SOLVENT EXTRACTION IN THE WINNING OF COPPER, NICKEL AND COBALT

A.J. VAN DER ZEEUW

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PROEFSCHRIFT

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Anneke, Eveline en Erik
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mijn Ouders.

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INTRODUCTION

Liquid/liquid extraction of metals (either as ions or salts) from an aqueous into an organic phase has been observed already long ago. In 1842 Péligot found that uranium could be extracted from nitric acid with ether. Despite various other examples found in later years the possibilities remained largely unobserved until H. Fischer introduced "dithizone" as a selective analytical reagent for various metal ions in 1924. "Dithizone" complexes often precipitated and gravimetric methods were then used for their quantitative determination. In other cases however the complexes could be extracted into organic solvents and then determined spectrophotometrically. From then on liquid/liquid extraction (or solvent extraction, SX, in the further text) became a very important tool in the hands of the analytical chemist, and this has been so ever since.

As a general term, liquid/liquid extraction or solvent extraction would be taken to cover such different processes as furfural extraction of aromatics in petroleum refining, extractions with supercritical CO_2 in food technology and pharmaceutical chemistry, and liquid metal - liquid slag exchange reactions in metallurgy[1]. However, for the present purpose the terms shall be used in the more restricted meaning defined in the opening paragraph.

The process can then be described as one in which an inorganic phase containing a solute is intimately contacted with an organic phase with which it is immiscible, in order to transfer the solute in some form into the organic phase. To this end the organic phase may or may not contain an extractant. Once the goal is achieved the contact is terminated and the phases are separated. Often this process of extraction is followed by its reverse, in which the solute-loaded organic phase is contacted with a second inorganic phase to transfer the solute into the latter. This is often referred to as "stripping" or "back-extraction".

Nowadays SX of metals finds application in a multitude of fields, from quantitative and qualitative analysis of trace metals, via waste water purification, to large scale metal production.

First industrial use of SX of metals dates back to the Manhattan project for the production for pure uranium compounds. During and after World War II SX as a unit operation was further developed and yielded advanced methods for the recovery of uranium, hafnium, zirconium and some other relatively low-volume metals[1]. The great industrial breakthrough in base metals came in the mid sixties, when it became possible to apply SX in the winning of copper, to purify and concentrate the copper solutions prior to electrowinning.

Although from a technological point of view SX of metals can be considered a unit operation, its position as a link in a chain of operations which should lead ultimately to the winning, in one form or another, of the pure metal(s) requires fine adaptation to the other processes involved.

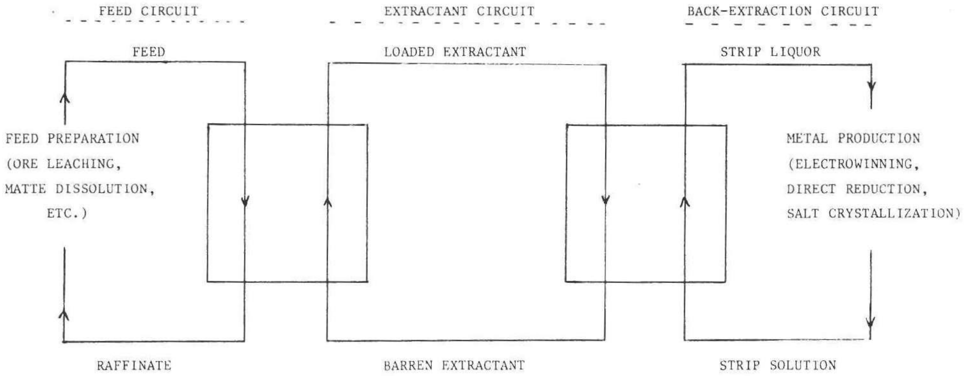


Fig. 1
A simple SX circuit in its context

In its (ideally) completely cyclic operation the organic extractant phase comes into contact with inorganic feed and back-extraction phases which differ greatly.

Factors like concentration and nature of feed impurities, concentration of the metal(s) wanted, flow rate of the feed, possibility of bacterial or fungoid growths, etc., will influence the attitude of the operations manager on items in which he has some liberty: choice of reagent, reagent concentration, choice of diluent, ratio between organic and inorganic phase volumes. They will however also confront him with some "facts of life", like rate and quality of phase separations throughout the process, presence of "crud" (a muddy semi-solid containing quite high reagent and diluent concentrations, which tends to collect at the interface in the settlers and to increase in volume with time, thus necessitating the operator to shut down his plant at intervals for cleaning), etc.

The often rather severe highly acidic conditions used in the stripping operation put high demands on the stability of the reagent. Requirements of purity on the inorganic back-extraction solution which proceeds to further metal-winning operations often dictate criteria of reagent selectivity. Inversely, in cases where this selectivity cannot be achieved, a bleed stream from the back-extraction circuit may be necessary to keep some contamination at an acceptable level of concentration.

From the designers' point of view the unpredictability and often also the changeability of feed factors such as indicated above, together with an unsatisfactory level of knowledge on the reagent's performance and properties puts limitations on the accuracy with which plant can be designed.

Other limiting conditions are being put to designer and operator by two more properties inherent to the reagents used. Firstly, many of the reactions in SX practice occur between two immiscible phases and between (hydrated) metal ions and largely or totally non-ionized reagent molecules. This makes such reactions inherently slow. Achieving equilibrium takes considerable time, and more often than not stage efficiencies fall short of 100 %. Hence plant design must be adapted to this fact. Secondly, especially the chelating type of SX reagents have rather high molecular weights (LIX 65 N: 339). In order to ensure handlability of the solutions, reagent concentrations cannot be increased too much. The stoichiometry of the reactions is often (for a bivalent metal) 1 ion to 2 molecules of the reagent. Frequently some extra free reagent is needed to keep the complexes in solution. Hence large volume streams of reagent solutions are often necessary to achieve a good extraction.

The impossibility per se, at least at an acceptable cost, to run the various circuits involved fully cyclic and self-contained may cause problems of an environmental nature, which have to be recognized by plant designer, reagent supplier and plant operator alike.

REFERENCE

1. Rosenbaum, J.B., Proc. AIME Meeting on Hydrometallurgy, Chicago 1973, p. 169. AIME, New York 1973.

SURVEY OF THE THESIS

In the first part a survey will be given of the various methods of SX for metals, indicating existing and potential applications for each method in actual metal-winning practice. Considering the enormous number of papers, books, conference proceedings etc. no attempt will be made to achieve completeness. In this part also some information will be given on the composition of various reagents which are, or have been, available on the market and on their most usual modes of application.

The second part contains the full text of the author's papers on several aspects of SX of metals.

In the third part a historic overview of the development of the author's interest in the field of SX and related areas will be given. Also comments are provided to the papers presented, which have been made necessary by the progress of science in the field. At the end a rather speculative view to the future of SX is given, together with a brief comparison of SX with some related processes.

PART ONE

A. CLASSIFICATION OF SX METHODS FOR METALS

Solvent extraction for metals can be classified in 4 categories:

1. SX by means of salt formation with anions,
2. SX by means of salt formation with cations,
3. SX by means of chelation,
4. "real" SX.

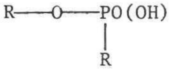
These categories will be discussed in the above sequence.

1. SX by means of salt formation with anions

Most metal ions are capable of forming salts with suitable acids. If the acid can be chosen such that both the acid and its metal salt are soluble in an organic phase but insoluble in water, SX of the metal ion from an aqueous medium is, at least in principle, possible.

Suitable acids may be carboxylic and sulfonic acids of reasonably high molecular weights, di-esters of phosphoric acid, mono-esters of phosphonic acids, etc.:

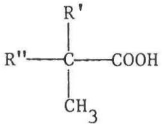
$R{-}COOH$ $R{-}SO_3H$ $(R{-}O)_2PO(OH)$



$R{-}O{-}PO(OH){-}R$

Amongst the carboxylic acids three types have been studied often:

highly branched aliphatic acids:

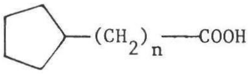


$R''{-}C(R')(CH_3){-}COOH$

VERSATIC acids (Shell)

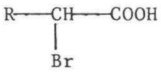
cyclo-alkyl substituted aliphatic acids:

(example)



naphthenic acids (Shell and others)

functionalized aliphatic acids:



$R{-}CH(Br){-}COOH$

α-bromolauric acid (Israeli Mining Institute)

Of these, VERSATIC acids find the widest application also in hydrometallurgical processes.

Of the phosphoric acid derivatives its di-ester with 2-ethylhexanol has been studied most frequently, and it is also applied in practice. It can be found in the SX literature under a number of names and abbreviations, a.o. di-(2-ethylhexyl) phosphoric acid, bis-(2-ethylhexyl) phosphoric acid, and often as DEHPA or D-2EHPA.

In principle the reaction between the acids described sofar and the metal ion is a simple salt formation. Hence, for carboxylic acids:

$$Me^{x+}_{aq} \quad + \quad x \quad R\text{—}COOH \rightleftharpoons (R\text{—}COO)_x Me_{org} \quad + \quad x \quad H^{+}_{aq}$$

Apart from formal objections one might have against writing H^+, this equation is grossly simplified, as will come to be discussed in part three of this thesis. Nevertheless the general idea is valid: acidity is generated, and the reaction is an equilibrium one.

It follows that the reaction is pH dependent, and that each metal ion is extracted best at an own specific pH value. Roughly it can be stated that for any metal the pH of optimum extraction for normal non-functionalized carboxylic acids (e.g. VERSATIC or naphthenic acids) is that at which the hydroxide of the metal starts to be formed. For such an acid an extraction/pH sequence for a number of important metal ions is for example:

$$\begin{array}{ccccccccc} Fe^{3+} & Cu^{2+} & Zn^{2+} & Ni^{2+}/Co^{2+} & Mn^{2+} & Fe^{2+} & Ca^{2+} & Mg^{2+} & Na^{+}/K^{+} \end{array}$$
$$2 \longleftarrow \text{pH} \longrightarrow 8$$

For acids having a greater strength, like α-bromolauric or sulfonic acids, the sequence remains largely the same, but the scale shifts to lower pH values and might get somewhat compressed. For an acid like DEHPA, which shows a selectivity for Zn^{2+}, this ion shifts to lower pH values and changes position with e.g. Cu^{2+}.

An implication of the pH dependence is that in general the extraction of a metal ion with such a reagent consumes a neutralizing agent if one aims for complete reaction. This is of course a cost factor, and up to now this has been a hindrance for a real breakthrough of carboxylic acid extraction of base metals.

In general it will not be economic to extract metals of which the optimum pH value of extraction lies above 6. In practice this means that in the above sequence SX by carboxylic acids might be feasible for metals up to Ni^{2+}/Co^{2+} and perhaps Mn^{2+}.

The fact that each metal has its own pH of optimum extraction implies that quite often separations between two or more metals are possible by adjusting the pH of operation. Two cases are illustrated in figures 1 and 2. In fig. 1 the pH "gap" between the two metals is so wide that a complete separation can be achieved in one stage by keeping the pH at the value indicated. The first metal A is completely extracted, whereas metal B remains totally in aqueous solution. Extraction of Fe^{3+} (A) and Cu^{2+} (B) from sulfate solutions is typical for this case.

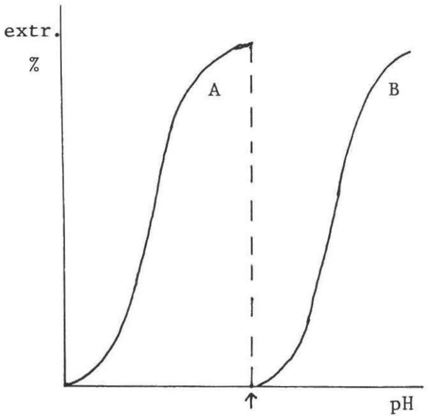


fig.1

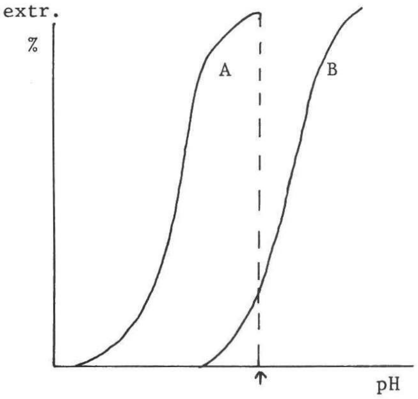


fig. 2

Fig. 2 is slightly more complicated. At the pH where A is extracted best, some B is already co-extracted. In many cases this problem can be overcome by using a multi-stage countercurrent operation. The small amount of B which is co-extracted in the first stage is then gradually replaced in the following stages by A. The extraction of Cu^{2+} (A) and Ni^{2+} (B) from sulfate solution is typical. For the couple Ni^{2+} and Co^{2+} the difference in optimum pH of extraction has already become so small that an uneconomically large number of stages would be required to accomplish a satisfactory separation.

Applications in practice

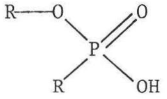
SX of copper and nickel from aqueous streams containing platinum group metals (PGM) was until recently applied at Rustenburg (South Africa) with VERSATIC acid. This acid has also been considered for the separation of cobalt and nickel contained in highly concentrated ammonium sulfate solutions obtained after application of the Sherrit-Gordon reduction of cobalt/nickel solutions.[1] In Japan Sumitomo use VERSATIC acid for the simultaneous extraction of cobalt and nickel.[2] The metals are then stripped together with aqueous HCl, and separation is then accomplished by selective extraction of the cobaltochloridate complex with tri-isooctylamine. Also in Japan, VERSATIC acid is used in a complicated multi-stage separation process for rare earth metals.

A process which is now being studied by Lurgi and approaches commercialization is the removal of ferric ions from zinc sulfate electrolyte, using an exchange reaction with the zinc salt of VERSATIC acid[3,4,5]:

$$2\ Fe^{3+}_{aq} + 3\ ZnV_{2\ org} \rightleftharpoons 2\ FeV_{3\ org} + 3\ Zn^{2+}_{aq}$$

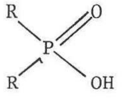
DEHPA is used in the extraction of zinc from various solutions at rather low pH.[6] Two processes using DEHPA have been developed for the separation of cobalt from nickel. The first,[7] carried out at normal temperature, has been piloted and subsequently shelved. The second one,[8] which applies higher temperatures, is now operational at Matthey Rustenburg Refiners in South Africa. It is a very interesting process, in that it uses the temperature-dependent transition of Co^{2+} from the octahedral six-co-ordination to the tetrahedral four-co-ordination.[9] The four-co-ordinated Co^{2+} is much more selectively extracted than the six-co-ordinated ion.

A phosphonic acid ester is used by Nippon Mining to extract cobalt selectively from nickel sulfate solutions.[10,11] Separation between cobalt and nickel is much better than for DEHPA. The formula of the product is



R = 2-ethylhexyl

Even better prospects for the separation of cobalt from nickel have been opened by the announcement of phosphinic acids by Cyanamid[12]:



These have apparently even better separation factors in favour of cobalt than the phosphonic acids.

2. SX by means of salt formation with cations

Some metal-containing anions may be extracted into organic layers by suitable cationic species, such as long-chain aliphatic tertiary or secondary amine salts, ammonium or sulfonium compounds, etc. The most widely known examples are the Alamine/Aliquat range (Henkel) and the almost identical Adogens (Sherex Chemicals):

$(\text{iso-}C_8H_{17})_3N$ Alamine 336
$(\text{iso-}C_8H_{17})_3N^+\!-\!CH_3\ \ Cl^-$ Aliquat 336

The most interesting category of metal-containing anions that may be extracted with these compounds are the complex halides: $FeCl_4^-$, $CoCl_4^{2-}$, $CuCl_3^-$, $CdCl_4^{2-}$, $ZnCl_4^{2-}$ and some others.

The reaction sequence of the extraction is illustrated for $CoCl_4^{2-}$ below.

$$Co^{2+}_{aq} + 4\ Cl^-_{aq} \rightleftharpoons CoCl^{2-}_{4\ aq}$$

$$2\ R_4N^+\ Cl^-_{org} + CoCl^{2-}_{4\ aq} \rightleftharpoons (R_4N^+)_2\ CoCl^{2-}_{4\ org} + 2\ Cl^-_{aq}$$

Although both reactions are equilibria, the second one lies far to the right. The first one is strongly dependent on the Cl^- concentration. Therefore the overall reaction is $[Cl^-]$ dependent, in about the same way as the carboxylic acid extraction is $[H^+]$ dependent. Hence the metals concerned can be put on a $[Cl^-]$ scale:

$$Cd^{2+}\quad Bi^{3+}\quad Fe^{3+}\quad Zn^{2+}\quad Cu^{2+}\quad Co^{2+}\quad Fe^{2+}\quad Mn^{2+}$$

$$0 \longleftarrow [Cl^-],\ M \longrightarrow 8$$

With respect to separations etc. the same considerations are valid as discussed previously for carboxylic acid extractions, but now of course related to $[Cl^-]$. A very attractive aspect of this type of reaction is that (since the overriding factor is $[Cl^-]$) back-extraction of the metal from the extractant can be carried out by decreasing the chloride concentration in the aqueous phase, in other words quite often stripping with plain water is sufficient.

Applications in practice

In the sequence given above Ni^{2+} is manifestly absent: under normal conditions Ni^{2+} does not form anionic halide complexes. This marked difference with Co^{2+} provides an excellent means of separating Co^{2+} from Ni^{2+} in chloride medium with very high selectivity.

It is therefore understandable that several variations of this separation have found technical applications in the metal-winning industry.[13]

Falconbridge Nikkelverk in Norway apply the principle to two different solutions: Adogen 281 (a secondary amine) is used to extract Cu^{2+} and Co^{2+} from a chloride nickel matte leach liquor, and tri-isooctylamine (Alamine 336 ?) is used to extract Co^{2+} from a solution of impure nickel hydroxide in aqueous HCl. Société Le Nickel (now Minemet) use Adogen 381 (a tertiary amine) to extract Co^{2+} from impure nickel electrolyte. Nippon Mining use "trioctylamine" for the same purpose. Métallurgie Hoboken-Overpelt find several applications for Alamine 336.

The Zincex process of Tecnicas Reunidas[6] uses a secondary amine (Amberlite LA2) for extracting zinc (and small amounts of other metals that form halide complexes, mainly copper, cadmium and iron) from their complex sulfide leaching solution.

In the nuclear industry Alamine 336[14] or similar products are of use in the purification of plutonium-containing solutions.

3. SX of metals by means of chelate formation

Chelating agents have available a salt-forming and an electron-donating function in one molecule. The salt-forming function is in most cases a group containing active hydrogen: aliphatic or phenolic OH groups, carboxylic acid groups, thiol or sulfonic acid groups. The electron-donating function may be any atom or group which is able to complex with metal ions through lone electron pairs:

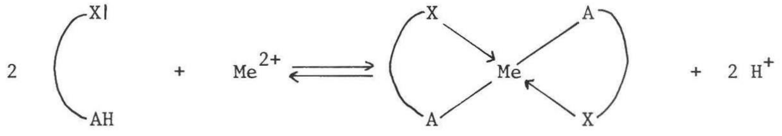
$$=\!O,\quad -S-\quad,\quad -O-\quad,\quad =\!N-\quad,\ \text{etc.}$$

Apart from the combination of salt-forming and electron-donating capacity in one molecule, several other criteria must be met by a "good" chelating agent. The most important one is ring size: the ring formed by the metal ion, the salt-forming function, the electron-donating group and all the atoms in between should be five- or six-membered.

The net chemical reaction between an appropriate (arbitrarily bivalent) metal ion and a chelating reagent can, simplified, be given as:

$$2\ RH_{org} + Me^{2+}_{aq} \rightleftarrows MeR_{2\ org} + 2\ H^{+}_{aq}$$

In a schematic structural way it can be pictured as:



It will be clear that chelating reagents will only form complexes as shown in this equation with metal ions that are keen to absorb the electrons donated by the reagent. Such metal ions almost all have partly empty inner d-electron shells.

In most chelating reagents used in analytical chemistry or industry the salt-forming function has a relatively low acidity. Reagents with alcoholic or phenolic OH groups are often used. In fact the acidity of these groups is so low that the remarkable stability of many chelates cannot be explained on that basis alone. It is the electron-donating function which is responsible for the strength of the complexes.

Towards metals which do not accomodate the electron-donating function the chelating reagents behave like (very) weak acids, forming normal salts at the expected high pH values.

It will be clear from the introduction that an important stimulus for SX came from the needs of analytical chemistry. A very large number of organic compounds with chelating properties have been proposed over the years to satisfy these requirements, and many still find applications in this field.

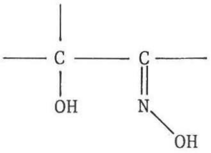
Two virtues have been of extensive use here. Firstly, the ability of the reagents to complex a metal ion selectively or even specifically from a mixture allowed the separation and quantitative determination of such a metal in preference of other ones, in dependence on reaction conditions. Secondly, many chelates have very specific light absorptions, which can be used for their determination by spectrophotometric methods.

After appropriate chemical adaptation some of the compounds can be made to serve in industrial applications. Such categories have to meet at least the following criteria:

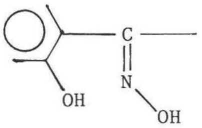
solubility in suitable organic diluents,
stability upon storage and in use,
acceptable properties with respect to toxicity etc.,
reversible chelation properties,
acceptable cost performance to the user.

Compounds that satisfy these criteria and are or have been available in commercial quantities fall in four classes:

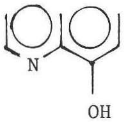
aliphatic hydroxy-oximes



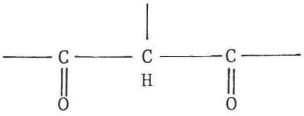
aromatic hydroxy-oximes



8-hydroxyquinolines



β-diketones



$$-\underset{\underset{\textstyle O}{\|}}{C}-\overset{|}{\underset{H}{C}}-\underset{\underset{\textstyle O}{\|}}{C}-$$

The net chemical reaction given earlier in this section is in many respects very similar to that given for the extraction of a metal ion with a carboxylic acid: it is an equilibrium, and pH dependent. For such a reaction to be applicable in the metal-winning industry it is required that the extraction is reversible under practicable conditions. Because of the remarkable stability of many of the chelates they are often formed at low pH values, and one can easily go to far: a toluene solution of 1,2-dioximino-4-alkylcyclohexane extracts copper from 2N H_2SO_4 [15], which means that the reaction is irreversible under acceptable conditions.

However, if the proper choice of reagent can be made, the extraction can often be carried out almost or completely without neutralization of the acidity generated. This explains why SX by chelation is so popular in the industry. Using one of the commercial reagents available, extraction of copper for instance can be carried out directly from the solutions coming from a leaching operation at a pH of 0.5 - 2, because the copper complexes are still stable at the lower end of the above range.

Applications in practice

By far the most important application is the extraction of copper from moderately acidic solutions. Several hundreds of kT/y of copper are being produced via SX. Section B of part one of this thesis will be devoted to this application.

As already indicated metal ions that will react with chelating agents often have only partially filled d-shells. Ni^{2+} and Co^{2+} also belong to this category and many chelating reagents therefore will react with these ions, beit mostly at considerably higher pH values than with copper. Practical application of chelating extraction to systems which contain Ni^{2+} and Co^{2+} is seriously hampered by the fact that Co^{2+} complexes in contact with air are very rapidly oxidized to Co^{3+} complexes [16,17] which are extremely difficult to decompose.[17,18] Co^{2+} acts effectively as a poison for chelating reagents. Many methods of recovering a partly poisoned reagent have been devised to enhance the feasibility of SX for Ni^{2+}/Co^{2+} systems [19,20] including back-extraction of the cobalt with concentrated HCl, concentrated H_2SO_4 at elevated temperatures, concentrated salt solutions, reduction of the Co^{3+} with cobalt powder, etc. Apart from being often aggressive for the reagent, these methods were found by us to be at best only partially successful. The only method known to date which is really successful is precipitation of the cobalt with H_2S.[16,18]

The best way to cope with the cobalt problem is to avoid it. In ammoniacal medium Co^{2+} is very easily oxidized to Co^{3+}, which is virtually not extracted by chelating agents.[21] Therefore deliberate oxidation of Co^{2+} could be considered. Whether this solution is acceptable depends on the overall economics.

Applications of chelating extraction in the winning of other metals are rare. Matthey Rustenburg are building a plant at their Royston (U.K.) site in which Pd will be extracted from a PGM solution in aqueous HCl with a solution of a hydroxy-oxime. Métallurgie Hoboken-Overpelt have patented a process for the extraction of Ge with LIX 63, an aliphatic hydroxy-oxime.[22] Rhône-Poulenc have a process in operation in which Ga^{3+} is extracted with an alkylsubstituted 8-hydroxyquinoline derivative.[23]

4. "Real" SX of metal ions

In this method both the metal ion and the counterion are extracted from the aqueous phase. The reagents used do normally not contain cationogenic or anionogenic functions, but do have available lone electron pairs, through which they form weak complexes with the metal ions. Because of the absence of functions in the reagents the metal ions must take their own counterions.

Well-known reagents for "real" solvent extraction are higher alcohols, ketones, ethers, phosphate esters, etc. Sometimes β-diketones are erroneously reckoned to belong to this category as well. In fact they are weak chelating agents, because they react in the enol form, with the second carbonyl oxygen acting as the electron-donating function.

Practical applications

From the beginning of the industrial application of SX of metals tributyl phosphate has been in use for the extraction of uranium compounds in the nuclear industry, and this is still so.[24]

B. SOLVENT EXTRACTION IN THE COPPER INDUSTRY

By its definition a SX process needs solutions to work on, and will yield solutions as its end product. From the latter the metal or metal salt may then be won using methods which are known: crystallization to give metal salts, electrowinning or direct reduction to produce the metal, etc.

Inclusion of a SX step may be warranted if a sequence of processes at some stage yields an aqueous metal salt solution which is too dilute or (and) too impure to proceed directly to a metal winning stage, or to be treated otherwise or disposed of. Such dilute or (and) impure solutions may in the copper winning practice arise for instance:

1. through direct leaching of ores,
2. through leaching of flotation tailings,
3. through natural leaching, as mine waters,
4. as waste streams, electrowinning bleed streams, etc.,
5. after dissolution of scrap metal etc.

1. SX after direct leaching of copper ores

Use of SX on solutions obtained through direct leaching of sulfidic copper ores, mainly chalcopyrite, was pioneered by Arbiter [13,25] at Anaconda's Butte Montana plant. The ore, after concentration, was leached with ammonia and air to give an ammoniacal copper sulfate solution, which was then extracted with a selective copper extractant (LIX 64 N). The process has only been in operation for a short period, and was closed down in 1979,[26] partly for economic reasons and partly because of leaching problems with one of the modifications of chalcopyrite.

Direct leaching of oxidic copper ores is planned by Codelco (Chile) in their Chuquicamata mine. The ore is very pure, and the resulting solutions will hardly contain other metal ions, so that SX will serve mainly as a concentration step. A major problem in practice may be a rather high content of colloidal silica.

2. SX after leaching of flotation tailings

In the dressing of porphyric ores a flotation operation takes a predominant position. It aims at producing an ore concentrate which can be used directly in a pyrometallurgical step. Separating the last quantities of ore from the gangue is difficult, not only because of the low absolute amounts but also because the valuables remaining with the gangue have a less pronounced sulfidic, rather more oxidic character which makes them less amenable to simple flotation procedures. In practice therefore a "cut-off" grade is maintained: material with a lower quantity of valuables is dumped or stored. In the past cut-off grades used to be rather high. However, with time ever lower grade copper ores were considered worth mining, so at present many old tailings dumps are regarded as worthwhile sources for copper. Leaching of these dumps is being carried out or planned for the future at many copper mines in the world. Two main types of leaching can be distinguished: heap or dump leaching in which the lixiviant (often dilute H_2SO_4 or recycled raffinate from the SX operation) is simply dosed onto the tailings heaps and the copper-enriched acid is tapped, and agitation leaching in which the dissolution of the copper is achieved by agitation (e.g. in Pachuca's). The latter system is used in the biggest copper SX plant in operation, ZCCM's Chingola plant in Zambia.

3. SX on mine waters

In some places a combination of natural conditions exists which leads to dissolution of copper from ores without human action. Important potential applications, which may come to realization in the (near) future, are at Bougainvillea (Papua New Guinea) and El Teniente (Chile).

4. SX on waste streams etc.

The electrowinning bleed stream from Phelps Dodge's El Paso refinery used to be worked up by SEC Corp. They extracted copper from this solution with LIX 64 N, then made the solution strongly alkaline with ammonia, and extracted nickel with the same reagent.[13]

5. SX on scrap metal solutions

Imperial Smelting Processes are operating an extraction of copper from ammoniacal solutions of zinc dross in their Avonmouth plant.[27] Although the original set-up was for LIX 65, it is now believed that they have re-designed the plant for LIX 54. The advantage of the latter (a diketone) is that co-extraction of ammonia is markedly less.

In 1979 Brookside Metals in the U.K. closed down a plant in which copper had been extracted from silver nitrate solutions with SME 529.[28] Very careful regulation of pH was necessary in this process. If pH was allowed to fall below 1, increasing amounts of copper could not be stripped from the organic reagent. In co-operation between the owners and Shell it was established that this was due to nitration of the copper complex in the position ortho to the phenolic group.[29] This resulted in the formation of a complex of an extremely strong reagent, displaying the corresponding resistance towards aqueous acid.

Several other projects based on the dissolution of scrap metal have been studied, but the present economic situation is not favourable for their realization, and most plans have been shelved.

Economics of SX

The total contribution of SX to the world's copper production is substantial. This may be illustrated by the following (fairly comprehensive) list of copper SX plants in operation, and their estimated production.

ZCCM, Chingola, Zambia	80,000 tpa
Anamax, Twin Buttes, Arizona (USA)	40,000 "
Ranchers Bluebird, Arizona	7,000 "
Cyprus Bagdad, Arizona	7,000 "
Cyprus Johnson, Arizona	5,000 "
Cities' Service, Arizona	15,000 "
Inspiration, Arizona	30,000 "
Kennecott Ray, Arizona	20,000 "
Duval Battle Mountain, Nevada (USA)	4,000 "
Pinto Valley, New Mexico (USA)	?
Noranda Lakeshore, Arizona	30,000 "
Cananea, Mexico	20,000 "
Cerro Verde, Peru	25,000 "
Centromin, Peru	5,000 "
Lo Aguirre, Chile	20,000 "

Worldwide, on a total copper production in 1980[30] of 7 x 10^6 tons, this makes some 4.5 %. However, locally the contributions may be much higher: in Zambia 12 - 15 % of the copper is produced using SX methods, and in the USA this figure is approaching 10 %.

Numerous factors determine the overall economics of a SX process as part of a metal-producing operation. In many cases the very costly mining and ore dressing, heavy contributors to the final product costs, are superfluous. Costs of lixiviants may be substantial if the operation stands on its own. Mostly however the SX is part of a large scale production site where

H_2SO_4 is easily obtained by conversion of SO_2 from the pyrometallurgical operation.

Often a pre-neutralization step is necessary prior to SX to neutralize excess acid, or to precipitate excessive amounts of e.g. iron salts. If the neutralizing agent (often lime) has to be transported over long distances this may be a heavy cost factor.

Energy consumption per unit of product in a SX/electrowinning plant is some 4 times higher than in a "conventional" pyrometallurgical/electrorefining operation.[26] However, in places with cheap energy this is not a problem.

Losses of reagent by physical means (entrainment) and decomposition cannot be completely avoided. Such losses range from 20 ppm total solvent (i.e. reagent + diluent) in the aqueous raffinate of a new, well-operated plant to 100 ppm or more in an old one. Considering that a plant like ZCCM's Chingola operation produces about 3000 m^3 of raffinate per hour, it is clear that the absolute costs of lost reagent are high. The fact that in most operations the raffinate is recycled to the leaching does not improve the situation very much: in the leaching most of the reagent contained in the aqueous phase disappears into the leaching residue or is decomposed and cannot be recovered.

All in all however it can be stated that most SX plants have shown considerable cost advantage over conventional processes. For instance, ZCCM's costs for copper produced through SX are in the US $ 0.45 - 0.55 per pound bracket, against proceeds of US $ 0.85/lb. This makes SX the only profitable part of the operation: "conventional" copper at ZCCM costs around US $ 0.90/lb.*

Similar considerations hold for most plants in operation, and the realization of more new projects is in fact only hindered by lack of capital.

Mutual influences of SX and other parts of metal-winning processes

Inclusion of SX in an integrated metal-winning process may have consequences for both upstream and downstream parts of such a process, and the operation of the SX part in turn may be influenced by the way in which other process parts are conducted.

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* 1981 data. Private communications from ZCCM staff.

Upstream process parts

Flotation reagents or residues thereof which may be present in (e.g.) the flotation tailings may end up in the aqueous feed to the SX process. Such contaminations almost invariably do great harm to the process of layer separation in the settler part of the SX plant. Also rates of extraction might be decreased.

Some ores contain constituents which dissolve, properly or colloidally, in the leaching liquor. A prime example is SiO_2, which in some cases may attain a high concentration and seriously inhibit layer separation. Moreover voluminous highly adsorbing precipitates of hydrated silica may be formed, which give rise to severe solvent losses.

In some cases a pre-neutralization step has to be carried out prior to SX. A very common neutralizing agent is lime. Obviously $CaSO_4$ will be formed, which shows a well-known tendency to supersaturated solutions. Consequently gypsum precipitates may be generated and again layer separation will suffer.

Downstream process parts

The use of SX leads to contamination of the downstream aqueous phases. Firstly, both the reagents used and the diluents show a certain (usually low) degree of solubility in water. Secondly, incomplete layer separation causes mutual entrainment of the phases. The degree of the latter can to an extent be restricted by adequate process operation, but never fully excluded. If the raffinate is not recycled but disposed of as waste water it may be necessary to bring the level of such contaminants down in order to compel with regulations and environmental considerations.

If the aqueous stream considered is a strip liquor, meant to be processed further in an electrowinning operation, it is also necessary to keep organic contamination at a low level. If this is not done properly, the cathode metal very often shows "organic burning". The very thin layer of organic phase floating in the electrolysis cells causes discolouration and contamination of the part of the cathode which is in contact with the organic. A technique often used to diminish the risk of organic burning is air flotation: a stream of air is used to drive the entrained organic phase to the surface of the aqueous layer, from which it is skimmed off as completely as possible before the aqueous stream enters the electrowinning unit.

In electrowinning cells in which a high current density is applied one often finds "acid mist". Due to the high rate of gas evolution a blanket of highly corrosive and very disagreeable acid droplets is maintained over the cell. Various means of restricting this phenomenon are used. One of these is addition of "anti mist agents". One of the types of products used for this purpose are aromatic sulfonic acids. Because of their character they display a certain solubility in organic phases. Since normally solutions from electrowinning operations are recycled, the organic reagent solutions may take up such strongly acidic compounds from the aqueous phases. Losses of reagent through acid hydrolysis may then result.[31]

Safety aspects

SX involves handling of highly inflammable products. It therefore requires a complex system of safety measures of a nature which is not per se common to the metal-winning industry. A very important value in this respect is the flash point of the diluent. A few years ago the uranium SX plant at Rossing (Namibia) was severely damaged by a fire caused, amongst others, by the use of a diluent with too low a flash point.

C. COMPOSITION AND MODE OF APPLICATION OF SOME COMMERCIAL REAGENTS

1. Commercial forms

Anionogenic reagents are mostly sold as virtually pure compounds in a non-diluted form. An exception are naphthenic acids which are impure because of their origin. They usually contain considerable amounts of neutral compounds, mostly hydrocarbons, and it is customary to identify naphthenic acids by their acid value, i.e. the number of milligrams of KOH required to neutralize the acid contained in one gram of the impure mixture. This figure is then quite straightforwardly found back in the product description.

Cationogenic and "real" SX reagents are also usually sold as pure compounds without diluents.

Most chelating reagents are sold in a more or less diluted form. The diluents are mostly hydrocarbons (kerosine fractions) or higher alcohols or alkylphenols.

2. Modes of application

Anionogenic reagents are used in solutions in hydrocarbon diluents, in active matter concentrations typically ranging from 0.1 to 2 M. Dependent on the particular reagents, the diluent and the process it is sometimes necessary to add a modifier, that is a co-diluent of a more polar character than the main one. Typical examples are cases where layer separation needs improvement, or in which the metal complexes might precipitate. Alcohols and alkylphenols are the most widely used modifiers. In pH dependent extractions addition of such compounds often causes a decrease in selectivity and a shift of the optimum pH range to higher values.

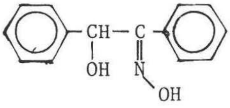
Cationogenic reagents are normally applied in highly aromatic diluents, sometimes in combination with a modifier, e.g. a higher aliphatic alcohol. Alternatively chlorinated hydrocarbons may be used as the sole diluent. Active matter concentrations in use are typically $\leqslant 0.5$ M.

"Real" SX reagents are used as such, or mixed with hydrocarbons or other diluents.

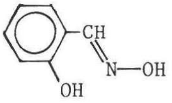
Chelating reagents are mostly used in hydrocarbon solutions, concentrations typically between 2 and 15 % active matter, or 0.05 to 0.5 M. It may be necessary to add a modifier.

3. Survey of commercial copper chelating reagents

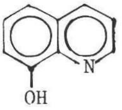
As already indicated four types of chelating reagents for copper are or have been available: 2 types of hydroxy-oximes, hydroxyquinolines, and diketones. Their structural groups can be found back in compounds that have been known in analytical chemistry for years:



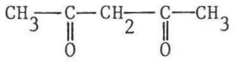
benzoin oxime
(cupron)



salicylaldoxime



8-hydroxy-
quinoline
(oxine)



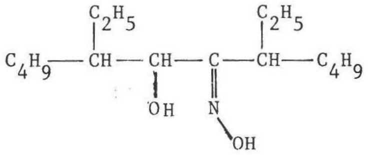
$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$

acetylacetone

Such simple compounds and their metal chelates are often not very soluble. By suitably substituting them with sufficiently long alkyl chains the molecular weights can be increased, so that both the reagent and the complexes acquire an appropriate level of solubility in organic diluents. This principle was first successfully used by General Mills Inc.[x] in their product LIX 63. Over the years a number of reagents have become available, which are discussed below.

3.1 Oxime reagents

LIX 63 5,8-diethyl-6-hydroxy-7-oximinododecane[32]



$C_4H_9-\overset{\overset{C_2H_5}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-\underset{\underset{N-OH}{\|}}{C}-\overset{\overset{C_2H_5}{|}}{CH}-C_4H_9$

This product extracts copper from aqueous solutions of $pH \geqslant 3$ at a high rate. However, this pH range was not attractive to the copper-winning industry. Since normally copper-bearing acidic leach liquors have pH values of $\leqslant 2$ use of LIX 63 would necessitate addition of neutralizing agents. At present LIX 63 is mainly used as an accelerator for other Henkel products, as discussed below.

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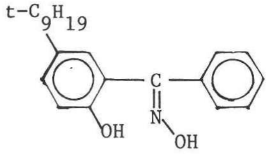
[x] The former mining chemicals division of General Mills Inc. is now the property of Henkel (USA). The products are sold under the Henkel label.

LIX 65 N 2-hydroxy-5-tert-nonylbenzophenone oxime[33]



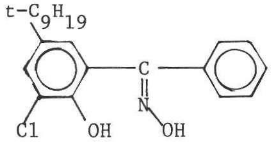
This compound met the requirements of the copper industry with respect to pH: its activity starts to be attractive as low as pH 1.5. Its rate of extraction for copper at this pH level however is too low at normal temperature. This could be improved by mixing LIX 65 N and LIX 63. The blend is commercially known as LIX 64 N. In cases where it is possible or desirable to carry out SX of copper at higher temperatures than normal, say up to 50° C, LIX 65 N alone can be used quite well.

LIX 64 N[34]

Early products contained LIX 65 N and LIX 63 in a molar ratio of about 4 : 1. This changed rapidly over the years, and the present commercial product probably contains about 3 % of LIX 63, at an active LIX 65 N content of 1 M.

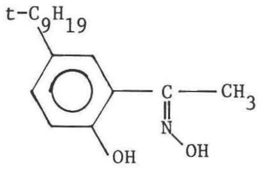
In the early days of LIX technology a grade LIX 64 has been in existence. It contained LIX 63 and 5-dodecyl-2-hydroxybenzophenone oxime. It was soon superseded by the much better LIX 64 N.

LIX 70[35] a blend of 2-hydroxy-3-chloro-5-tert-nonylbenzophenone oxime



and LIX 63. With respect to pH functionality LIX 70 is a much stronger reagent than LIX 65 N, due to the influence of the Cl substituent. It is active down to pH 0.5 and hence requires rather strong acid to release its complexed copper. Moreover, it is not a very fast reagent. With the aim to reduce the complexing power to a more acceptable level and to improve the rates of extraction and stripping various blends of LIX 70, LIX 65 N and LIX 63 have been proposed (LIX 71, LIX 73[35]), but neither has been able to match the commercial and technical success of LIX 64 N.

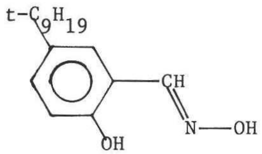
SME 529 [36] 2-hydroxy-5-tert-nonylacetophenone oxime



With respect to pH functionality Shell Metal Extractant 529 is a slightly stronger reagent than LIX 65, and it has faster kinetic performance than LIX 64 N. It is sold as a 50 % active matter solution in a hydrocarbon diluent.

Acorga P 5000 series[x]

base compound: 2-hydroxy-5-tert-nonylsalicylaldoxime[37]



This is an extremely potent reagent which extracts copper at pH values as low as 0.5. Consequently it will release the complexed copper only in contact with highly concentrated acid, which is an unacceptable proposition in relation to present day electrowinning practice. ICI have devised formulations modified with nonylphenol[38] which are more easily stripped, at the cost of only a limited and therefore acceptable loss of pH functionality. The P 5000 range of extractants can be characterized as fast reagents. Currently the range comprises:

name	ratio base compound/nonylphenol
P 5100	1/1
P 5200	1/2
P 5300	1/3

The products also contain small quantities of a hydrocarbon diluent. The base compound, P 5000, is not sold as such. Recently a product PT 5050 has appeared, which is probably a blend of P 5000 modified with tridecanol.

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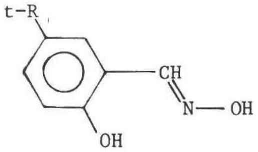
[x] Acorga is a 50/50 joint venture between Anglo American and ICI.

LIX 617, LIX 622, etc.

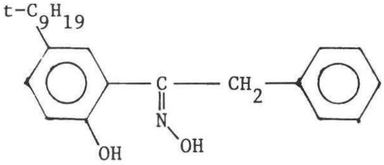
base compound(s): 5-tert-alkyl-2-hydroxysalicylaldoxime [39]



Under above and other codenames various products are around. They may differ in chain length of the alkyl substituent, or in concentration of active matter. They are presumably all modified with a higher alcohol. Our analysis has shown LIX 622 to be 5-tert-dodecyl-2-hydroxysalicylaldoxime with tridecanol as modifier and a kerosine diluent.

Compounds of the very similar formulas proposed by Henkel and ICI/Acorga are the subjects of a mutual law suit by these companies in the USA. Recent information is that this case has in first instance been won by ICI. The consequences of this result cannot easily be estimated.

Acorga P 17 2-hydroxy-5-tert-nonylphenyl benzyl ketoxime [40]



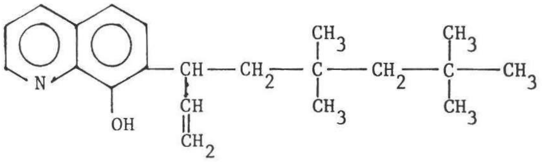
This product has only been available for a short time. It was comparable to SME 529 with respect to pH functionality, but was slower in action. It was superseded by the P 5000 range.

3.2 Hydroxyquinoline derivatives

Kelex 100/120

Base compound:

7-(1-ethenyl-3,3,5,5-tetramethylhexyl)-8-hydroxyquinoline [41]



This is a very strong and fast reagent. The strength of the copper complex makes modification for improved stripping necessary. Ashland/Sherex[x] have achieved this by blending the pure compound (sold as Kelex 100) with nonylphenol. Thus, a blend of 20 % Kelex 100 and 80 % nonylphenol was sold as Kelex 120.

The products have never attained a good position in the market, and have now been withdrawn. They had basically two drawbacks.

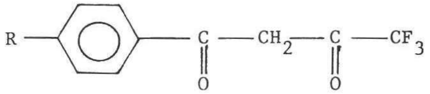
Firstly, as an "oxine" derivative the base compound is not very selective, and will complex many metals. Especially in the area of copper winning, where selectivity over Fe^{3+} is very important, the Kelex reagents have problems. "Oxine" complexes with Fe^{3+} are stronger than those with copper,[42] and the same is probably true for the complexes with the Kelex reagents. The selectivity obtained for Cu^{2+} over Fe^{3+} in the practical use of Kelex is therefore of a kinetic nature, instead of thermodynamic, as with the hydroxy-oximes.

Secondly, the basic quinoline nitrogen tends to form a salt with sulfuric acid used in stripping. This necessitates an extra operation to recover the reagent after copper stripping.

3.3 Diketone reagents

LIX 54

Presumably 1-(4-alkylphenyl)-4,4,4-trifluoro-1,3-dioxobutane[43]



This product has been developed especially for ammoniacal liquors and is presumably being used in Imperial Smelting Processes' plant in Avonmouth (UK). The advantage of diketone reagents in general is their very low ammonia co-extraction.

Application of diketone reagents for extraction of copper from acidic liquors is not feasible, because under such conditions the rate of reaction is very slow.

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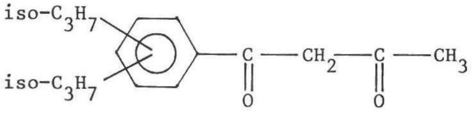
[x] Kelex used to be a registered trade mark of Ashland Oil Comp. Their mining chemicals business was recently taken over by Schering. The products are sold under the Sherex label.

Hostarex DK 16[x]

Presumably 1-(di-isopropylphenyl)-1,3-dioxobutane [44]



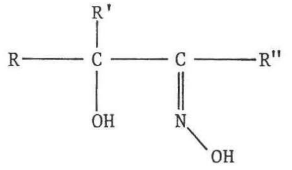
No practical uses of this product are known. As LIX 54, it is especially recommended for ammoniacal leach liquors.

4. Chelating reagents without present or past commercial status

In the course of the years some reagents have been proposed, mainly by General Mills Inc/Henkel, which have never achieved even a temporary commercial status. Two of these are discussed briefly below.

LIX X18A

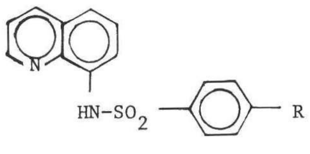
An aliphatic hydroxy-oxime with formula [39]



$$R-\overset{R'}{\underset{OH}{C}}-\underset{N-OH}{\overset{\|}{C}}-R''$$

in which presumably $R = R'' = n\text{-}C_4H_9$ and $R' = n\text{-}C_6H_{13}$. (See also paper B 3 in part two of this thesis). This reagent was not specifically designed for copper extraction, but rather for cobalt/nickel separation from sulfate medium. It has never been a success, probably mainly because of the cobalt problems already discussed.

LIX 34, an 8-sulfonamidoquinoline derivative of formula [45]



It is outstanding in its virtually total iron rejection, but is slow and could not be accelerated with the common accelerators.

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[x] Hostarex is a registered Hoechst trademark.

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PART TWO

PAPERS

A 1. STUDY OF THE HYDROGENATION OF THE VERSATIC ACID SALTS OF COPPER, NICKEL AND COBALT.

A.J. van der Zeeuw and L. Gandon.

Proc. Tenth Int. Mineral Processing Congress, IMM London 1973.

INTRODUCTION

The reduction of cupric salts of organic acids by hydrogen has been known for some time. Chalk and Halpern[1] carried out the reduction of cupric heptanoate in organic solvents at temperatures above 120 and 150° C and at atmospheric pressure. They concluded that the reaction proceeds autocatalytically via a cuprous species. Because this system has catalytic properties, it was used for the reduction of benzoquinone, etc. Stouthamer[2] employed a slightly different system for the preparation of unsaturated fatty alcohols from unsaturated fatty acids.

Application of this type of reaction to the preparation of metal powders has also been investigated. In a recent patent application[3] Burkin described the reduction of a single metal salt of a highly branched carboxylic acid (VERSATIC acid[x]) in kerosene solution. The reaction is generally carried out at elevated temperature and pressure, often in the presence of a catalyst and/or nucleating agent (Pd on charcoal, prefabricated metal powder) and in some instances without a catalyst. Because the VERSATIC acids used for the investigation are highly branched in the α-position they themselves are resistant against hydrogenation under the conditions employed. Our own investigations were undertaken with the aim of establishing whether this reaction could be so guided as to achieve selectivity - so as to enable one metal to be separated, by reduction, from a system containing different metal salts of VERSATIC 10 acid. The present paper deals with the systems Cu, Cu - Ni, and Cu - Co. Because the cupric salt of VERSATIC 10 acid can be reduced at atmospheric pressure and moderate temperatures, it was possible to follow the reaction kinetics without difficulty.

EXPERIMENTAL

Preparation of metal solutions

Kerosene solutions of metal salts of VERSATIC acid were prepared by mixing VERSATIC acid in kerosene and an aqueous solution of a suitable metal salt and neutralizing the briskly stirred mixture slowly with concentrated ammonia until the pH of the aqueous layer had a value of 6.5. At this value metal extraction is virtually quantitative, whereas co-extraction of NH_4^+ is still negligible.

After suitable dilution the metal contents of the solutions were determined

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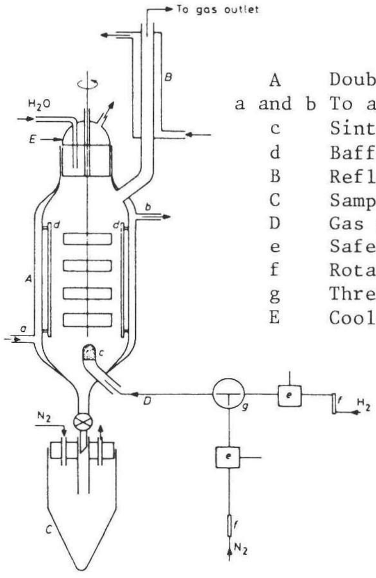
[x] Shell trade mark.

by atomic absorption spectrometry and the values were related to the infrared spectra. Excellent agreement was found for all metals up to 0.1 M concentrations. Free VERSATIC 10 concentrations were determined by titration. Up to 0.15 M, the values thus found were in agreement with those obtained by infrared measurement.

Apparatus and reaction conditions

The reactions were carried out in an all-glass apparatus comprising a stirred baffled vessel as depicted in Fig. 1. Purified hydrogen of atmospheric pressure was used. The stirring rate was 530 rev/min, which is safely beyond the measured mass transfer limiting value of 180 rev/min. Samples were taken under a stream of purified nitrogen into a cooled receiver and transferred into the infrared cell immediately. It was found that the samples could be kept for hours without change, provided that air was carefully excluded.



A	Double-walled reaction vessel
a and b	To and from thermostat bath
c	Sintered-glass gas supply tube
d	Baffles (4)
B	Reflux condenser
C	Sampling device
D	Gas supply
e	Safety valve and bubble counters
f	Rotameters
g	Three-way cock
E	Cooled all-glass stirrer head

Fig. 1
Apparatus for atmospheric pressure reductions

Kinetic measurements

The reactions were followed by infrared measurement of the frequencies of free VERSATIC acid (1700 cm^{-1}), the metal salts (1602 - 1604 cm^{-1}), and of partially reduced species (1545 cm^{-1}). The spectra were recorded on a Perkin-Elmer 225 Grating infrared spectrometer.

RESULTS

Reduction of the cupric salt of VERSATIC acid

The experimental set-up enabled us to follow three variables at a time, i.e. the decrease of the cupric salt concentration, the increase of the free acid concentration and the increase and decrease of a species absorbing at 1545 cm.$^{-1}$ Fig. 2 gives the result of a typical copper salt reduction. The cupric carboxylate absorption follows an autocatalytic curve. Fig. 3 shows that the maximum rate is at about 50 % conversion (this holds for all experiments referred to in this paper).

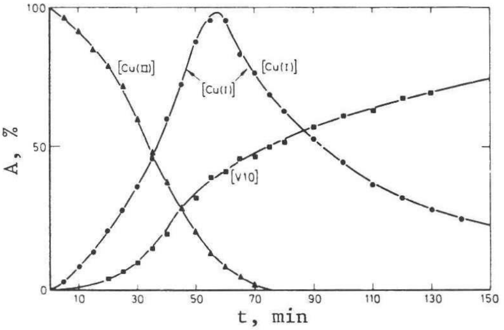
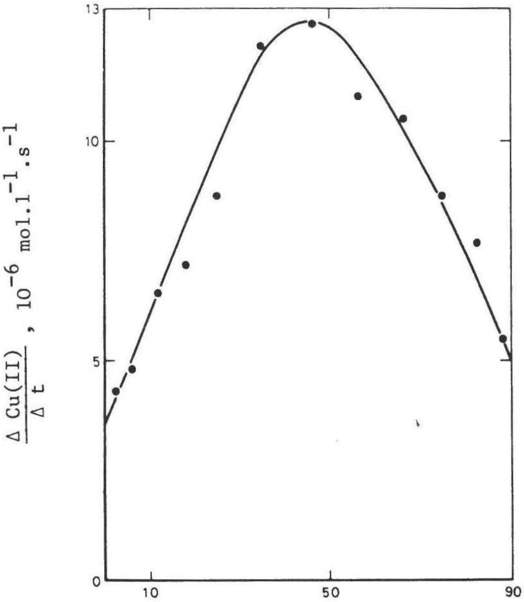


Fig. 2

Atmospheric pressure reduction of Cu(II) VERSATIC salt (0.033 M) in kerosene in presence of free VERSATIC 10 (0.033 M) at 140^{o} C. See Appendix 1.

At the same time the concentration of the species absorbing at 1545 cm^{-1} increases approximately as the mirror image of the cupric salt concentration. It reaches a maximum when the cupric concentration has dropped to a value near to zero, and the free VERSATIC acid concentration has increased by about half the maximum growth (i.e. the growth expected upon completion of the reaction Cu(II)$\longrightarrow$ Cu^{o}). The conclusion seems warranted that this absorption is due to a cuprous carboxylate species. At this point of the reaction the solution is practically colourless.

Any situation obtained in this reaction before or until all Cu(II) has been completely converted into Cu(I) can be frozen at will by merely stopping the hydrogen supply, and it can be maintained almost indefinitely. This supports the observation by Chalk and Halpern[1] that under the circumstances applied the cuprous species is stable to disproportionation.



conversion, %

Fig. 3

Rate of disappearance of Cu(II) in reduction of 0.033 M Cu(II) VERSATIC salt in kerosene at 140° C/1 atm H_2. (initial free VERSATIC acid concentration 0.033 M)

When an experiment was stopped at maximum Cu(I) concentration, the hydrogen replaced by nitrogen, an extra amount of cupric salt of VERSATIC acid equal to the Cu(I) concentration added and hydrogen addition resumed after suitable thermostatting the newly added Cu(II) was converted at a continuously decreasing rate.

After going through its maximum, the cuprous carboxylate absorption decreases again in a clear first-order way (Fig. 4). The pseudo first-order rate constant at 140° C is 2.66×10^{-4} sec^{-1}. A duplicate experiment gave a value of 3.0×10^{-4} sec^{-1}.

Since the hydrogen pressure in our experiments was fixed at 1 atm and an excess of hydrogen was maintained, only three variables are of interest in the system - temperature, VERSATIC acid concentration and initial copper concentration.

High concentrations (above 0.1 M) of free VERSATIC acid do not influence the decrease of cupric salt concentration or the ascending part of the cuprous carboxylate curve, but they have a remarkable, and as yet unexplained, accelerating effect upon the later stages of the reaction.

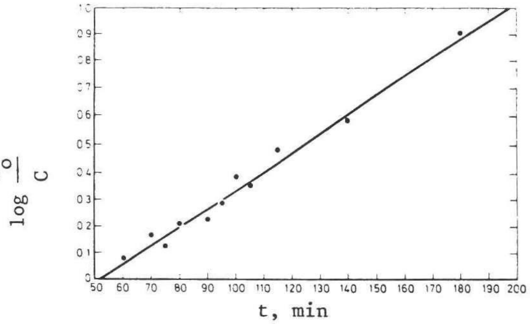


Fig. 4

First-order plot of decrease of [Cu(I)] vs. time (see Fig. 2 for reaction conditions)

We will further restrict ourselves to the first part of the reactions, i.e. until all Cu(II) has been converted to Cu(I).
Chalk and Halpern[1] showed that in the case of reduction of cupric heptanoate activation of hydrogen occurred through both Cu(II) and Cu(I). Their measurements, however, did not necessitate a cuprous/cupric-dependent term by way of explanation. We would like to suggest a modification of Chalk and Halpern's rate law for our reaction:

$$\frac{d\,[\mathrm{Cu(II)}]}{dt} = k_a\,[\mathrm{Cu(II)}] + k_b\,[\mathrm{Cu(II)}]\,[\mathrm{Cu(I)}] \qquad (1)$$

in which k_a and k_b evidently depend on $[H_2]$ (see Appendix 2), or, since:

$$[\mathrm{Cu(I)}] = [\mathrm{Cu(II)}]_o - [\mathrm{Cu(II)}]$$

and writing X for [Cu(II)] and X_o for the initial cupric concentration, $[\mathrm{Cu(II)}]_o$

$$-\frac{dX}{dt} = k_a X + k_b (X)(X_o - X)$$

$$= -k_b X^2 + (k_a + k_b X_o).X \qquad (2)$$

Equation 2 represents a parabola with a maximum, which is in agreement with our results. The second term of equation 1 is a typical example of an autocatalytic reaction first-order in both components, resulting in an S-shaped conversion curve[4].

A possible mechanism, which is in agreement with the above rate law, is presented in Appendix 2.

A graphical representation of equation 1 may be derived from the conversion curves by plotting increments $\Delta X/\Delta t$ against the conversion, as is shown in Fig. 3. In principle, the point of intersection of the curve thus obtained with the ordinate represents $k_a X_o$, whereas the maximum rate should have the value

$$k_a \frac{X_o}{2} + k_b \frac{X_o^2}{4}$$

Because the maximum rate is achieved at 50 % conversion. We should therefore be able to calculate all constants from our plots, and also the relation with X_o could come to the fore. Particularly at the beginning of an experiment, however, accuracy is expected to be low, owing to the necessity of calculating small differences between strong absorptions, and a safety margin of about 5 % on absolute conversion at either end of the reaction should be kept.

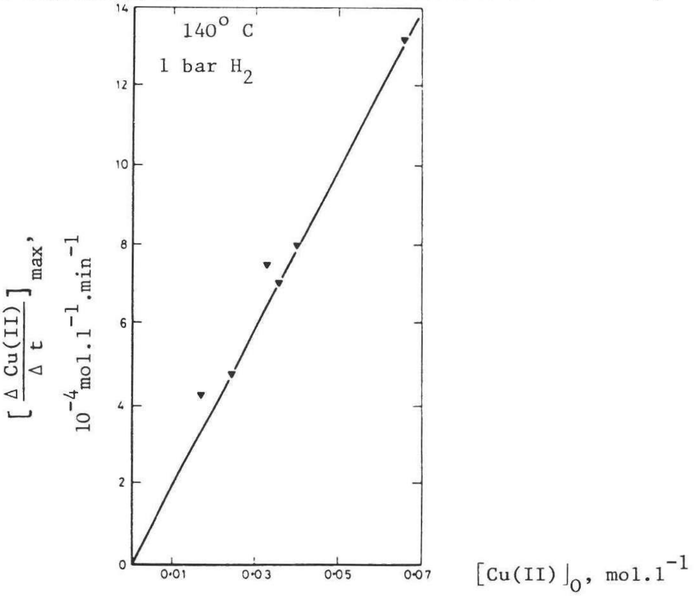


Fig. 5

Maximum rate of decrease of $[Cu(II)]$ as a function of $[Cu(II)]_0$

The values of the maximum may be measured accurately, but it does not seem warranted to use them for calculation purposes. With regard to the dependence of the maximum rate and X_o, it is shown in Fig. 5 that a first-order relation fits reasonably well.

Reduction of the cupric salt of VERSATIC acid in the presence of nickel and cobalt salts.

In the presence of the nickel salt of VERSATIC acid the reduction of the cupric salt proceeds considerably faster (cf. Figs. 2 and 6). We have varied the nickel concentration at a given, constant, initial copper concentration and evaluated the results in the same way as before, i.e. by plotting increments $\Delta X/\Delta t$ versus conversion.

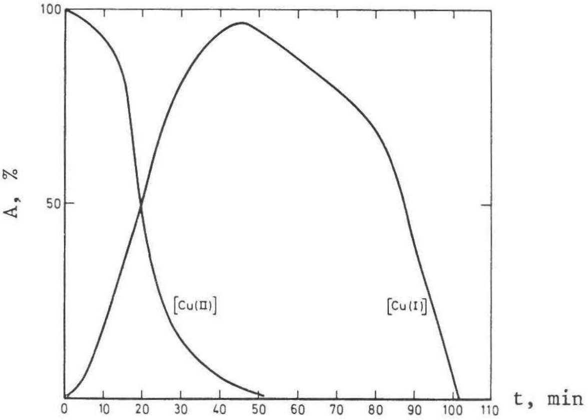


Fig. 6
Atmospheric pressure reduction of Cu(II) VERSATIC salt (0.030 M) in kerosene in presence of Ni(II) VERSATIC salt (0.030 M) and free VERSATIC 10 (0.1 M) at 140^o C.

The maximum rates of the various reactions occurred again at about 50 % conversion. The values of the maximum increased strongly with higher nickel concentrations. Since the copper concentrations were kept the same, and the value of the maximum can be estimated fairly accurately, they may be used for estimation of the influence of the nickel concentrations. Fig. 7 indicates that a second-order relation of the form $R_{max} = R^o_{max} + a[\mathrm{Ni}]^2$ exists, in which R_{max} is the maximum rate of the nickel-catalysed reaction and R^o_{max} that of the uncatalysed reaction. The nickel salts also accelerate the second step of the reaction sequence, i.e. the reduction of the cuprous species to give metallic copper (see Fig. 6); however, this influence is rather complex, and we did not study it in any detail.

Surprisingly, cobalt salts of VERSATIC acid do not influence the reaction at all in the temperature range investigated, even when used in rather high concentrations ($\geqslant$ 0.1 M). An explanation for this remarkable difference in behaviour between cobalt and nickel may be offered by the infrared spectra of samples of nickel and cobalt salts of VERSATIC acid in kerosene before and after treatment with either hydrogen or nitrogen. It has been observed that as a kerosene solution of the nickel salt is heated with hydrogen at 140 - 180^o C the -COOH absorption increases and the $-COO^-$ peak decreases. Furthermore, the spectrum shows a small absorption at the same wavelength at which the assumed cuprous carboxylate peak appears in the Cu(II) reduction (see Fig. 8). Replacement of the hydrogen stream by nitrogen results in reversal of the reaction. We tentatively assume, therefore, that there is a partial reduction of Ni(II) to a lower-valent Ni species, e.g. Ni(I). In the temperature range studied no further reaction to Ni(o) follows.

Judged from the spectra, the reaction occurring might be an equilibrium between Ni(II) and Ni(I), e.g.

$$2\ NiV_2 \ + \ H_2 \rightleftharpoons 2\ HV \ + \ 2\ NiV$$

Under the reaction conditions applied this equilibrium is established within 2 min, i.e. rapidly as compared to the normal reaction period for the copper reductions. At equilibrium the Ni(II) carboxylate absorption of a 0.03 M kerosene solution of the nickel salt of VERSATIC acid shows, upon treatment with hydrogen at 140, 160 and 180^o C, a decrease of 18, 21 and 44 %, respectively, which points to Ni(II)/Ni(I) ratios of 4.55, 3.76 and 1.27.

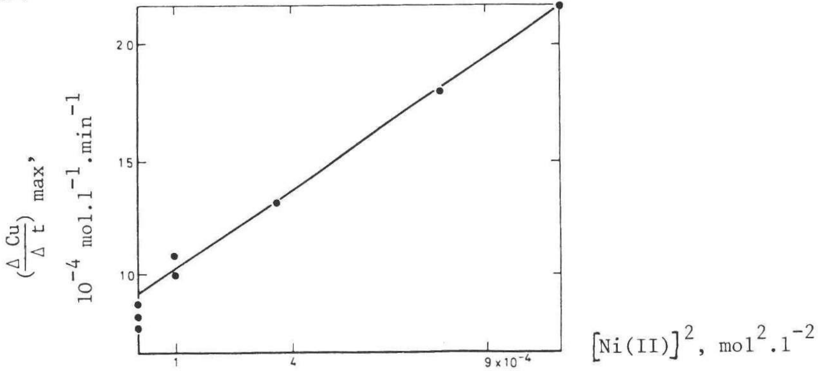


Fig. 7

Relation between maximum rate of Cu(II) disappearance and $[Ni(II)]^2$
Initial [Cu(II)] 0.033 M, temp. 140^o C.

1	1700 cm^{-1}
2	1670 "
3	1604 "
4	1545 "

A	Heated to 140° C under N_2
B	After 15 min with H_2 at 140°C

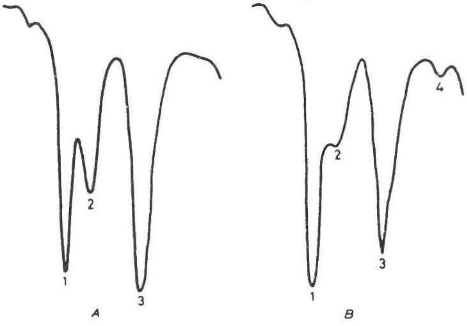


Fig. 8

Reaction of Ni(II) VERSATIC salt (0.031 M) + free VERSATIC (0.037 M) in kerosene with hydrogen at 140° C.

1	1700 cm^{-1}
2	1670 "
3	1604 "
4	1570 "

A	Fresh solution
B	After 1 h treatment with N_2 at 140° C
C	After 1 h treatment with H_2 at 140° C
D	Sample B after keeping in N_2 at room temp. for 3 h

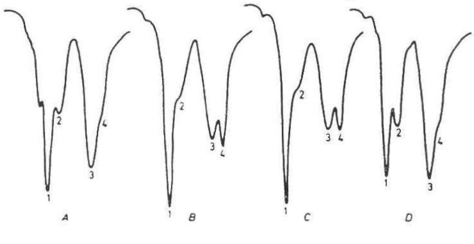


Fig. 9

Spectra of Co(II) VERSATIC salt (0.036 M) + free VERSATIC (0.042 M) in kerosene.

When the cobalt salt of VERSATIC acid is treated in the same way, the spectrum also changes considerably. Contrary to what happens with the nickel salt, however, this change may also be induced by heating with nitrogen. By cooling down under nitrogen the original situation is slowly restored (see Fig. 9). No sign of a reduced cobalt species is found in the spectra. It may, therefore, safely be assumed that at the temperatures applied cobalt salts of VERSATIC acid are not reduced to any measurable extent.

CONCLUSIONS

With the aid of infrared measurements it has been demonstrated that the reduction of the cupric salt of VERSATIC acid in kerosene essentially consists of two steps, i.e. the reduction of Cu(II) to Cu(I), catalysed by the Cu(I) formed, and the pseudo first-order reduction of Cu(I) to Cu(o). No metallic copper is precipitated before all Cu(II) has disappeared. The maximum rate of the $Cu(II) \longrightarrow Cu(I)$ reaction is approximately proportional to the initial Cu(II) concentration. The mechanism proposed in Appendix 2 involves heterolytic splitting of hydrogen molecules by the cupric and homolytic splitting by the cuprous salt of VERSATIC acid.

In the presence of nickel salts of VERSATIC acid the copper reduction reaction is considerably accelerated. The maximum rate at constant initial Cu(II) concentration is proportional to the square of the Ni(II) concentration. Evidence has been found that the Ni(II) is partially converted into a lower-valent species - probably a Ni(I) salt. This reaction proceeds to an equilibrium, and in the temperature range investigated there is no further reduction to metallic nickel.

Cobalt salts of VERSATIC acid have no influence upon the cupric-cuprous reduction at the temperatures applied. Since no indication of the presence of a lower-valent cobalt species could be found in the spectra, it is tentatively assumed that the ineffectiveness of cobalt salts is due to the impossibility of Co(I) being formed.

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APPENDIX I

Quantitative evaluation of infrared measurements

The most useful absorption of free VERSATIC 10 in kerosene was seen at 1700 cm^{-1}. Its absorbance was easily correlated with titrimetric values. A perfectly straight line was obtained up to 0.15 M. The extinction coefficient calculated was 765 $l.mol^{-1}.cm^{-1}$.

The metal(II) carboxylate absorptions at 1602 cm^{-1} for Cu(II) and 1604 cm^{-1} for Co(II) and Ni(II) were chosen to determine the concentration of metal of the higher valency. Absorbances were correlated with quantitative atomic absorption analyses. Excellent straight lines were obtained up to 0.1 M. The extinction coefficients were 1225 $l.mol^{-1}.cm^{-1}$ for Cu(II) VERSATIC salt and 840 $l.mol^{-1}.cm^{-1}$ for Co(II) and Ni(II) VERSATIC salts.

As is evident measuring these absorptions gives a direct absolute value for the concentration. This is not the case for the absorption at 1545 cm^{-1}, which is supposed to represent the lower-valent Cu(I) and Ni(I) carboxylates. Since no direct test for the Cu(I) concentration was applied, we determined the maximum value for the absorbance of this species from the experiment (if necessary by extrapolation), and expressed all other values as percentages of this figure, which was supposed to represent 100 % Cu(I) concentration. In the Ni(II) reductions the peak at 1545 cm^{-1} has an equilibrium value; hence, no calculations can be based upon it.

For the Ni and Co salts an extra absorption was found at 1670 cm^{-1}, very near the free VERSATIC peak and not very well separated from it. This made calculations more difficult and somewhat less reliable with respect to the free acid concentration.

In order to facilitate comparison the values on the ordinates of Fig. 2 and 6 are given as a percentage of the maximum possible change of the absorbance, i.e.

$$A_t\ (\%) = \frac{A_t - A_o}{A_{max} - A_o} \times 100$$

For mixed Cu-Ni or Cu-Co reductions use was made of the additivity of absorbances, the final value of the absorbance at 1602-1604 cm^{-1} being regarded as the contribution of the Ni or Co salt. Despite the observed partial reduction of the Ni salt, this is permissible at low Ni concentrations, the error then having only little influence.

APPENDIX II

Proposed mechanism

The observed influence of the cuprous ion on the reduction of the cupric salt of VERSATIC acid may be explained by the following reaction sequence:

$$CuV_2 + H_2 \xrightarrow{k_1} CuV.H + HV \qquad (1)$$

$$CuV.H + CuV_2 \xrightarrow{k_2} 2\ CuV + HV \qquad (2)$$

$$2\ CuV + H_2 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} 2\ CuV.H \qquad (3)$$

Equations 1 and 2 are identical with those put forward by Chalk and Halpern.[1] Formally, equation 1 refers to the heterolytic splitting of hydrogen. Equation 3 deviates considerably from the mechanism of Chalk and Halpern in that it assumes the homolytic splitting of hydrogen by cuprous salt, ultimately giving a species formally equal to that from equation 1. Equations 2 and 3 bear a close resemblance to those found by Calvin and Wilmarth[2] in the reduction of cuprous acetate in quinoline. The only difference is that our results require that both k_{-3} and $k_3 > k_2$, whereas Calvin and Wilmarth supposed $k_2 >> k_{-3} >> k_3$.

Comparing our results with those of Chalk and Halpern and Calvin and Wilmarth, the obvious conclusion is that the splitting of hydrogen may be homolytic or heterolytic, and can be influenced not only by varying the solvent but also by suitable change of the anion. Clearly, VERSATIC acid anions have a fundamentally different influence on the reduction as compared with heptanoate.[1] It is logical to assume that the fact that there are two branchings so close to the carboxylic group is responsible for the difference. This, however, is an assumption and would need further investigation.

The reactions described in this paper are much faster than those investigated by Chalk and Halpern. This is illustrated in Table 1, which lists the half-lives of Cu(II) - Cu(I) reductions in both systems.

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1. Chalk, A.J. and Halpern, J., J. Am. Chem. Soc. 1959, <u>81</u>, 5846
2. Calvin, M. and Wilmarth, W.R., J. Am. Chem. Soc. 1956, <u>78</u>, 1301

Table 1

Half-lives of Cu(II) - Cu(I) reduction in the system Cu(II) VERSATIC acid salt in kerosene at 140° C and 1 atm H_2.
Below dotted line: half-lives of same reduction in Chalk and Halpern's systems.

$Cu(II)_o$, M	half-life, min.
0.016	42
0.033	34
0.033	42
0.042	48
0.126	22
0.03^x	ca 110
0.35^{xx}	ca 125

^{x} Cupric heptanoate in heptanoic acid at 145° C

^{xx}Cupric heptanoate in octadecane at 145° C.

From the above reaction sequence, together with the assumption that k_{-3}, $k_3 > k_2 > k_1$, it follows that

$$[\text{ CuV.H }] = [\text{ CuV }]\sqrt{\frac{k_3\,[H_2]}{k_{-3}}} = [\text{CuV}]\sqrt{K'_3}$$

or, since

$$[\text{ CuV }] = [\text{CuV}_2]_o - [\text{CuV}_2]$$

$$[\text{CuV.H}] = (X_o - X)\sqrt{K'_3}$$

Moreover,

$$-\frac{d\text{Cu(II)}}{dt} = -\frac{dX}{dt} = k'_1\,X + k_2\,X\,[\text{CuV.H}] \qquad (4)$$

in which $k'_1 = k_1[\,H_2\,]$

Substitution of the value for CuV.H into equation 4 gives

$$-\frac{dX}{dt} = k'_1\,X + k_2\sqrt{K'_3}\,(X)(X_o - X) \qquad (5)$$

which is completely equivalent to the rate law of equation 2.

For the nickel-catalysed Cu(II) - Cu(I) reduction the following mechanism is proposed:

$$2\ NiV_2 + H_2 \xrightleftharpoons{K_1} 2\ NiV + 2\ HV \qquad (6)$$

$$2\ NiV + H_2 \xrightleftharpoons{K_2} Ni_2V_2H_2 \qquad (7)$$

$$CuV_2 + Ni_2V_2H_2 \xrightarrow{k_3} CuV.H + HV + 2\ NiV \qquad (8)$$

$$CuV.H + CuV_2 \xrightarrow{k_4} 2\ CuV + HV \qquad (9)$$

$$2\ CuV + Ni_2V_2H_2 \xrightleftharpoons{K_5} 2\ CuV.H + 2\ NiV \qquad (10)$$

This scheme as a whole appears to be a plausible extension of the Cu(II) - Cu(I) reduction described before. That a reduced nickel species (probably a Ni(I) compound) plays an important role is evident from our measurements. The one speculative element is that this species is a dimer. The justification for this lies in the experimental evidence that the relation between maximum rate and nickel concentration is second-order.

In the above scheme $Ni_2V_2H_2$ plays a part only in increasing the actual concentration of 'activated hydrogen'. Assuming that the equilibria 6, 7 and 10 are established rapidly as compared to the rates of 8 and 9, it follows that

$$[Ni_2V_2H_2] = K_1'' K_2' [NiV_2]^2 \qquad (11)$$

in which $K_1'' = K_1 [H_2] / [HV]^2$ and $K_2' = K_2 [H_2]$. Further, from 8 and 9 it follows for the rate of decrease of Cu(II):

$$-\frac{dX}{dt} = k_3 [Ni_2V_2H_2] (X) + k_4 [CuV.H] (X) \qquad (12)$$

in which $X = [CuV_2]$.

Also

$$[CuV.H] = K_5 \sqrt{\frac{[CuV]^2 [Ni_2V_2H_2]}{[NiV]^2}} = [CuV] \sqrt{K_2' K_5}$$

$$= (X_o - X) \sqrt{K_2' K_5} \qquad (13)$$

Substitution of equations 11 and 13 into 12 gives for the rate:

$$-\frac{dX}{dt} = k_3 K_1 K_2' [NiV_2]^2 (X) + k_4 \sqrt{K_2' K_5} (X_o - X) (X) \qquad (14)$$

The maximum value of this equation at constant X_o is evidently proportional to the square of the initial Ni concentration.

A 2. METALS EXTRACTION WITH CARBOXYLIC ACIDS

I. Composition of complexes with nickel, cobalt(II) and iron(III)

A.J. van der Zeeuw.

Hydrometallurgy 1979, 4, 21

INTRODUCTION

The results of the liquid/liquid extraction of a metal from an aqueous solution with acidic reagents are often reported as a plot of log D, i.e. the logarithm of the distribution coefficient, versus pH. The distribution coefficient is then usually defined as the quotient of the analytical concentrations of the metal in the organic and in the inorganic phase.

Ideally, such a plot is a straight line with a slope equal to the number of extractant groups bound to the metal through covalent bonds. However, for several reasons this ideal is seldom attained. First, the ionic strength in the aqueous solution and the activities of the species in the organic layer are not always constant throughout the extraction. It is therefore generally accepted that slope analysis is only warranted when low concentrations of metal ions (e.g. $< 10^{-3}$ M) are extracted from aqueous solutions containing high concentrations of a bulk ion (usually having an opposite charge) with relatively large excesses of the extractant. Even when these conditions are satisfied, effects such as extensive hydrolysis of the metal ions in the aqueous phase and polymerization of the organic metal complexes may disturb the picture.

In the past, the composition of extracted complexes was usually estimated by subjecting a number of log D/pH curves, obtained under different carefully chosen sets of conditions with respect to concentration of extractant and extracted ion, to a combined graphical analysis[1-4]. Jaycock and Jones[5] have devised a graphical method that needs only one log D/pH curve. A common feature of all these methods is that the measurements have taken place under conditions which approach the ideal as closely as possible.

The present paper describes a non-graphical treatment which makes it possible to obtain an idea of the composition of complexes in experiments performed at concentrations of extractant and metal that are more realistic. It is clearly illustrated that in many cases theoretical disadvantages do not hamper its practical applicability. As a rule, one log D/pH curve will suffice to give satisfactory results. The procedure has been applied to the extraction of metals with organic acids, e.g. VERSATIC and octanoic acids. It must be stated that the method only reveals the most likely compositions.

The actual composition(s) cannot be established this way. As the method attempts to study the composition of organic phase metal complexes under realistic conditions, its application to commercial extractants seems justified especially as the components of VERSATIC 10 are so similar that they may be safely regarded as a single acid type.

DERIVATION OF EXTRACTION EQUATION AND COMPUTATIONAL METHOD

The symbols used in this section are listed at the end of the paper.
In the most generalized way the overall extraction of a metal ion from an aqueous layer with an acidic extractant may be written as follows:

$$M_{aq} + \frac{n+m}{p} (HA)_{p,org} \rightleftarrows \frac{1}{x} (MA_n . m\, HA)_x + n\, H^+_{aq} \tag{1}$$

The complex $(MA_n . m\, HA)_x$ will further be denoted as C. In this generalized concept n is not necessarily equal to the valency of the metal ion M.

We may now define an overall equilibrium constant for this reaction:

$$K' = \frac{[C]^{1/x}_{org}\ [H]^{n}_{aq}}{[M]_{aq} \left[(HA)_p\right]^{(n+m)/p}_{org}} \quad \frac{\gamma^{1/x}_{C,org}\ \gamma^{n}_{H,aq}}{\gamma_{M,aq}\ \gamma^{(n+m)/p}_{(HA)_p,org}} = KB \tag{2}$$

The results of the measurements generally are values of the analytical distribution coefficient D, defined as:

$$D = [M]_{org} / [M]_{aq} \tag{3}$$

$$[C]^{1/x}_{org} = \left[\frac{1}{x}\ M\right]^{1/x} = [M]^{1/x}_{org}\left(\frac{1}{x}\right)^{1/x} = [M]_{org}[M]^{(1-x)/x}_{org}\left(\frac{1}{x}\right)^{1/x}$$

Further, it follows from eq. 3 that $[M]_{org} = D\,[M]_{aq}$, and hence

$$[C]^{1/x}_{org} = D[M]_{aq}[M]^{(1-x)/x}_{org}\left(\frac{1}{x}\right)^{1/x} . \tag{4}$$

Substitution of eq. 4 into 2 gives for K':

$$K' = \frac{\left\{D\,[M]^{(1-x)/x}_{org}\left(\frac{1}{x}\right)^{1/x}\right\}[H]^{n}_{aq}}{\left[(HA)_p\right]^{(n+m)/p}}\ B$$

or, taking logarithms:

$$\log D = \log K' - \log B + ((x-1)/x)\log [M]_{org} + (1/x)\log x + n\mathrm{pH} + \\ + ((n+m)/p)\log (HA)_p . \tag{5}$$

We may further write:

$$[\mathrm{HA}]_o = [\mathrm{HA}]_{org} + [\mathrm{HA}]_{aq} + [\mathrm{A}]_{aq} + (n + m)[\mathrm{M}]_{org}$$

Since the solubility of HA and the complex in the aqueous phase will be low, we may neglect $[\mathrm{A}]_{aq}$ and $[\mathrm{HA}]_{aq}$, which gives:

$$[\mathrm{HA}]_o = [\mathrm{HA}]_{org} + (n + m)[\mathrm{M}]_{org} \qquad \text{or}$$

$$[\mathrm{HA}]_{org} = [\mathrm{HA}]_o - (n + m)[\mathrm{M}]_{org}$$

Substitution of this value into eq. 5 gives:

$$\log D = \log K' - \log B + ((x-1)/x)\log [\mathrm{M}]_{\mathrm{org}} + (1/x)\log x + n\mathrm{pH} + \\ + \frac{n+m}{p}\log\left(\frac{[\mathrm{HA}]_0 - (n+m)[\mathrm{M}]_{\mathrm{org}}}{p}\right)$$

or, by rearrangement and assuming that log B is constant:

$$\log K = \log D - ((x-1)/x)\log [\mathrm{M}]_{\mathrm{org}} - (1/x)\log x - n\mathrm{pH} - \\ - \frac{n+m}{p}\log\left(\frac{[\mathrm{HA}]_0}{p} - \frac{n+m}{p}[\mathrm{M}]_{\mathrm{org}}\right)^{*}. \qquad (6)$$

Apart from the parameters n, m, x, and p, this formula only contains known or measurable values. If eq. 6 holds, choosing a suitable set of n, m, x and p should give an approximately constant value for log K over the range of measurements.

The simplification in the derivation that log B is constant is only warranted in three cases. First, if all activity coefficients are equal to 1, log B will be 1 and K' = K. Second, if all activity coefficients, although different from 1, are constant throughout the series of measurements, log B will be a constant and therefore a constant (though not realistic) value will be found for log K (i.e. log K equals log K' minus a constant). In our opinion these two situations are not likely to occur. The third possibility is that any changes in the activity coefficients during extraction result in a value of log B which, considering the inaccuracies of measurement, will hardly, if at all, affect the computations. This seems to be the case, since in practice the proposed formula can be used with confidence for judging the constancy of log K, and hence for finding the best fitting compositions for the complex over a considerable range of measurements.

The evaluation was carried out with the aid of a computer program by which the permutation of values for n, m and x was performed. The results of the computations are reported here as: (a) an average value for log K over the range of measurements, (b) a slope coefficient for the best fitting straight line through all calculated log K values, (c) an estimation of the possibility of a straight line with slope zero being drawn through all log K values. This estimation was made via Student's t-test. For any set of measurements a t-value was calculated and compared with a critical t-value, known from statistical tables, using 95 % probability two-sided. A straight line with slope 0 was assumed to be possible if $t_{calc} \leqslant t_{crit}$; this has been indicated in the tables by an asterisk. In addition, the tables in most cases also give the measured values of pH and log D.

EXPERIMENTAL

The metals to be extracted were dissolved in the form of their sulfates. The total amount of sulfate was adjusted to 0.55 M by the addition of $MgSO_4$ or Na_2SO_4.

The extractions were carried out in a cylindrically shaped separatory funnel equipped with an electric stirrer (2000 rev/min) and an inlet for the neutralizing agent. For the extraction 90 ml of the metal solution was contacted with 100 ml of the organic acid solution, and, while stirring, 10 ml of a dilute aqueous NH_3 solution was slowly added. The dilution of the NH_3 was chosen so as to reach pre-estimated extraction. For each measurement this procedure was repeated. This method was followed in order to have a constant phase ratio at equilibrium of 1/1 and a constant sulfate concentration of 0.5 M.

All stirring times were 3 min after addition of the neutralizing agent. Settling times were kept at 5 min. The temperature was 25^{o} C.

Metal concentrations were determined by atomic absorption spectrophotometry (Perkin Elmer 403): in the inorganic layers after suitable dilution with 1 N HNO_3 and in the organic layers after backwashing with 1 N HNO_3 followed by suitable dilution of the stripping layer with 1 N HNO_3.

RESULTS

Cobalt and nickel

For cobalt and nickel the extraction behaviour with VERSATIC solutions proved to be strongly dependent on the concentrations involved, and more particularly on the ratio R between the extractant and metal concentrations and its variation during the extractions.

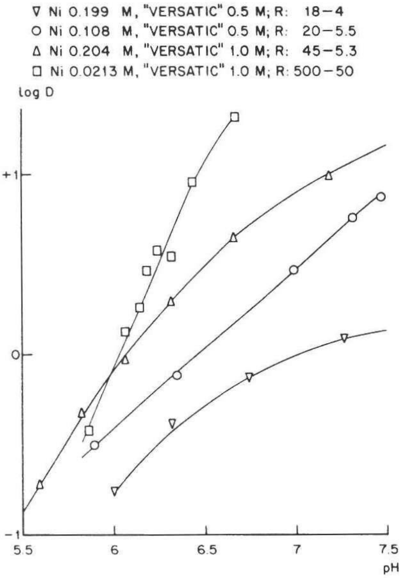

Fig. 1

Extraction of nickel with VERSATIC 10 solutions. Background: 0.5 M $MgSO_4$

Fig. 1 illustrates for nickel that upon decreasing R the slope of the log D/pH graph decreases. At high R this slope is $\geqslant 2$, whereas at low R it ultimately becomes <1; the line also becomes curved. The latter is mainly caused by the rapid changes in concentration of free VERSATIC during the extraction. For cobalt the situation is almost identical, albeit that this metal is extracted at a slightly higher pH level.

The evaluation[x] according to the outlined procedure suggests that at high R the complexes formed have (n,m,x) = (2,2,2) for nickel (see Table 1) and (2,0,2) for cobalt (see Table 2), which means formulas $(NiV_2.2\ HV)_2$ and $(CoV_2)_2$, respectively, where V stands for the VERSATIC anion. In the nickel case sets for (n,m,x) of (2,0,2) and (2,1,2) appear to be acceptable too, but (2,2,2) gives a better fit, i.e. has a lower calculated value for t and a lower slope coefficient[xx].

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[x] In the evaluation of experiments with carboxylic acids p has been taken to be 2. It is known from the literature (ref. 1-5) that carboxylic acids in various non-aqueous apolar solvents are dimeric.

[xx] See however the discussion section.

Table 1

Extraction of 0.0213 M Ni with 1.00 M VERSATIC. Background: 0.5 M $MgSO_4$

Exp. no.	pH	Metal in org. layer (mol/l)	Metal in inorg. layer (mol/l)	log *D*
1	5.80	0.0046	0.0167	−0.5600
2	6.00	0.0097	0.0114	−0.0701
3	6.20	0.0153	0.0060	0.4065
4	6.40	0.0189	0.0024	0.8963

Number of observations = 4
Critical *t* value for B1 = 4.30 (95% two-sided and 2 degrees of freedom); *t* values below the critical level are marked with an asterisk.

Permutations

No.	*n*	*m*	*x*	log *K* (mean value)	*B*1 (slope coeff.)	Student's *t*
1	1	0	1	− 5.7787	1.427	1.574×10^{2}
2	2	0	1	−11.7201	4.442×10^{-1}	5.204×10^{1}
3	1	1	1	− 5.6201	1.444	1.692×10^{2}
4	2	1	1	−11.5560	4.717×10^{-1}	6.060×10^{2}
5	1	2	1	− 5.4560	1.471	1.890×10^{1}
6	2	2	1	−11.3864	5.111×10^{-1}	7.165×10^{2}
7	1	0	2	− 4.9430	9.182×10^{-1}	1.002×10^{1}
8	2	0	2	−10.8845	-6.552×10^{-2}	$^{*}7.213 \times 10^{-1}$
9	1	1	2	− 4.7845	9.344×10^{-1}	1.029×10^{1}
10	2	1	2	−10.7204	-3.796×10^{-2}	$^{*}4.236 \times 10^{-1}$
11	1	2	2	− 4.6204	9.620×10^{-1}	1.074×10^{1}
12	2	2	2	−10.5507	1.359×10^{-3}	$^{*}1.546 \times 10^{-2}$

In the cases of very low R the evaluations give an average formula $(NiV.2\ HV)_2$ for nickel (or (n,m,x) = (1,2,2)), see Table 3, and $(CoV.1$ or $2\ HV)_2$ for cobalt (or (n,m,x) = (1, 1 or 2, 2)). For nickel a set (1,1,1) would seem to be equally acceptable, but for reasons to be discussed later we prefer (1,2,2).

For values of R in the intermediate range sets (n,m,x) of (1½,2,2) for nickel (Table 4) and (1½,1 or 2, 2) for cobalt were found to give the best fit, i.e. the compositions were $Ni_2V_3.4\ HV$ and $Co_2V_3.2\text{-}4\ HV$, respectively.

In the extraction of cobalt with a large excess of octanoic acid (1 M acid vs. 0.05 M cobalt) the complex formed had the composition $CoA_2.0\text{-}1\text{-}2\ HA$ (Table 5). Some dimeric compositions, esp. $(CoA_2.2\ HA)_2$, also fit. However, the best fitting straight line through all log D/pH measurements as determined by the computer had a slope of exactly 2 at an explanation level of over 98 %. It is a well-known fact (see e.g. ref. 1) that the presence of

Table 2

Extraction of 0.02 M Co with 0.50 M VERSATIC. Background: 0.5 M $MgSO_4$

Exp. no.	pH	Metal in org. layer (mol/l)	Metal in inorg. layer (mol/l)	log *D*
1	6.40	0.0037	0.0163	−0.6440
2	6.60	0.0085	0.0115	−0.1313
3	6.80	0.0141	0.0059	0.3784
4	7.00	0.0177	0.0023	0.8862
5	7.20	0.0192	0.0008	1.3802
6	7.40	0.0198	0.0002	1.9956

Number of observations = 6
Critical *t* value for *B*1 = 2.78 (95% two-sided and 4 degrees of freedom); *t* values below the critical level are marked with an asterisk.

Permutations

No.	*n*	*m*	*x*	log *K* (mean value)	*B*1 (slope coeff.)	Student's *t*
1	1	0	1	− 5.9487	1.613	3.860×10^1
2	2	0	1	−12.5289	6.361×10^{-1}	1.611×10^1
3	1	1	1	− 5.6289	1.636	4.143×10^1
4	2	1	1	−12.1958	6.759×10^{-1}	1.881×10^1
5	1	2	1	− 5.2958	1.675	4.663×10^1
6	2	2	1	−11.8486	7.340×10^{-1}	2.299×10^1
7	1	0	2	− 5.1387	1.270	1.149×10^1
8	2	0	2	−11.7190	2.930×10^{-1}	*2.729
9	1	1	2	− 4.8190	1.293	1.204×10^1
10	2	1	2	−11.3859	3.329×10^{-1}	3.264
11	1	2	2	− 4.4859	1.332	1.307×10^1
12	2	2	2	−11.0387	3.910×10^{-1}	4.143

polymeric species in the organic phase may lead to an increase in slope. Our extractions with VERSATIC under comparable conditions gave slopes considerably higher than 2. We therefore believe that for octanoic acid the monomeric compositions fit better with all known facts, whereas VERSATIC 10 forms mainly polymeric (dimeric) complexes.

At a very high loading (0.2 M Co vs. 0.5 M octanoic acid) the most probable complexes were found to be (in this sequence): $(CoA_2)_2$, CoA_2, $CoA_2.2\,HA$ and $(CoA_2.2\,HA)_2$. In this case we cannot rule out the dimeric compositions, since the simple reasoning given above will certainly not be valid under these extreme conditions. At these high loadings it was observed that the complex precipitated from the organic layer at a log D of about 1.0, i.e. at a cobalt concentration in the organic layer of about 0.18 M. The precipitate had a composition (after thorough drying at 50°C and 133 Pa) of CoA_2.

Table 3

Extraction of 0.199 M Ni with 0.5 M VERSATIC. Background 0.3 M $MgSO_4$

Exp. no.	pH	Metal in org. layer (mol/l)	Metal in inorg. layer (mol/l)	log *D*
1	6.00	0.0300	0.1690	−0.7508
2	6.20	0.0470	0.1520	−0.5097
3	6.40	0.0624	0.1366	−0.3403
4	6.60	0.0770	0.1220	−0.1999
5	6.80	0.0893	0.1097	−0.0894
6	7.00	0.0995	0.0995	0.0000

Number of observations = 6
Critical *t* value for *B*1 = 2.78 (95% two-sided and 4 degrees of freedom); *t* values below the critical level are marked with an asterisk.

Permutations

No.	*n*	*m*	*x*	log *K* (mean value)	*B*1 (slope coeff.)	Student's *t*
1	1	0	1	− 6.4821	-2.285×10^{-1}	3.412
2	2	0	1	−12.5725	−1.097	1.604×10^{1}
3	1	1	1	− 6.0725	-9.722×10^{-2}	*1.421
4	2	1	1	−12.0542	-7.971×10^{-1}	1.283×10^{1}
5	1	2	1	− 5.5542	2.028×10^{-1}	3.265
6	2	2	1	−11.3527	-1.236×10^{-1}	7.505
7	1	0	2	− 6.0309	-4.807×10^{-1}	1.392×10^{1}
8	2	0	2	−12.1213	−1.349	3.748×10^{1}
9	1	1	2	− 5.6213	-3.494×10^{-1}	9.704
10	2	1	2	−11.6030	−1.049	3.518×10^{1}
11	1	2	2	− 5.1030	-4.938×10^{-2}	*1.655
12	2	2	2	−10.9015	-3.758×10^{-1}	1.507×10^{1}

Table 4

Extraction of 0.204 M Ni with 1.00 M VERSATIC. Background 0.3 M $MgSO_4$

log *D*	pH	Metal in org. layer (mol/l)	log *K* for *n*, *m*, *x*			
			1,2,2	1.5,2,2	2,2,2	1.5,1,2
−0.8800	5.50	0.0238	−5.2190	−7.8758	−10.5298	−8.0592
−0.6900	5.60	0.0346	−5.1871	−7.8851	−10.5786	−8.0846
−0.5200	5.70	0.0473	−5.1567	−7.8935	−10.6237	−8.1133
−0.3600	5.80	0.0620	−5.1211	−7.8929	−10.6570	−8.1389
−0.2100	5.90	0.0778	−5.0813	−7.8876	−10.6801	−8.1622
−0.0800	6.00	0.0926	−5.0502	−7.8893	−10.7098	−8.1945
−0.0600	6.10	0.1090	−4.9997	−7.8672	−10.7097	−8.2102
−0.1800	6.20	0.1228	−4.9642	−7.8613	−10.7261	−8.2397
−0.3000	6.30	0.1359	−4.9243	−7.8496	−10.7337	−8.2654
−0.4200	6.40	0.1478	−4.8821	−7.8349	−10.7363	−8.2886
−0.5200	6.50	0.1567	−4.8627	−7.8469	−10.7698	−8.3318
−0.6100	6.60	0.1638	−4.8556	−7.8735	−10.8207	−8.3854

Table 5

Extraction of 0.05 M Co with 1.00 M octanoic acid in kerosene. Background 0.5 M Na_2SO_4

Exp. no.	pH	Metal in org. layer (mol/l)	Metal in inorg. layer (mol/l)	log *D*
1	5.42	0.0210	0.0300	−0.1549
2	5.55	0.0320	0.0190	0.2264
3	5.89	0.0437	0.0073	0.7772
4	6.10	0.0500	0.0021	1.3767
5	6.21	0.0510	0.0021	1.3854
6	5.42	0.0190	0.0300	−0.1984
7	5.55	0.0300	0.0190	0.1984
8	5.89	0.0420	0.0073	0.7599
9	6.10	0.0480	0.0021	1.3590
10	6.21	0.0490	0.0021	1.3680

Number of observations = 10
Critical *t* value for B1 = 2.31 (95% two-sided and 8 degrees of freedom); *t* values below the critical level are marked with an asterisk.

Permutations

No.	*n*	*m*	*x*	log *K* (mean value)	*B*1 (slope coeff.)	Student's *t*
1	1	0	1	− 4.9652	1.014	1.040×10^{1}
2	2	0	1	−10.6222	4.013×10^{-2}	*4.065×10^{-1}
3	1	1	1	− 4.7882	1.040	1.054×10^{1}
4	2	1	1	−10.4261	8.628×10^{-2}	*8.550×10^{-1}
5	1	2	1	− 4.5921	1.086	1.076×10^{1}
6	2	2	1	−10.2094	1.550×10^{-1}	*1.487
7	1	0	2	− 4.3969	7.809×10^{-1}	9.041
8	2	0	2	−10.0540	-1.929×10^{-1}	*2.216
9	1	1	2	− 4.2200	8.070×10^{-1}	9.269
10	2	1	2	− 9.9578	-1.467×10^{-1}	*1.661
11	1	2	2	− 4.0238	8.532×10^{-1}	9.652
12	2	2	2	− 9.6411	-7.799×10^{-2}	*8.610×10^{-1}

Trivalent iron

The complexes formed when trivalent iron is extracted with a large excess of VERSATIC acid (see Table 6) all have in common that the stoichiometrically expected number of carboxylate groups is present. Four out of five of the complexes are dimers, which only differ in the number of solvating acid molecules. The possible complexes as indicated by our evaluation then are $(FeV_3.3\ HV)_2$, $(FeV_3.2\ HV)_2$, $(FeV_3.HV)_2$, $(FeV_3)_2$, and $(FeV_3.3\ HV)_3$, in decreasing order of probability.

When a more concentrated trivalent iron solution is extracted with a more dilute VERSATIC solution (Table 7), three complexes lie within the limits of probability, viz. $(FeV_2)_3$, $(FeV_3.HV)_2$ and $(FeV_3.HV)_3$. Of these we prefer the first, because a good value for Student's t-factor is combined with the lowest factor for the slope coefficient.

Table 6

Extraction of 0.02 M Fe(III) with 1.00 M VERSATIC 10 in kerosene. Background 0.5 M Na_2SO_4

Exp. no.	pH	Metal in org. layer (mol/l)	Metal in inorg. layer (mol/l)	log *D*
1	2.70	0.0030	0.0168	-0.7482
2	2.76	0.0044	0.0150	-0.5326
3	2.80	0.0060	0.0134	-0.3490
4	2.84	0.0074	0.0119	-0.2063
5	2.90	0.0107	0.0098	0.0382
6	2.90	0.0121	0.0080	0.1797
7	3.00	0.0134	0.0066	0.3076
8	3.06	0.0152	0.0042	0.5586
9	3.25	0.0179	0.0012	1.1737

Number of observations = 9
Critical *t* value for *B*1 = 2.36 (95% two-sided and 7 degrees of freedom); *t* values below the critical level are marked with an asterisk.

Permutations

No.	*n*	*m*	*x*	log *K* (mean value)	*B*1 (slope coeff.)	Student's *t*
1	1	0	1	-2.7127	2.473	1.527×10^{1}
2	2	0	1	-5.4678	1.492	9.127
3	3	0	1	-8.2183	5.255×10^{-1}	3.161
4	1	1	1	2.5555	2.492	1.524×10^{1}
5	2	1	1	-5.3061	1.525	9.176
6	3	1	1	-8.0521	5.723×10^{-1}	3.364
7	1	2	1	-2.3939	2.525	1.519×10^{1}
8	2	2	1	-5.1399	1.572	9.243
9	3	2	1	-7.8811	6.334×10^{-1}	3.616
10	1	3	1	-2.2276	2.572	1.512×10^{1}
11	2	3	1	-4.9689	1.633	9.325
12	3	3	1	-7.7054	7.095×10^{-1}	3.910
13	1	0	2	-1.8322	1.773	1.686×10^{1}
14	2	0	2	-4.5873	7.933×10^{-1}	7.518
15	3	0	2	-7.3379	-1.738×10^{-1}	*1.637
16	1	1	2	-1.6751	1.793	1.699×10^{1}
17	2	1	2	-4.4256	8.261×10^{-1}	7.784
18	3	1	2	-7.1716	-1.270×10^{-1}	*1.185
19	1	2	2	-1.5134	1.826	1.721×10^{1}
20	2	2	2	-4.2594	8.729×10^{-1}	8.143
21	3	3	2	-7.0007	-6.589×10^{-2}	*6.051×10^{-1}
22	1	3	2	-1.3472	1.872	1.747×10^{1}
23	2	3	2	-4.0884	9.341×10^{-1}	8.577
24	3	3	2	-6.8249	1.014×10^{-2}	*9.103×10^{-2}
25	1	0	3	-1.4970	1.540	1.344×10^{1}
26	2	0	3	-4.2521	5.602×10^{-1}	4.903
27	3	0	3	-7.0027	-4.069×10^{-1}	3.578
28	1	1	3	-1.3399	1.560	1.365×10^{1}
29	2	1	3	-4.0905	5.930×10^{-1}	5.215
30	3	1	3	-6.8365	-3.601×10^{-1}	3.183
31	1	2	3	-1.1783	1.593	1.401×10^{1}
32	2	2	3	-3.9242	6.398×10^{-1}	5.655
33	3	2	3	-6.6655	-2.990×10^{-1}	2.652
34	1	3	3	-1.0120	1.639	1.449×10^{1}
35	2	3	3	-3.7533	7.009×10^{-1}	6.218
36	3	3	3	-6.4898	-2.229×10^{-1}	*1.978

Table 7

Extraction of 0.1 M Fe(III) with 0.50 M VERSATIC 10 in kerosene. Background 0.4 M Na_2SO_4

Exp. no.	pH	Metal in org. layer (mol/l)	Metal in inorg. layer (mol/l)	log D
1	2.35	0.0027	0.1039	1.5853
2	2.57	0.0121	0.0923	-0.8824
3	2.60	0.0161	0.0887	0.7411
4	2.60	0.0188	0.0806	-0.6322
5	2.60	0.0205	0.0793	-0.5875
6	2.67	0.0216	0.0756	0.5441
7	2.65	0.0242	0.0728	-0.4783
8	2.66	0.0258	0.0710	-0.4396
9	2.70	0.0276	0.0685	-0.3948
10	2.70	0.0297	0.0652	-0.3415
11	2.70	0.0323	0.0638	-0.2956
12	2.79	0.0355	0.0609	-0.2344
13	2.76	0.0373	0.0577	-0.1895
14	2.80	0.0430	0.0529	-0.0900
15	2.80	0.0459	0.0502	-0.0389
16	2.84	0.0491	0.0471	0.0181
17	2.81	0.0505	0.0437	0.0628
18	2.85	0.0534	0.0403	0.1222
19	2.90	0.0565	0.0376	0.1769
20	2.93	0.0605	0.0339	0.2516

Number of observations = 20.
Critical t value for $B1$ = 2.10 (95% two-sided and 18 degrees of freedom); t values below the critical level are marked with an asterisk.

Permutations

No.	n	m	x	log K (mean value)	$B1$ (slope coeff.)	Student's t
1	1	0	1	-2.7401	2.187	1.696×10^{1}
2	2	0	1	-5.1052	1.362×10^{-1}	1.040×10^{1}
3	3	0	1	7.4321	6.911	5.029
4	1	1	1	-2.3912	2.362	1.803×10^{1}
5	2	1	1	-4.7181	1.691	1.231×10^{1}
6	3	1	1	-6.9993	1.221	7.799
7	1	2	1	-2.0041	2.691	1.958×10^{1}
8	2	2	1	-4.2853	2.221	1.418×10^{1}
9	3	2	1	-6.5100	2.030	9.858
10	1	3	1	-1.5713	3.221	2.057×10^{1}
11	2	3	1	-3.7960	3.030	1.471×10^{1}
12	3	3	1	-5.9460	3.259	1.034×10^{1}
13	1	0	2	-2.1140	1.092	1.375×10^{1}
14	2	0	2	4.4790	2.672×10^{-1}	3.052
15	3	0	2	6.8059	-4.040×10^{-1}	3.808
16	1	1	2	-1.7650	1.267	1.447×10^{1}
17	2	1	2	-4.0919	5.959×10^{-1}	5.617
18	3	1	2	6.3732	1.263×10^{-1}	*8.819×10^{-1}
19	1	2	2	-1.3779	1.595	1.504×10^{1}
20	2	2	2	3.6592	1.126	7.862
21	3	2	2	-5.8839	9.356×10^{-1}	4.406
22	1	3	2	-0.9452	2.126	1.484×10^{1}
23	2	3	2	-3.1699	1.935	9.115
24	3	3	2	-5.3198	2.164	6.399
25	1	0	3	-1.8636	7.273×10^{-1}	1.007×10^{1}
26	2	0	3	-4.2287	-9.782×10^{-2}	*1.182
27	3	0	3	-6.5555	-7.691×10^{-1}	7.312
28	1	1	3	-1.5147	9.021×10^{-1}	1.090×10^{1}
29	2	1	3	-3.8415	2.308×10^{-1}	2.195
30	3	1	3	-6.1228	-2.387×10^{-1}	*1.626
31	1	2	3	-1.1275	1.230	1.170×10^{1}
32	2	2	3	-3.4088	7.613×10^{-1}	5.187
33	3	2	3	-5.6335	5.706×10^{-1}	2.596
34	1	3	3	-0.6948	1.761	1.200×10^{1}
35	2	3	3	-2.9195	1.570	7.144
36	3	3	3	-5.0694	1.799	5.156

DISCUSSION

In most experiments considerable amounts of Mg^{2+} and SO_4^{2-} were present in the aqueous phase, since conditions had been chosen to resemble those met with in a practical problem under investigation. The presence of these ions might cause complications in interpreting the results of the extractions.

First, Mg^{2+} is extracted by VERSATIC 10 in the higher pH ranges. At pH 7.0 the log D_{Mg} values from a 0.5 M $MgSO_4$ solution against 0.5, 1 and 2 M VERSATIC 10 are - 1.8, - 1.0 and - 0.4, respectively. At this level the amount of extractant used to complex Mg in the experiment of Table 3 is less than 5 %, and hence we chose 7.0 to be the highest pH value used in the calculation in this case. At pH 6.4 the log D_{Mg} values from a 0.5 M $MgSO_4$ solution against 0.5, 1 and 2 M VERSATIC 10 are < -4, < -4, and ca. - 2, respectively. In the experiments presented in Table 1, 6.4 was therefore chosen as a safe maximum pH for the calculations. Similar criteria were applied in other experiments which are not tabulated here.

The second complication might arise from complexing of the metals with sulfate anions in the aqueous phase. Flett[6] observed that zinc forms strong complexes with sulfate giving undissociated $ZnSO_4$ and the anion $[Zn(SO_4)_2]^{2-}$, and he calculated the association constants. In this case these associations exert a clear influence upon the extraction of Zn with naphthenic acid. Ashbrook[7] found that cobalt in the presence of sulfate ions shows a degree of association to $CoSO_4$, and also found an influence upon the extraction, though less pronounced than in the case studied by Flett.

A correction term, analogous to that given by Flett[6], might be inclueded in eq. 6. In the study of a single log D/pH curve at constant sulfate concentration (as is done in this work) the experimental conditions should lead to a constant value for this correction term, and this would therefore not affect the basic calculations. The extent of sulfate complexing, it was found, can safely be neglected, since the variation of pH_{50} with $\log[SO_4^{2-}]$ was virtually nil (Table 8).

From the results given it appears that the parameters n (the number of covalently bound carboxylate groups) and x (the degree of polymerization of the organic complex) can be determined unambiguously in most cases. The parameter m (the number of solvating acid molecules per metal ion), however, is not always strictly defined (i.e. affects the calculations to

Table 8

Influence of SO_4^{2-} concentration on extraction of Fe(III), Ni and Co with VERSATIC 10. Metals solutions made up from (Mg + metal) sulfates.

Metal ion	Concentration (mol/l)	Versatic (mol/l)	SO_4^{2-} (mol/l)	log SO_4^{2-}	pH_{50}
Fe(III)	0.005	2	1.50	0.176	2.2
			0.20	−0.699	2.2
Ni(II)	0.05	1	1.45	0.161	5.97
			0.45	−0.347	5.92
Co(II)	0.02	1	1.48	0.170	6.31
			0.48	−0.319	6.28

a lesser extent). Although this mathematical insufficiency might only be due to inaccuracy of measurement, it could also indicate the simultaneous existence of several complexes. Obviously these would then mainly differ with respect to the number of solvating ligands, rather than with respect to the - more important - number of covalently bound groups. In the discussion below such different complexes are only referred to in a few cases, only the complexes giving the best fit are usually mentioned.

When large excesses of VERSATIC acid are available and the nickel concentration in the aqueous layer is relatively low, this metal (in complete agreement with literature data[1]) tends to form complexes $(NiV_2.2\ HV)_2$. At smaller ratios R it was found that complexes with less than two covalently bound carboxylate groups per nickel atom are formed. This apparent violation of the bivalency of nickel may be most easily explained by assuming that the remaining valencies are occupied by covalent bonds with an anion X, the nature of which is not revealed by the present procedure. Then the real formulae would be $Ni_2V_3X.4\ HV$ and $(NiVX.2\ HV)_2$, respectively. As regards the nature of the ligand X we assume that a 'real' anion from the solution (e.g. sulfate) would probably render the complex much less readily extractable than it is in practice. A logical assumption is that X = OH. The structure of the complexes might then be a twinned octahedron, with one or two hydroxyl groups as bridges. This is also the reason for rejecting the formula NiV.HV (or, for that matter, NiVOH.HV) for the nickel complex obtained at low R: this complex is covalently saturated, but co-ordinately unsaturated and, furthermore, would have a rather pronounced 'hydroxide' character, which in our opinion would mean a poor extractability.

Co-extracted water can hardly make a sizeable contribution as a ligand. It can be seen from Table 9 and 10 that the amount of co-extracted water is less than stoichiometric both for low and high loadings. The gradual increase in water co-extraction is probably due to the emulsifying action of the metal VERSATIC salts.

The ambiguity of m referred to above is not very marked for our nickel experiments. In the case of cobalt however it is hardly possible to define the parameter for extraction with VERSATIC. It is highly likely that in this specific case several complexes with different numbers of solvating acid molecules are present simultaneously. This is confirmed by the fact that during the extraction of cobalt with VERSATIC 10 the colour of the organic solution shifts from a distinct pink (typical of octahedral co-ordination[8]) at low loadings to purple and ultimately bluish at higher loadings. At very high loadings the solution is dark blue (typical of tetrahedral co-ordination[8]). It has also been observed[9] that in the extraction of cobalt with

Table 9

Co-extraction of water in the extraction of nickel with 1.0 M VERSATIC 10. Values corrected for solubility of water in VERSATIC solution. Karl Fischer titrations. (^{x} Checked and confirmed by GLC).

Org. Ni. conc. (mol/l)	Org. H_2O conc. (Karl Fischer) (mol/l)	Corrected org. H_2O conc. (mol/l)	$\frac{H_2O_{org\ (corr.)}}{Ni_{org}}$
—	0.020	—	—
0.002	0.024	0.004	2
0.0056	0.025	0.005	0.9
0.009	0.029	0.009	1
0.011	0.030^x	0.01	0.9
0.016	0.026	0.006	0.4

Table 10

Co-extraction of water in the extraction of nickel with 0.5 M VERSATIC 10. Values corrected for solubility of water in VERSATIC solution. Karl Fischer titrations.(^{x} checked and confirmed by GLC).

Org. Ni conc. (mol/l)	Org. H_2O conc. (Karl Fischer) (mol/l)	Corrected org. H_2O conc. (mol/l)	$\frac{H_2O_{org\ (corr.)}}{Ni_{org}}$
—	0.018	—	—
0.006	0.024	0.006	1
0.024	0.028	0.008	0.33
0.042	0.036^x	0.018	0.43
0.056	0.048	0.030	0.53
0.103	0.070^x	0.052	0.50

VERSATIC 911 (a grade slightly different from VERSATIC 10, with a wider molecular weight distribution) the visible spectrum shows two distinct peaks, one in the red and one in the blue region, whose ratio of magnitude shifts in favour of the blue one as the extraction proceeds. In our extraction of cobalt with octanoic acid we did not observe any colour shift, even at very high loadings. However, Crabtree and Rice[9] found that also in this case several species are present, although the solutions remained pink.

It is not easy to explain why, at high loadings, nickel and cobalt complexes with VERSATIC tend to incorporate other ligands rather than use the available solvating acid molecules, as do cobalt-octanoic acid complexes. Besides being heavily branched, VERSATIC is a considerably weaker acid than octanoic acid. Whereas the latter has an acid dissociation constant of 4.89[10], the pK_a of VERSATIC 911 is about 7.14[7], and we see no reason why VERSATIC 10 should differ greatly from VERSATIC 911 in this respect. A comparison of the results pertaining to VERSATIC 10 and octanoic acid suggests that the latter, stronger, acid tends to form monomeric complexes whereas the weaker VERSATIC acid mainly forms dimeric complexes. On the other hand, Fletcher and Flett[1] found a dimeric structure for the cobalt-naphthenic acid complex, while naphthenic acid is about as strong as a normal aliphatic fatty acid[11]. In this context it is interesting to note that the slopes found by Fletcher and Flett[11] for the cobalt extractions were almost exactly 2.0, whereas for VERSATIC extractions under comparable conditions slopes higher than 2 were found in the present study. It has been observed in the foregoing that a higher slope might point to polymerization in the organic phase. It could be illuminating to evaluate the numerical data of the above authors by the present method.

For iron similar reasoning to that for cobalt and nickel can be applied. This evaluation suggests that various complexes with three carboxylate groups per metal atom may exist, whereas under suitable conditions a complex $(FeV_2)_3$ may also be formed. Since the valency of the trivalent iron must be satisfied a third covalently bound ligand, most probably OH, must be present and therefore the complex may have the formula $(FeV_2OH)_3$. Tanaka et al.[4] concluded that trivalent iron is extracted by capric acid as an unsolvated trimer, but they could not distinguish between $(FeA_3)_3$ and $Fe_3(OH)_{9-p}A_p$. The latter formula is a generalized form of our $(FeV_2OH)_3$. The existence of complexes between trivalent iron and acetic acid with the formula $[\mathrm{Fe_3(OH)_2(OAc)_6}]$ OAc is known from the literature[12], and may give some support to our view.

At the moment no conclusion can be drawn with respect to the differences between Tanaka's results for iron and our own. As was the case with cobalt, they may be due to differences between the acids used, but for a complete understanding more work would be necessary.

NOMENCLATURE

M	metal ions (without a charge sign) in any possible complex
HA	acid extractant
A	anion of extractant
B	activity coefficient product
$[HA]_o$	initial extractant concentration, taken as monomer
$\gamma_{a,b}$	activity coefficient of species a in phase b
p	degree of polymerization of extractant in diluent
n	number of covalently bound extractant groups in complex
m	number of extractant molecules bound as solvation molecules
x	degree of polymerization of the extracted complex
C	extracted complex
K	equilibrium constant with respect to concentrations
K'	equilibrium constant with respect to activities

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A 3. METALS EXTRACTION WITH CARBOXYLIC ACIDS

II. Effect of temperature on the extraction of Cu, Ni, Co(II), Zn, Fe(III) and Co(III).

A.J. van der Zeeuw.

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INTRODUCTION

The effect of the extraction temperature on the liquid/liquid extraction of metals with reagents containing active hydrogen has never been investigated in much detail. Some fragmentary reports exist[1,2] which in general show that in many cases the distribution coefficient decreases with increasing temperature.

Further to our work[3] on the composition of metal complexes with VERSATIC acid a study of the effect of temperature on the distribution coefficients and complex compositions in these systems is now reported.

EXPERIMENTAL

Metal solutions

Unless stated otherwise, all metal solutions were 0.05 M. A sulfate background concentration of approximately 0.5 M was used, either as Na_2SO_4 or as $(NH_4)_2SO_4$. The Co(III) solution was prepared as follows: a stock solution 0.15 M in Co(II) and 0.075 M in H_2SO_4 was made ammoniacal to pH 9.5 and oxidized in an autoclave with air at 80° C for 4 h. The oxidation level was then 100 %, as confirmed by the absence of cobalt extraction with LIX 63[x]. Then the solution was diluted with water to about 0.05 M Co, 0.5 mol/l $(NH_4)_2SO_4$ was added and the pH was brought down to 2.41 by the addition of a small amount of concentrated H_2SO_4.

Extractant solutions

The extractant used was VERSATIC 10. It was mostly used as a 1 M solution in low-aromatic kerosene. Exceptions are indicated in the tables and figures.

Apparatus

A cylindrically-shaped, double-walled stirred glass vessel was used. It was specially designed to mix very effectively at low stirrer speeds. The vessel was connected to a thermostatted bath, which allowed temperature control to within 0.5° C.

Procedure

In the preliminary experiments the solutions (after a rough adjustment of the pH of the aqueous layer to the desired value) were mixed at 20 or 25° C for 5 min, which in all cases proved sufficient to reach equilibrium. After settling for 10 min the two layers were sampled and the pH of the aqueous layer was carefully determined. This was done at the extraction temperature, with reference to buffer solutions brought to the same temperature. Then, without any other modification, the temperature of the solution was increased to the next desired value and the procedure repeated.

In the complete extraction experiments with Fe(III) and Co(III) neutralization was carried out during mixing by addition of 25 % aq. NH_3 at a rate of 0.1 ml/min with the aid of a Braun depletion pump. This addition was continued for a predetermined period and then stopped, mixing being continued for 5 min. After 10 min settling the layers were sampled and the pH determined as described above. The neutralization was resumed for another predetermined period, and so on to complete extraction. Metal analyses were performed by atomic absorption spectrophotometry as described in Part I.[3]

RESULTS AND DISCUSSION

Table 1 shows that for Cu, Ni, Co(II) and Zn the distribution coefficient changes only marginally when the extraction temperature is varied between 20 and 80° C. The extraction of Fe(III), however, is strongly affected by the temperature, as will be obvious from Table 2. Hence complete Fe(III) extractions were done at 20 and 60° C and the results were evaluated using

Table 1

Extraction of Cu, Ni, Co(II) and Zn with VERSATIC. Preliminary results.

Metal	Temp.	pH	log *D*	pH	log *D*	pH	log *D*
Cu	25	4.15	-0.68	4.24	-0.01	4.38	0.24
	40	3.91	-0.65	4.21	+0.01	4.23	0.25
	60	3.80	-0.60	4.13	+0.03	4.18	0.26
	80	3.80	-0.51	4.06	+0.06	4.20	0.28
Ni	25	5.88	-0.76	5.95	-0.52	6.12	-0.03
	40	5.71	-0.73	5.86	-0.51	6.08	0.0
	60	5.67	-0.73	5.83	-0.51	6.02	0.0
	80	5.54	-0.72	5.79	-0.51	5.93	0.01
Co(II)	25	6.05	-0.84	6.20	0.53		
	40	5.80	-0.82	6.00	0.58	6.34	+0.08
	60	5.79	-0.79	5.75	0.52	6.18	+0.10
	80	5.64	-0.87	5.74	0.62	6.05	+0.05
Zn	20	5.47	-0.20				
	40	5.36	-0.22				
	60	5.19	-0.20				
	80	4.97	-0.22				

Table 2

Extraction of Fe(III) with VERSATIC

Temperature	pH	Log *D*
25	2.54	-0.82
42	2.39	-0.37
60	2.57	-0.13
80	2.63	+0.15
25	2.62	-0.36
42	2.69	-0.14
60	2.80	+0.04
80	2.86	+0.31
25	2.81	-0.17
41	2.70	+0.07
60	2.82	+0.37
80	2.82	+0.60
25	2.18	-1.14
81	2.10	-0.30
25[a]	—	-0.71
25[b]	2.09	-0.97

[a] Solution cooled down overnight and stirred for 10 min next day. [b] Same solution, after 3 h additional stirring.

the method described previously[3] (see fig. 1). It was calculated that the most probable complex compositions occurring in the extraction of Fe(III) with a large excess of VERSATIC 10 (short: HV) at 20° C are (in this order): $(FeV_3.2\ HV)_2$, $(FeV_3.HV)_2$, $(FeV_3)_2$ and $(FeV_3.3\ HV)_3$; see Table 3 and also the previous paper.[3]

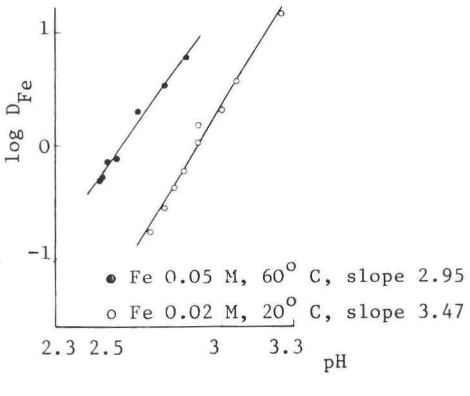

Fig. 1

Extraction of Fe(III) with 1 M VERSATIC 10 in kerosene, Na_2SO_4 0.5 M.

Table 3

Extraction of 0.02 M Fe(III) with 1.00 M VERSATIC 10 at 20° C (background: 0.5 M Na_2SO_4)

Exp. no.	pH	Metal in org. layer (mol/l)	Metal in inorg. layer (mol/l)	log *D*
1	2.70	0.0030	0.0168	-0.7482
2	2.76	0.0044	0.0150	-0.5326
3	2.80	0.0060	0.0134	-0.3490
4	2.84	0.0074	0.0119	-0.2063
5	2.90	0.0107	0.0098	0.0382
6	2.90	0.0121	0.0080	0.1797
7	3.00	0.0134	0.0066	0.3076
8	3.06	0.0152	0.0042	0.5586
9	3.25	0.0179	0.0012	1.1737

Number of observations = 9
Critical *t* value for *B*1 = 2.36 (95% two-sided and 7 degrees of freedom); *t* values below the critical level are marked with an asterisk.

Permutations

No.	*n*	*m*	*x*	log *K* (mean value)	*B*1 (slope coeff.)	Student's *t*
1	1	0	1	-2.7127	2.473	1.527×10^{1}
2	2	0	1	-5.4678	1.492	9.127
3	3	0	1	-8.2183	5.255×10^{-1}	3.161
4	1	1	1	-2.5555	2.492	1.524×10^{1}
5	2	1	1	-5.3061	1.525	9.176
6	3	1	1	-8.0521	5.723×10^{-1}	3.364
7	1	2	1	-2.3939	2.525	1.519×10^{1}
8	2	2	1	-5.1399	1.572	9.243
9	3	2	1	7.8811	6.334×10^{-1}	3.616
10	1	3	1	2.2276	2.572	1.512×10^{1}
11	2	3	1	-4.9689	1.633	9.325
12	3	3	1	-7.7054	7.095×10^{-1}	3.910
13	1	0	2	-1.8322	1.773	1.686×10^{1}
14	2	0	2	-4.5873	7.993×10^{-1}	7.518
15	3	0	2	-7.3379	-1.738×10^{-1}	*1.637
16	1	1	2	-1.6751	1.793	1.699×10^{1}
17	2	1	2	-4.4256	8.261×10^{-1}	7.784
18	3	1	2	-7.1716	-1.270×10^{-1}	*1.185
19	1	2	2	-1.5134	1.826	1.721×10^{1}
20	2	2	2	-4.2594	8.729×10^{-1}	8.143
21	3	2	2	-7.0007	-6.589×10^{-2}	*6.051×10^{-1}
22	1	3	2	-1.3472	1.872	1.747×10^{1}
23	2	3	2	-4.0884	9.341×10^{-1}	8.577
24	3	3	2	-6.8249	1.014×10^{-2}	*9.103×10^{-2}
25	1	0	3	-1.4970	1.540	1.344×10^{1}
26	2	0	3	-4.2521	5.602×10^{-1}	4.903
27	3	0	3	-7.0027	-4.069×10^{-1}	3.578
28	1	1	3	-1.3399	1.560	1.365×10^{1}
29	2	1	3	-4.0905	5.930×10^{-1}	5.215
30	3	1	3	-5.8365	-3.601×10^{-1}	3.183
31	1	2	3	-1.1783	1.593	1.401×10^{1}
32	2	2	3	-3.9242	6.398×10^{-1}	5.655
33	3	2	3	-6 6655	2.990×10^{-1}	2.652
34	1	3	3	-1.0120	1.639	1.449×10^{1}
35	2	3	3	-3.7533	7.009×10^{-1}	6.218
36	3	3	3	-6.4898	-2.229×10^{-1}	*1.978

The slope of the log D/pH plot is 3.47 (Fig. 1), i.e. higher than 3, which suggests the possibility of polymerization of the complex.[4]

According to this evaluation, at higher temperatures monomeric complexes such as FeV_3, $FeV_3.HV$ and $FeV_3.2\ HV$ may be formed, although some polymeric species cannot be rules out (see Table 4). In particular the formation of the first complex is highly probable. The slope of the log D/pH plot is 2.95 . This value, very close to 3, suggests complexes of a monomeric nature.

Table 4

Extraction of 0.05 M Fe(III) with 1.00 M VERSATIC 10 at 60° C (background: 0.5 M Na_2SO_4)

Exp. no.	pH	Metal in org. layer (mol/l)	Metal in inorg. layer (mol/l)	log *D*
1	2.49	0.0168	0.0330	-0.2932
2	2.50	0.0176	0.0322	-0.2623
3	2.52	0.0211	0.0290	-0.1381
4	2.56	0.0210	0.0272	-0.1123
5	2.65	0.0330	0.0168	0.2932
6	2.76	0.0370	0.0113	0.5151
7	2.85	0.0400	0.0068	0.7696

Number of observations = 7
Critical *t* value for *B*1 = 2.57 (95% two-sided and 5 degrees of freedom); *t* values below the critical level are marked with an asterisk.

Permutations

No.	*n*	*m*	*x*	log *K* (mean value)	*B*1 (slope coeff.)	Student's *t*
1	1	0	1	2.3519	1.966	1.256×10^{1}
2	2	0	1	4.8020	1.013	6.292
3	3	0	1	7.2394	9.594×10^{-2}	*5.676×10^{-1}
4	1	1	1	2.1834	2.013	1.250×10^{1}
5	2	1	1	4.6208	1.095	6.483
6	3	1	1	7.0448	2.163×10^{-1}	*1.198
7	1	2	1	2.0022	2.095	1.240×10^{1}
8	2	2	1	-4.4262	1.216	6.737
9	3	2	1	-6.8362	3.791×10^{-1}	*1.934
10	1	3	1	-1.8077	2.216	1.227×10^{1}
11	2	3	1	4.2176	1.379	7.036
12	3	3	1	-6.6127	5.887×10^{-1}	2.725
13	1	0	2	1.7029	1.429	1.481×10^{1}
14	2	0	2	4.1529	4.768×10^{-1}	4.752
15	3	0	2	6.5903	4.411×10^{-1}	4.115
16	1	1	2	-1.5344	1.476	1.472×10^{1}
17	2	1	2	3.9717	5.588×10^{-1}	5.217
18	3	1	2	6.3957	-3.207×10^{-1}	2.734
19	1	2	2	1.3532	1.558	1.455×10^{1}
20	2	2	2	3.7772	6.792×10^{-1}	5.788
21	3	2	2	6.1871	1.580×10^{-1}	*1.201
22	1	3	2	1.1586	1.679	1.431×10^{1}
23	2	3	2	3.5685	8.420×10^{-1}	6.403
24	3	3	2	5.9636	5.164×10^{-2}	*3.441×10^{-1}
25	1	0	3	-1.4449	1.250	1.533×10^{1}
26	2	0	3	3.8949	2.977×10^{-1}	3.516
27	3	0	3	6.3323	-6.202×10^{-1}	6.858
28	1	1	3	1.2764	1.297	1.532×10^{1}
29	2	1	3	3.7137	3.797×10^{-1}	4.199
30	3	1	3	6.1377	-4.998×10^{-1}	5.024
31	1	2	3	1.0952	1.379	1.526×10^{1}
32	2	2	3	3.5192	5.001×10^{-1}	5.027
33	3	2	3	5.9291	-3.370×10^{-1}	2.995
34	1	3	3	0.9006	1.500	1.508×10^{1}
35	2	3	3	3.3105	6.629×10^{-1}	5.892
36	3	3	3	-5.7056	-1.274×10^{-1}	*9.793×10^{-1}

In this respect it is interesting to note that on cooling a solution from 80 to 25° C log D_{Fe} decreases and ultimately reaches a value very close to the original one at 25°C (Table 2). These facts together suggest that the change (increase) in distribution coefficient is caused by a reversible change in complex composition. In the case of Fe(III) the general reaction would then be:

$$(FeV_3.x\ HV)_y \underset{-\,T}{\overset{+\,T}{\rightleftarrows}} y\ \ FeV_3.\ x\ HV$$

or a simple change from a polymeric into a monomeric complex and vice versa. The same might happen to acetates and propionates of palladium[5]. It is obvious, however, that not all metals that form polymeric complexes at room temperature, such as Ni, Co and Cu[3,4] show changes in log D value at higher temperatures. It would be interesting to know whether in these cases the complex composition changes with temperature. But here the present method[3] cannot be used, the only variables taken into account being extractant concentration, metal concentration, log D and pH.

A very interesting case of increase in distribution coefficient with rising temperature is the extraction of trivalent cobalt with a large excess of VERSATIC. The results of extraction experiments at 20 and 80°C are plotted in Fig. 2, and reported and evaluated in Tables 5 and 6. The slope of the log D/pH plot at 20° C is 0.90, which is considerably less than the stoichiometrically expected value of 3 and suggests that at room temperature Co(III) forms complexes with less than 3 carboxylate groups. In fact the computer evaluation (Table 6) shows that four complexes lie within the limits of probability, viz. (in this order) CoV.3 HV, CoV.2 HV, CoV.HV and CoV. As was observed in our previous work[3] such an apparent violation of the valency of the metal is explained very easily by assuming the presence of ligand X, the nature of which is not indicated by the evaluation procedure, but which is possibly OH. This would change the formulae into: $CoV(OH)_2.0\text{-}3\ HV$. This high percentage of non-organic ligands would also account for the rather poor extractability of Co(III) as compared with Co(II). Two points of Co(II) extraction, measured under comparable circumstances and indicated in Fig. 2, illustrate that at room temperature Co(III) is about 100 times more difficult to extract than Co(II).

Table 5

Extraction of 0.05 M Co(III) with 2.00 M VERSATIC 10 at 80° C. Background 0.5 M $(NH_4)_2SO_4$

Exp. no.	pH	Metal in org. layer (mol/l)	Metal in inorg. layer (mol/l)	log *D*
1	5.92	0.0042	0.0490	−1.6069
2	6.15	0.0180	0.0340	−0.2762
3	6.60	0.0420	0.0110	0.5819
4	6.89	0.0500	0.0049	1.0088
5	7.00	0.0540	0.0027	1.3010
6	7.24	0.0570	0.0014	1.6097
7	7.31	0.0550	0.0007	1.8953

Number of observations = 7

Critical *t* value for *B*1 = 2.57 (95% two-sided and 5 degrees of freedom); *t* values below the critical level are marked with an asterisk.

Permutations

No.	*n*	*m*	*x*	log *K* (mean value)	*B*1 (slope coeff.)	Student's *t*
1	1	0	1	− 6.0037	9.882×10^{-1}	9.651
2	2	0	1	−12.7202	1.017×10^{-3}	*9.863×10^{-3}
3	3	0	1	−19.4274	-9.771×10^{-1}	9.364
4	1	1	1	− 5.9902	1.001	9.707
5	2	1	1	−12.6974	2.283×10^{-2}	*2.188×10^{-1}
6	3	1	1	−19.3948	-9.458×10^{-1}	8.913
7	1	2	1	− 5.9674	1.022	9.802
8	2	2	1	−12.6649	5.418×10^{-2}	*5.106×10^{-1}
9	3	2	1	−19.3521	-9.044×10^{-1}	8.336
10	1	3	1	− 5.9349	1.054×10^{-2}	9.934
11	2	3	1	−12.6221	9.559×10^{-1}	*8.812×10^{-1}
12	3	3	1	−19.2987	-8.523×10^{-1}	7.642
13	1	0	2	− 5.3991	6.360×10^{-1}	1.106×10^{1}
14	2	0	2	−12.1157	-3.511×10^{-1}	6.147
15	3	0	2	−18.8229	−1.329	2.351×10^{1}
16	1	1	2	− 5.3857	6.488×10^{-1}	1.136
17	2	1	2	−12.0929	-3.293×10^{-1}	5.823
18	3	1	2	−18.7903	−1.298	2.323×10^{1}
19	1	2	2	− 5.3629	6.706×10^{-1}	1.186×10^{1}
20	2	2	2	−12.0603	-2.980×10^{-1}	5.333
21	3	2	2	−18.7475	−1.256	2.274×10^{1}
22	1	3	2	− 5.3303	7.019×10^{-1}	1.256×10^{1}
23	2	3	2	−12.0176	-2.565×10^{-1}	4.643
24	3	3	2	−18.6941	−1.204	2.193×10^{1}
25	1	0	3	− 5.1560	5.186×10^{-1}	8.519
26	2	0	3	−11.8726	-4.685×10^{-1}	7.809
27	3	0	3	−18.5797	−1.446	2.471×10^{1}
28	1	1	3	− 5.1426	5.314×10^{-1}	8.857
29	2	1	3	−11.8497	-4.467×10^{-1}	7.630
30	3	1	3	−18.5471	−1.415	2.501×10^{1}
31	1	2	3	− 5.1197	5.532×10^{-1}	9.448
32	2	2	3	−11.8172	-4.154×10^{-1}	7.340
33	3	2	3	−18.5044	−1.374	2.533×10^{1}
34	1	3	3	− 5.0872	5.845×10^{-1}	1.033
35	2	3	3	−11.7744	-3.739×10^{-1}	6.896
36	3	3	3	−18.4510	−1.321	2.559×10^{1}

In the extraction of Co(III) at 80° C the slope of the log D/pH plot is very near to 2, which suggests complexes with two carboxylic groups. In agreement with this, our evaluation, assuming that bonds not carrying acid bear OH ligands, suggests the complexes CoV_2OH, $CoV_2OH.HV$, $CoV_2OH.2\ HV$, and $CoV_2OH.3\ HV$, the first being particularly acceptable.

Table 6

Extraction of 0.05 M Co(III) with 2.00 M VERSATIC 10 at 20° C. Background 0.5 M $(NH_4)_2SO_4$

Exp. no.	pH	Metal in org. layer (mol/l)	Metal in inorg. layer (mol/l)	log *D*
1	6.41	0.0150	0.0307	−0.3110
2	6.96	0.0285	0.0133	0.3310
3	7.41	0.0353	0.0058	0.7843
4	7.95	0.0395	0.0029	1.1342
5	8.06	0.0402	0.0022	1.2618
6	8.17	0.0429	0.0017	1.4020
7	8.34	0.0433	0.0016	1.4324

Number of observations = 7
Critical *t* value for *B*1 = 2.57 (95% two-sided and 5 degrees of freedom); *t* values below the critical level are marked with an asterisk.

Permutations

No.	*n*	*m*	*x*	log *K* (mean value)	*B*1 (slope coeff.)	Student's *t*
1	1	0	1	− 6.7484	-9.870×10^{-2}	*2.156
2	2	0	1	−14.3510	−1.094	2.367×10^{1}
3	3	0	1	−21.9456	−2.086	4.442×10^{1}
4	1	1	1	− 6.7367	-9.402×10^{-2}	*2.034
5	2	1	1	−14.3313	−1.086	2.313×10^{1}
6	3	1	1	−21.9176	−2.074	4.320×10^{1}
7	1	2	1	− 6.7170	-8.603×10^{-2}	*1.832
8	2	2	1	−14.3033	−1.074	2.238×10^{1}
9	3	2	1	−21.8811	−2.059	4.168×10^{1}
10	1	3	1	− 6.6891	-7.458×10^{-2}	*1.553
11	2	3	1	−14.2668	−1.059	2.144×10^{1}
12	3	3	1	−21.8358	−2.040	3.991×10^{1}
13	1	0	2	− 6.1595	-2.065×10^{-1}	6.703
14	2	0	2	−13.7621	−1.201	3.852×10^{1}
15	3	0	2	−21.3567	−2.193	6.887×10^{1}
16	1	1	2	− 6.1478	-2.018×10^{-1}	6.470
17	2	1	2	−13.7424	−1.193	3.748×10^{1}
18	3	1	2	−21.3287	−2.182	6.654×10^{1}
19	1	2	2	− 6.1282	-1.938×10^{-1}	6.086
20	2	2	2	−13.7145	−1.182	3.605×10^{1}
21	3	2	2	−21.2922	−2.167	6.366×10^{1}
22	1	3	2	− 6.1002	-1.824×10^{-1}	5.561
23	2	3	2	−13.6779	−1.167	3.429×10^{1}
24	3	3	2	−21.2469	−2.148	6.033×10^{1}
25	1	0	3	− 5.9215	-2.424×10^{-1}	9.094
26	2	0	3	−13.5242	−1.237	4.583×10^{1}
27	3	0	3	−21.1187	−2.229	8.081×10^{1}
28	1	1	3	− 5.9099	-2.377×10^{-1}	8.805
29	2	1	3	−13.5045	−1.229	4.456×10^{1}
30	3	1	3	−21.0908	−2.218	7.799×10^{1}
31	1	2	3	− 5.8902	-2.298×10^{-1}	8.327
32	2	2	3	−13.4765	−1.218	4.283×10^{1}
33	3	2	3	−21.0543	−2.203	7.448×10^{1}
34	1	3	3	− 5.8622	-2.183×10^{-1}	7.675
35	2	3	3	−13.4400	−1.203	4.067×10^{1}
36	3	3	3	−21.0089	−2.184	7.039×10^{1}

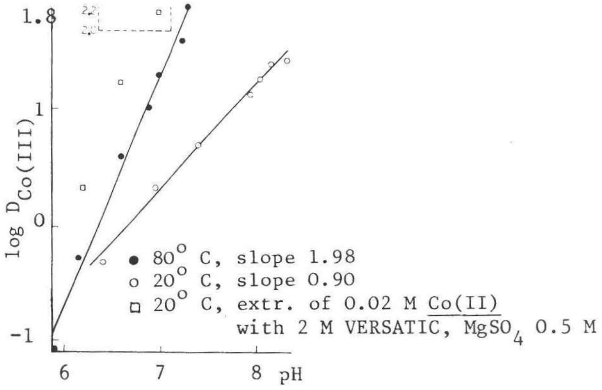

Fig. 2

Extraction of Co(III) with 2 M VERSATIC in kerosene, background 0.5 M $(NH_4)_2SO_4$

The above results suggest that in the case of Co(III) extraction the changes in the distribution coefficient may be attributed to the reaction:

$$CoV(OH)_2.x\ HV \xrightarrow{+\ T} CoV_2OH.y\ HV$$

Since, contrary to the Fe(III) case described previously, it this reaction both the character and the number of ligands changes, it might be expected that this reaction would be irreversible. It was indeed found (Table 7) that with decreasing temperature the log D value remains at its increased level.

In cobalt extraction co-extraction of ammonium need not be feared, since the ammonium salt of VERSATIC acid is hardly soluble in kerosene. Part of the VERSATIC salt will dissolve as the ammonium salt in the aqueous layer, but even at the highest pH value (8.34) this was found to be less than 5 % of the total amount present, and therefore can be neglected in the calculations. On the other hand, complexing of cobalt with NH_3 in the organic phase cannot be excluded. It was found, for example, in the extraction of bivalent cobalt with VERSATIC 9[6] and in the extraction of Co(III) with VERSATIC 911[7]. Ashbrook[8] however did not encounter such complexing in his

Table 7

Extraction of Co(III) with 1.00 M VERSATIC as a function of temperature.

Temp. ^{o} C	pH	log D
23	6.61	- 0.78
83	6.11	- 0.42
23[a]	5.99	- 0.40
23[b]	6.19	- 0.41

[a] Cooled down without stirring overnight, then stirred for 10 min.

[b] Same sample, but stirred for 4 h.

experiments with VERSATIC 911. Our measurements do not give an indication as to what will happen with trivalent cobalt. It would, however, not influence the basis of the calculation, since NH_3 would not consume extractant.

The possiblity of sulfate complexing of metal ions, especially cobalt and zinc, has been raised in the literature[8,9]. As pointed out earlier[3], there is no need to consider this in the study of a single log D/pH curve at constant sulfate concentration, since this would lead to a constant value for the correction term as given by Flett[9]. As to the effect it would have on these results it can be said that it would probably be even weaker at higher temperatures than at ambient temperature[9]. The relative unimportance of complexing in our work is confirmed by the fact that log D_{Zn} is hardly dependent on temperature in the range studied.

CONCLUSIONS

The distribution coefficients of Cu, Zn, Ni and Co(II) change only marginally, if at all, when the extraction temperature is increased from 20 to 80° C. The distribution coefficient of trivalent iron shows a considerable increase with temperature. Upon cooling, the distribution coefficient decreases again to approach its original value. Here the change is probably due to a simple reversible polymerization/depolymerization reaction:

$$(FeV_3.x\ HV)_y \underset{-\ T}{\overset{+\ T}{\rightleftarrows}} y\ FeV_3.\ x\ HV$$

At room temperature trivalent cobalt reacts with only one carboxylate group per atom. At 80° C it complexes with two carboxylate groups. The observed increase in distribution coefficient at higher temperatures might be due to the reaction:

$$\mathrm{CoV(OH)_2.x\ HV} \xrightarrow{+\ T} \mathrm{CoV_2OH.y\ HV}$$

which is irreversible, since the distribution coefficient does not decrease on cooling.

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A 4. PURIFICATION OF ZINC CALCINE LEACH SOLUTIONS BY EXCHANGE EXTRACTION WITH THE ZINC SALT OF 'VERSATIC' ACID

A.J. van der Zeeuw.

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INTRODUCTION

Zinc sulfate solutions that result from the leaching of zinc calcine with sulfuric acid generally contain appreciable amounts of contaminants. Prior to the final electrowinning of zinc these solutions have to pass through various purification steps, one of which involves the removal of iron. In recent years several methods have been proposed for this, the most commonly adopted procedures being the goethite[1] and jarosite[2-4] methods, The former uses precipitation as, nominally, FeO(OH) whereas in the jarosite procedure iron is precipitated as mixed basic iron ammonium sulfates with the general composition $(NH_4)Fe_3(SO_4)_2(OH)_6$. In both methods a more or less complete removal of contaminants such as As, Sb and Ge, the presence of which would be undesirable in the electrowinning procedure, is achieved.

Normally these iron-containing precipitates have to be dumped despite the fact that this is necessarily economically unattractive. In addition, the accumulation of large amounts of such materials containing undesirable co-precipitated compounds might well lead to environmental problems. However, the use of a liquid/liquid extraction technique could prove to be a more economical and environmentally acceptable solution to the purification problem. We have therefore investigated the removal of iron from zinc sulfate leach solutions by solvent extraction with the zinc salt of a highly-branched monocarboxylic acid, VERSATIC 10. We have also considered the fate of some valuable metals other than zinc in this extraction and the most suitable methods for handling the undesirable contaminants.

THE PURIFICATION PROBLEM

1. Composition of the zinc calcine leaching liquors

The leaching of zinc calcine with sulfuric acid is generally a two-step operation. In the first step the temperature is kept low and some 80 % of the zinc contained in the calcine in the oxide form is readily dissolved. The remaining 20 % of the zinc is left as a residue in the form of zinc ferrites, which are dissolved at higher temperatures (up to 95° C) in the second step to yield the hot acid leach solution (HAL). This solution contains substantial amounts of ferric ions which have to be removed before the two solutions can be combined and, after further purification, sent to electrowinning.

A typical HAL may have the following composition:

Zn	ca. 140 g/l
Fe	ca. 25 g/l
free H_2SO_4	ca. 40 g/l

Several other metals are also present, some of which are valuable and others detrimental. For example, cobalt and copper are present in most cases and, in the normal electrolytic zinc production process, these are removed in a separate precipitation step and the precipitates either worked or sold as valuable material. Manganese is also present, but can only be tolerated in the electrolyte up to a certain level, and therefore bleeding of spent electrolyte is usually necessary in order to avoid exceeding this level. However, since manganese cannot be tolerated in the environment to any appreciable extent, a separate additional removal step has to be used.

Arsenic, which is at least in quantity the most important, represents a number of elements including antimony and germanium that markedly decrease the current efficiencies during electrolysis, even when present in very small amounts. These elements must therefore be removed very carefully before the zinc is electrowon. In the processes known to date in which some form of precipitation is used to remove the iron, the bulk of these harmful elements are coprecipitated and thus effectively removed.

2. Statement of the problem

The basic problem therefore is to bring the HAL into a form in which it is suitable for the electrowinning of zinc. If, as proposed, the removal of iron is to be accomplished solely by a liquid/liquid extraction technique, then the following requirements should also be met:

1. The undesirable contaminants (mainly arsenic) should be removed.
2. The method used should not upset the rest of the system in terms of material balances etc.
3. The resulting aqueous zinc-sulfate-containing solution should be suitable for electrolysis.
4. The other valuable metals should not be lost.

3. Principles underlying the solution of the problem by solvent extraction

The extraction of metal ions from aqueous solutions with VERSATIC acid can in principle be represented as follows:

$$x\ \text{RCOOH} + M^{x+} \rightleftharpoons (\text{RCOO})_x M + x\ H^+$$

Although this is oversimplified, since it is known that in many cases amounts of acid in excess of the stoichiometric quantity are incorporated in the complexes as ligands, the equation clearly shows the pH dependency of the reaction. In order to shift the equilibrium sufficiently far to the right the protons must therefore be neutralized. This is most easily done by the addition of an alkali, e.g. sodium or potassium hydroxide or ammonia, preferably continuously during the extraction.

If this method is applied to a solution containing various metal ions, these are extracted consecutively in a sequence roughly given by the order of precipitation of their hydroxides in the absence of VERSATIC. For some common metals such a sequence would be:

$$Fe^{3+},\ Cu^{2+},\ Zn^{2+},\ Ni^{2+}/Co^{2+},\ Mn^{2+},\ Ca^{2+},\ Mg^{2+}$$

Most metals respond well to this procedure and even temporary precipitates of the hydroxides formed after a too rapid addition of alkali readily dissolve. The notable exceptions however are Cr^{3+}, which only forms a precipitate and is not extracted at all, and Fe^{3+}. A hydrated ferric oxide formed on overneutralization dissolves quite slowly in the VERSATIC and it is advisable to prevent its formation by a very slow continuous addition of alkali. Naturally this is hardly practicable in cases where substantial amounts of Fe^{3+} have to be extracted. Moreover, during neutralization the amount of free acid present also has to be taken into account.

Clearly, if the whole procedure were carried out as suggested above, massive amounts of "foreign" cations would be brought into the electrolyte. Apart from this being undesirable in the electrowinning process, an extensive waste of sulfuric acid would result and thus it is logical to reject this solution to the problem as being unattractive. Therefore exchange extraction using the zinc salt of VERSATIC acid as the extractant[5] has been investigated as a possible way out of the difficulties.

In the extraction sequence given above, zinc is sufficiently far removed from ferric iron to suggest that the exchange equilibrium:

$$2\ Fe^{3+}_{aq} \quad + \quad 3\ ZnV_{2\ org} \rightleftharpoons 3\ Zn^{2+}_{aq} \quad + \quad 2\ FeV_{3\ org}$$

(where aq and org represent the aqueous and organic phases respectively and V = VERSATIC) would lie well to the right. Moreover, since no true alkali would be used during the extraction, the exchange would probably occur without the intermittent liberation of metal hydroxides and therefore precipitation of ferric hydroxide should be avoided.

The VERSATIC can be re-used after stripping of the iron from the iron-loaded organic phase with a mineral acid. The recovered VERSATIC acid is then easily reconverted into its zinc salt.

EXPERIMENTAL

1. Solutions

In the various stages of our investigation three different aqueous zinc/iron solutions were used, the compositions of which are given in Table 1. Solution A was a solution of ferric sulfate and zinc sulfate and solution B was a synthetic HAL made up from ferric, zinc and manganese sulfates. Solution C was a true HAL.

Table 1

Composition of aqueous zinc/iron solutions.

Component	Content (g/1)		
	A	B	C
Fe^{3+}	19.85	25.0	25.0
Zn^{2+}	19.50	120.0	140.0
H_2SO_4	trace	10.0	40.0
As	-	-	0.3
Co	-	-	0.07
Cu	-	-	0.5
Mn	-	6.0	9.4
pH	1.0	0.8	not measured

The extractant solution (0.3 M in zinc) was prepared by dissolving the calculated amount of chemically pure ZnO in 2 M (344 g/1) VERSATIC 10 in Shell Diluent MSB 210 (a Shell hydrocarbon-type diluent of low-aromatic nature, suitable for liquid/liquid extraction) at 60° C. Later experiments have shown that zinc calcine can be used with equal success, provided an allowance is made for the content of "insoluble" zinc (the ferrites). Sulfuric acid and hydrochloric acid (both 6 N) were used for stripping.

2. Extraction and stripping

The apparatus consisted of a double-walled glass vessel with a six-bladed turbine stirrer, four baffles, a bottom sampling device and a Quickfit condenser. Water from a thermostatically controlled bath was circulated through the double wall of the vessel. The temperature was maintained at 60° C and the stirrer speed at 2000 rev/min throughout all the experiments.

The desired amount of extractant solution preheated to 60° C was added in portions to the aqueous solution in the glass vessel. After stirring for about 5 minutes the layers were allowed to settle and then analysed (see below). The stripping was done by adding the warm stripping solution to the iron-loaded organic while stirring.

3. Coprecipitation experiments

Glass beakers were used for these experiments, the precipitants being added as solids to the solutions while stirring with a magnetic stirrer. Stirring was continued for the arbitrarily chosen period of 30 minutes.

4. Analyses

With the exception of arsenic, the metals were analysed by atomic absorption spectrophotometry (Perkin-Elmer 403). The inorganic layers were first diluted as required with 0.5 N nitric acid. The organic layers were mixed with a known and suitable volume of 0.5 N nitric acid and then shaken under hot running water until completely backwashed; samples of the aqueous layer were used for the analyses. Arsenic was analysed by neutron activation.

RESULTS

1. Extraction performance

Although the reaction rates for extraction were not measured, it was observed that these were extremely high. The exchange obviously took place virtually instantaneously and no trace of iron hydroxide precipitation was observed. Settling was rapid at the temperature used.

In the stripping process it was found that the iron-loaded organic material reacted very quickly with hydrochloric acid and considerably more slowly with sulfuric acid. Virtually complete used of the hydrochloric acid could be made:

$$FeV_3 + 3\ HCl \rightleftarrows FeCl_3 + 3\ HV$$

Only a very small excess of the acid was required to keep the iron out of the organic layer and to prevent hydrolysis of the ferric chloride. In view of its slow stripping activity we found it was difficult to use sulfuric acid with equal efficiency.

As shown in Table 2, the iron was removed very efficiently from the synthetic zinc/iron solutions, and essentially complete iron removal could easily be achieved with an amount of zinc VERSATIC salt equivalent to the amount of iron plus the amount of free acid originally present in the aqueous solution.

The table also shows that the losses of zinc were low and the separation between iron and zinc ($\log S = \log D_{Fe} - \log D_{Zn}$, where $D_{Fe} = Fe_{org}/Fe_{aq}$) was very good.

Table 2

Efficiency of iron removal and accompanying zinc losses

Aqueous solutions	Molar ratio $Zn_{(org)}/Fe_{(aq)}$	Final pH	% Fe removed	% Zn[a] remaining i n organic phase	log *S*
A	1.44	2.40	97.0	0.15	4.3
A	1.48	2.80	99.5	1.00	4.3
B	1.73	2.45	96.0	0.12	4.3
B	1.76	2.70	99.0	0.80	4.1
B	1.82	3.00	99.8	2.20	4.3

[a] With respect to original zinc content of aqueous solution.

2. Fate of contaminants

Table 3 shows that both cobalt and copper remained in the aqueous layer up to virtually complete iron removal. Only for copper does there seem to be a risk that losses will occur when one aims at very high iron removal levels. For this reason (and others to be discussed) it appears advisable not to try and achieve very high efficiencies.

Table 4

Removal of ferric iron and arsenic from solution C by coprecipitation with various alkaline agents.

Fe^{3+} in solution before treatment		Precipitant used	Amount of precipitant added (equivalents[a]	Temperature (°C)	pH at equilibrium	Fe^{3+} in solution after treatment		As in solution after treatment (g/l)
(g/l)	(% on original HAL)					(g/l)	(% on original HAL)	
2.60	10.0	CaO	0	25	1.60	2.60	10.0	0.24
			1		2.55	2.53	9.73	—
			2		3.55	0.43	1.65	0.05
			3		4.60	0.01	—	< 0.01
			1	60	2.23	2.29	8.81	—
			2		3.90	0.04	0.15	—
			3		4.80	—	—	< 0.006
1.49	5.0	CaO	0	25	1.73	1.49	5.0	0.25
			1		2.35	1.31	4.4	—
			2		3.40	0.32	1.1	0.05
			3		4.23	0.025	< 0.1	0.003
			1	60	2.43	1.15	3.9	—
			2		3.60	0.06	0.2	0.008
			3		4.53	0.004	—	< 0.007
2.60	10.0	$Ca(OH)_2$	0	25	1.60	2.60	10.0	0.24
			1		2.60	2.21	8.5	—
			2		3.95	0.08	0.3	0.007
			3		4.82	nil	nil	—
			1	60	2.65	0.52	2.0	0.05
			2		4.27	nil	nil	< 0.008
1.49	5.0	$Ca(OH)_2$	0	25	1.73	1.49	5.0	0.24
			1		2.86	1.13	3.8	—
			2		4.04	0.17	0.6	0.04
			3		4.60	nil	nil	—
			1	60	2.90	0.10	0.7	0.01
			2		4.32	nil	nil	< 0.01

Table 4 (continued)

Fe^{3+} in solution before treatment		Precipitant used	Amount of precipitant added (equivalents[a])	Temperature (°C)	pH at equilibrium	Fe^{3+} in solution after treatment		As in solution after treatment (g/l)
(g/l)	(% on original HAL)					(g/l)	(% on original HAL)	
2.60	10.0	ZnO	0	25	1.60	2.60	10.0	0.24
			1		2.84	2.25	8.6	—
			2		4.57	0.01	0.04	< 0.006
			3		—	—	—	—
			1	60	2.82	0.88	3.4	0.017
			2		4.90	nil	nil	< 0.006
1.49	5.0	ZnO	0	25	1.73	1.49	5.0	0.24
			1		2.92	1.19	4.0	—
			2		4.30	nil	nil	< 0.008
			1	60	2.80	0.1	0.33	0.065
			2		4.56	nil	nil	< 0.008
2.60	10.0	Zinc calcine	0	25	1.60	2.60	10.0	0.24
			1[b]		2.60	2.41	9.3	—
			2[b]		3.75	0.16	0.6	0.14
			3[b]		4.85	nil	nil	< 0.002
			1[b]	60	2.23	1.97	7.6	—
			2		4.50	nil	nil	< 0.007
1.49	5.0	Zinc calcine	0	60	1.73	1.49	5.0	0.24
			1[b]		2.51	0.81	2.7	—
			2[b]		4.27	nil	nil	< 0.008
2.60	10.0	Basic zinc sulphate slurry	0	25	1.73	2.60	10.0	0.24
			1[c]		3.02	1.80	7.0	—
			2[c]		4.57	<0.004	—	—

[a] Calculated on $^3/_2$ Zn (or Ca) = 1 Fe.
[b] Calculated on Zn present in calcine.
[c] Calculated on Zn available as $Zn(OH)_2$.

Table 3

Analysis for loss of cobalt, copper and manganese from a HAL (solution C) as a function of iron removal

% iron removal	% of element remaining in aqueous solution		
	Co	Cu	Mn
51.8	100	100	100
88.0	100	100	100
95.4	100	99.5	100
97.4	100	98	100
98.1	100	95	100

It is not necessary to consider in this context the behaviour of other valuables e.g. cadmium. These metals lie sufficiently far to the right of zinc in the extraction sequence that they will not be extracted.

Of the various harmful elements that can in principle occur in a HAL, some (e.g. chlorine) need not be considered since the use of our proposed liquid/liquid extraction method makes no difference to their behaviour during the purification steps. Others such as manganese and arsenic require special mention, although since the results in Table 3 indicate that there was no detectable extraction of manganese, the procedures currently adopted for its removal can remain as they are.

In the case of arsenic, it was found that at nearly complete iron removal only 10 % of the element present (i.e. about 30 ppm) was co-extracted. At lower levels of iron removal the amount of arsenic co-extracted fell off rapidly to virtually zero. These results mean that the major part of arsenic (and probably of antimony and germanium as well) remain in the aqueous solution after the solvent extraction of iron. Therefore a separate removal step for these elements had to be devised and several possibilities were investigated. By far the most effective was one in which the arsenic was coprecipitated with a small amount of iron. This was done by removing 90 - 95 % of the iron by solvent extraction and then precipitating the remaining 5 - 10 % as hydroxide, preferably using reagents that did not introduce "foreign" ions into the solution, e.g. zinc oxide, zinc calcine and basic zinc sulfate slurry. However, calcium oxide and calcium hydroxide were also found to be effective. The results of these coprecipitation experiments are summarized in Table 4.

DISCUSSION

Clearly, solvent extraction is a very efficient technique for the removal of ferric iron from zinc sulfate liquors. The zinc losses are very low, especially if an iron removal similar to that achieved in the precipitation processes is satisfactory. For example, the zinc loss corresponding to a residual iron content of 1 g/l (normal for the jarosite process) after solvent extraction is only 0.1 % of the original amount present. This compares very favourably with figures of up to 3 % found in the jarosite process.

Losses of other valuables such as cobalt and copper are negligible, so that the existing methods and facilities for recovering these metals can be kept in operation. The same holds for the removal of some harmful elements like manganese. Other undesirable contaminants, such as arsenic, that are coprecipitated in the jarosite and goethite processes, are left in the solution. However, these are effectively removed by coprecipitation with a small amount of ferric iron left in the solution for this purpose.

At first sight this combination of liquid/liquid extraction and precipitation might seem somewhat illogical. However, at present no satisfactory large-scale liquid/liquid extraction technique is known for arsenic, particularly in view of the low residual levels required. In this respect it is necessary to acknowledge that the valency state of arsenic in the leach liquors is not precisely known and most probably both As(III) and As(V) are present. Several reagents capable of extracting either As(III) or As(V) are known, but their chemical nature is rather complex and they are not (yet) suitable for large-scale application. Therefore removal by precipitation is a reasonable alternative. The solution proposed is simple and the amount of solid waste to be disposed of by dumping or otherwise is far less than that produced in the jarosite or goethite processes.

The chemical stability of VERSATIC is so good that losses during stripping of the iron-loaded organic phase with hydrochloric acid can be neglected. The ferric chloride produced (which can be practically acid-free) could be introduced in a process to recover hydrochloric acid and produce ferric oxide, which might be salable. Alternatively, it could be used for water purification. The danger of contamination of the VERSATIC with chloride ions, which might end up poisoning the zinc sulfate electrolyte in a subsequent cycle, has been found to be negligible, provided adequate settling time after stripping is allowed; we found the chloride content of the stripped VERSATIC layer to be less than 3 ppm. If additional safety is desired, a simple water wash can be used.

CONCLUSIONS

We have demonstrated that ferric iron can be effectively removed from zinc sulfate electrolyte by a solvent extraction method using the zinc salt of VERSATIC acid as the extractant. The advantages of the proposed method over the well-known precipitation methods are the decreased minimum iron levels in the treated solutions, decreased zinc losses and the avoidance of the use of "foreign" ions. The VERSATIC can easily be recovered for re-use (after reconversion to the zinc salt) by stripping the iron-loaded organic phase with a mineral acid, preferably hydrochloric acid. Valuable metals, such as cobalt and copper are not or only slightly co-extracted, which means that the normal manganese removal stage may be used. Distinctly harmful elements such as arsenic are not extracted and therefore an extra step to effect As, Sb and Ge removal must be incorporated. This can be achieved by extracting the iron to a level not higher than 90 - 95 % of the original amount (i.e. a residual iron content of 1 - 2 g/l) and precipitating the last quantities of iron as hydroxide using zinc-oxide-containing precipitants or calcium oxide or hydroxide. The undesirable contaminants are thus precipitated.

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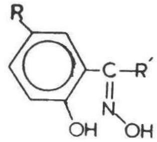
B 1. SELECTIVE COPPER EXTRACTANTS OF THE 5-ALKYL-2-HYDROXYPHENYL ALKYL KETOXIME TYPE

A.J. van der Zeeuw.

Inst. Chem. Eng. Symposium Series No. 42, 1975, p. 16.1

INTRODUCTION

Since 1969 Shell have been developing a class of selective copper extractants with the general formula[1]



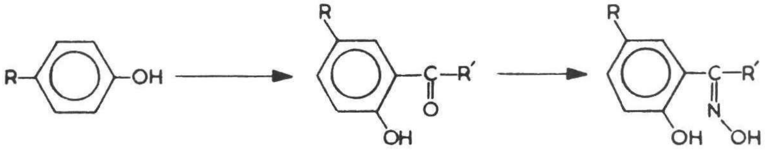
The present paper deals with the considerations that led to the ultimate choice of the side chains R and R'. The synthesis, the kinetics of extraction and stripping and the stability of the product as well as the availability of the starting materials had to be carefully evaluated.

The influence that the various components of kerosine diluents exert on the performance characteristics of hydroxy-oxime extractants can be illustrated with the aid of single component hydrocarbon diluents. It is stressed that in the author's view the composition of a kerosine diluent, as given by a type analysis, is of secondary importance, and that consideration of such phenomena as phase separation, absence of third-phase formation, entrainment, etc., properties that cannot be easily traced back to gross composition, should be given preference.

CHOICE OF REAGENT

Synthesis routes

The obvious synthesis route towards 5-alkyl-2-hydroxyphenyl alkyl ketoximes is:



The key chemical is the ketone, 5-alkyl-2-hydroxyphenyl alkyl ketone. This type of ketone can be produced in a variety of synthetic routes, the most important being:

1. Photo-Fries rearrangement of esters of 4-alkylphenols.
2. Ortho-acylation of 4-alkylphenols with an acid or acid chloride in the presence of a catalyst.
3. Chemically induced Fries rearrangement of esters of 4-alkylphenols.

The above routes are shown diagrammatically in fig. 1.

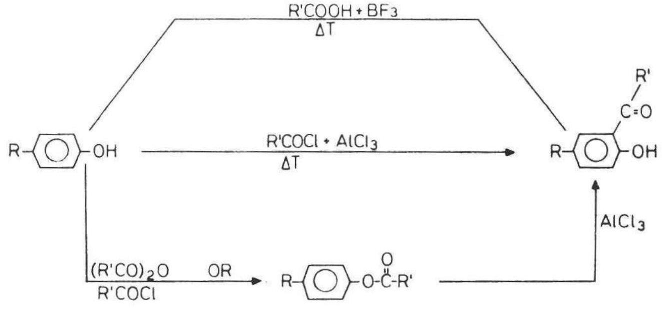


Fig. 1

Synthesis routes to 5-alkyl-2-hydroxyphenyl alkyl ketones.

The first route can be discarded because of the large quantities of product required. Methods 2 and 3 are both widely used in organic synthesis[2,3] but have some serious disadvantages when the production of a sufficiently pure and cheap copper extractant is the end objective.

Method 2, when carried out with an acid as the acylating agent, requires a Friedel-Crafts type catalyst which complexes the acid, but which is not decomposed by it. Boron trifluoride is the best catalyst, but is hazardous, expensive, and in practice not a readily recoverable chemical. Alternatively, an acid chloride can be used in combination with $AlCl_3$, but this is in fact a variation of method 3.

Both methods have the serious drawback that, according to the literature, the alkyl chains of the preferred starting phenols (see next section) are very easily degraded and (or) split off altogether.[2,3,4]
In the case of the acid/BF_3 variation of method 2 we have found that this is completely true and that little can be done to circumvent the problem.

The above considerations of price and feasibility made us focus our attention on method 3. Although it was stated only very recently[4] that in the Fries reaction e.g. with tertiary-butylphenyl esters de-alkylation always prevails, we have been able to find a means of overcoming the problem of degradation and the splitting off of the side chain. Virtually any p-alkylphenyl ester that has been found to suffer from these side reactions, such as p-tert-butylphenyl, p-tert-octylphenyl, p-nonylphenyl and p-dodecylphenyl esters, can now be converted into the desired ketone with the formation of $\leqslant$ 5 % of degraded or de-alkylated material. $AlCl_3$ may be used as catalyst. This method is the subject of a patent application.[x]

Availability of starting materials

For chemical reasons the only 4-alkylphenols that are readily available and thus reasonably cheap are, with the exception of p-cresol, those containing a tertiary or at least highly branched alkyl chain: 4-tert-butylphenol, 4-tert-octylphenol, 4-tert-nonylphenol[xx] and perhaps 4-tert-dodecylphenol.[xx]

Although in the course of our experimental work many products based on other 4-alkylphenols were made, often being specially synthesized for this purpose, it will be clear that the options for practical production are limited to those mentioned above.

The preparation of phenolic esters requires an acid anhydride or chloride. The only adequate acid anhydride which is commercially available in quantity is acetic anhydride. Some acid chlorides can be bought, but most others will have to be prepared by means of a separate step. Obviously the possibility of using acetic anhydride, which then automatically defines R' as methyl, would be advantageous. Fortunately the properties shown by products having acetic anhydride as a precursor were favourable and its use as an intermediate was therefore established.

Relation between structure and performance

Although the considerations given in the preceding section are of vital importance to the commercialization of the project, no sensible decision can be made when there are no rules that relate structure to performance. Therefore the determination of a satisfactory relationship was an immediate task.

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[x] Br. P. 1,458,659, to Shell Int. Research Maatschappij B.V.

[xx] Commercial quantities contain up to 10 % of ortho-alkylated material

The structure of the class of reagents synthesized allowed us to vary the chain length at two sides of the molecule (R and R') without major changes in the chemical properties of the active chelate-forming unit. Probably the best overall picture of these chelating properties is given in a normal log D/pH plot. Fig. 2 shows that even a marked "shifting" of the active group along the chain does not appreciably change the log D/pH graph.

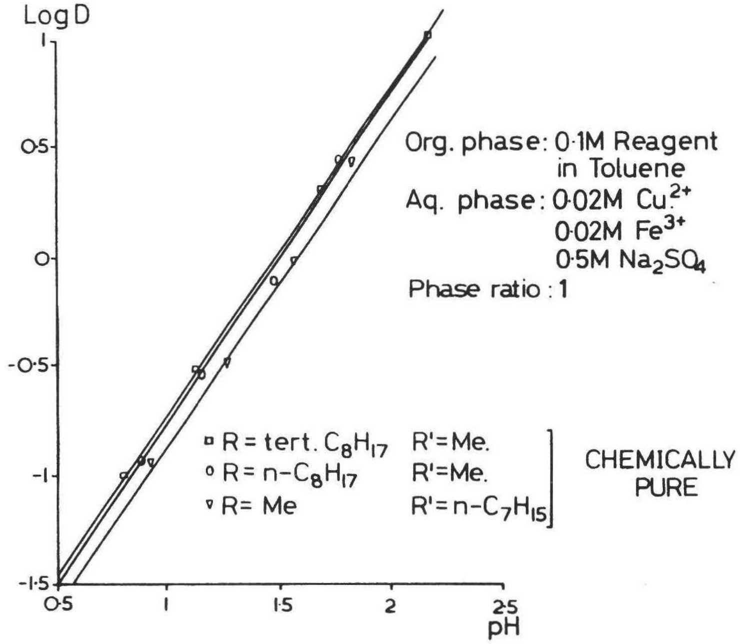

Fig. 2

Log D/pH plots of various reagents

A second class of important properties comprises the solubility of reagent and complex in the hydrocarbon diluent, the kinetics of extraction and stripping and the loading capacity. A schematic survey of the results of our work on these aspects is shown in table 1. From this table it is clear in which direction the search for the most suitable reagent should go: high molecular weights and long R' chains are undesirable, on the other hand too low molecular weights (too short R chains) ultimately lead to complete insolubility in kerosine.

Table 1

Generalized scheme relating performance parameters to structure properties*

Mol. Wt.	R	R'	Solubility in kerosine	Kinetics	Loading capacity
347	t-C_8	C_7	very good	poor	acceptable
C	+	-	+	C	C
C	-	+	-	C	C
-	C	-	-	+	+
-	-	C	-	-	-
-	-	-	-	+	+
+	C	+	-	-	-
+	+	C	+	-	-
+	+	+	+	-	-

* C = unchanged
+ = increased (improved)
- = decreased (worsened)

Of course, chemical stability of the chosen reagent is also important. As a class of compounds, oximes are in principle unstable in an acidic medium. In an aqueous-acidic medium they can undergo hydrolysis to give ketones. Since this is typically a reaction taking place in an aqueous phase, the amount of reagent dissolved in this phase should be decreased. This is most easily done by keeping the molecular weight as high as is acceptable. The effect of molecular weight on stability is shown in table 2.

Table 2

Percentage of loading capacity retained by various 5-alkyl-2-hydroxyphenyl alkyl ketoximes after 2 h contact with 3 N H_2SO_4 at 60° C.

Mol. Wt.	R	R'	Diluent[x]	
			MSB 210	**AB**
235	t-C_5	C_2	n.d.	53
263	t-C_8	C_1	83	100
277	t-C_9	C_1	100	n.d.

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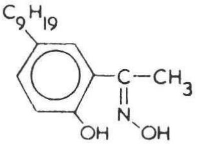
[x] Shell Diluent MSB 210 is low aromatic ($\leqslant$ 3 %), ShellSol AB is completely aromatic.

When the two values given for the stability of 2-hydroxy-5-tert-octylacetophenone oxime are compared, the better solvency properties of the aromatic diluent become apparent, in other words the oxime displays an improved stability in the more aromatic diluent.

Consideration of all the advantages and disadvantages led finally to the conclusion that it was worthwhile investigating two of the prepared compounds more thoroughly, viz. 2-hydroxy-5-tert-octylacetophenone oxime and 2-hydroxy-5-nonylacetophenone oxime. For this reason most of the work discussed in the remainder of this paper, which examines the influence of the diluent character upon the reagent, has been carried out with these two compounds. A large number of experiments have been conducted to enable a final choice between the two selected compounds to be made. Ultimately 2-hydroxy-5-nonylacetophenone oxime of formula



was chosen as the active part of Shell Metal Extractant 529.

INFLUENCE OF DILUENT CHARACTER ON THE PERFORMANCE OF REAGENTS

Experimental

It is important to note that the non-equilibrium (kinetic) behaviour of a system is strongly affected by the experimental procedure adopted. It is dependent on phase continuity, rate of stirring, use of baffles, etc. An outline of the experimental method used in our work is given below.

The apparatus consisted of a cylindrical vessel (diameter 80 mm, volume 500 ml) provided with a paddle stirrer (tip-to-tip diameter 58 mm) which was placed halfway in the lower phase, a bottom sampling cock and a top inlet. No baffles were used. Initial phase volumes were 100 ml each. The stirrer speed was 2000 rev/min and a temperature of 25° C was maintained throughout every experiment. During rate experiments the chosen phase continuity was ensured by starting agitation with only this phase in the cylinder and then rapidly adding the second phase to it. Time zero was taken to be when the addition was complete. Sampling was conducted by continuously draining the bottom cock while recycling the drainings via the top inlet. This was necessary to eliminate the effect of "dead space". At selected times aliquots of the draining mixture were set aside as samples. It was found that in this way completely homogeneous samples were obtained and that phase continuity could be maintained for a desired length of time.

Analysis of samples was performed as soon as all samples from one experiment had been collected, i.e. within 5 minutes after starting. All analyses were carried out by atomic absorption spectrophotometry. Aqueous phases were suitably diluted with 0.5 N HNO_3; organic phases were first stripped with 0.5 N HNO_3.

All inorganic solutions were made up from analytical grade metal sulfates and sulfuric acid. All diluents tested were chemically pure single hydrocarbon compounds or commercial hydrocarbon diluents. Some of the reagents used were purified either by recrystallization or by chromatography on silica using copper complexes. The reagents were mostly yellow to light-brown crystalline solids or semi-solids.[x] In the text and figures they have been marked c.p. Technical quality 2-hydroxy-5-tert-octyl - and 2-hydroxy-5-nonylacetophenone oximes were also used. These were brown viscous liquids. In the text and figures they have been marked t.p. All concentrations given are expressed as the calculated content of pure (c.p.) oxime.

pH functionality and selectivity

The pH functionality for copper shows a slight dependency on diluent character. It can be seen from fig. 3 that the log D/pH plot for c.p. 2-hydroxy-5-nonylacetophenone oxime in toluene has shifted over approx. 0.25 units towards higher pH values as compared to other diluents. This illustrates the well-known fact that the better the solvency power of the diluent for the extractant, the worse the extracting properties of the combination. It is interesting to know that the hydroxy-oximes, when dissolved in ether, do not extract copper below pH 5.5.

The overall "suitability order" for the single component hydrocarbons tested with respect to pH functionality for copper is:

iso-octane = n-heptane = methylcyclohexane > toluene

A comparison of the behaviour of t.p. Shell Metal Extractant 529 in two commercial hydrocarbon diluents shows that the less aromatic one has a slightly better pH functionality, which is in agreement with the above order (fig. 4). The type analyses of these hydrocarbon mixtures "A" and "B" are given in table 3.

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[x] The pure compounds are distinctly sensitive to light and tend to darken on standing.

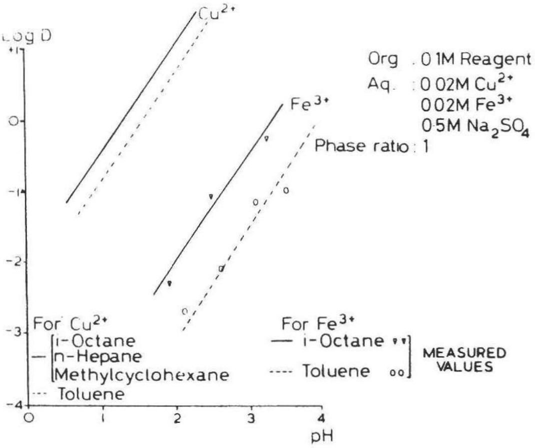


Fig. 3

Extraction of copper and ferric iron with c.p. 2-hydroxy-5-nonylacetophenone oxime in various diluents.

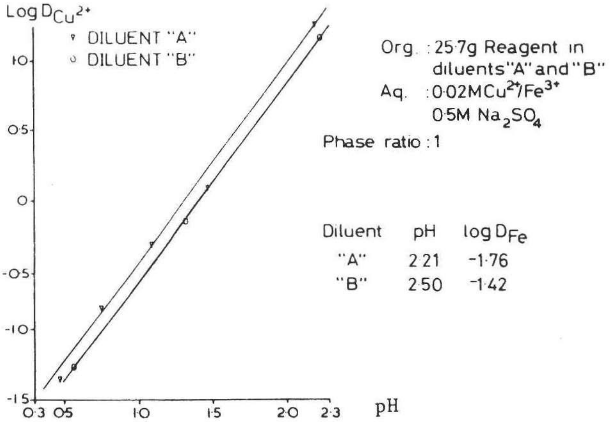


Fig. 4.

Extraction of copper with t.p. 2-hydroxy-5-nonylacetophenone oxime in two commercial diluents.

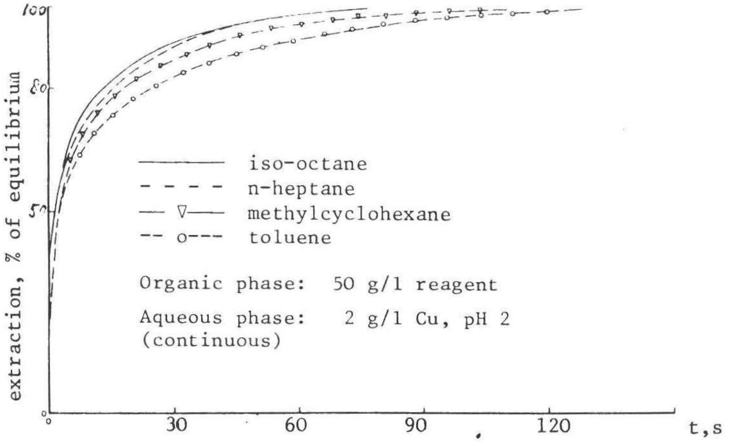


Fig. 5

Rate of copper extraction with c.p. 2-hydroxy-5-tert-octylacetophenone oxime as a function of diluent.

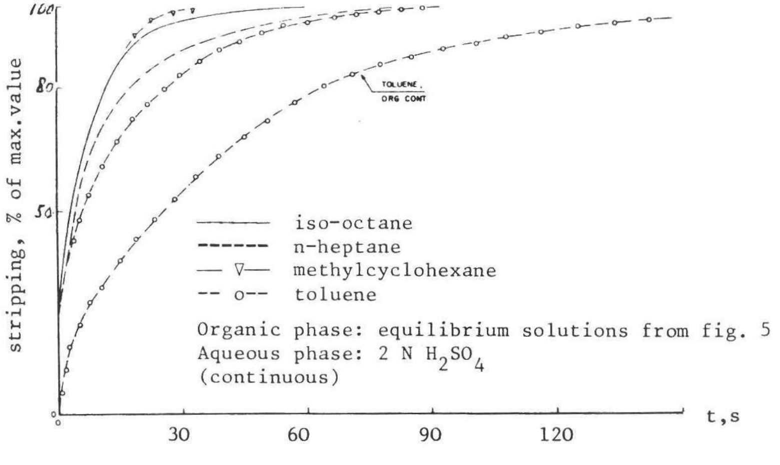
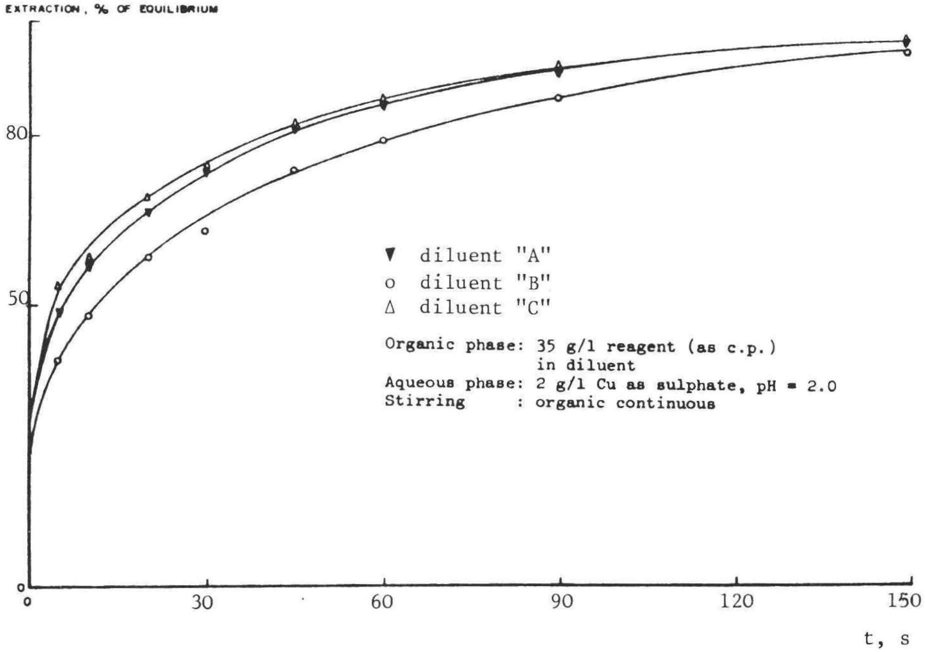


Fig. 6

Rate of copper stripping from c.p. 2-hydroxy-5-tert-octylacetophenone oxime as a function of diluent.

The change of position between the saturated compounds is probably brought about by minor differences in phase viscosities, interfacial tensions, etc. Nevertheless the position of toluene as the "worst" diluent is clear.

Although differences between the various types of hydrocarbons are evident, the values of these differences are relatively small. Therefore, one is led to expect that the effect of commercial diluents of varying composition might be too small. This is borne out in practice. Fig. 7 shows the behaviour of t.p. 2-hydroxy-5-nonylacetophenone oxime in diluents "A", "B" and "C" (see table 3 for the compositions). The non-aromatic "C" which contains high amounts of naphthenes and isoparaffins performs marginally better than the low-aromatic, high-naphthenic "A", which in turn is slightly better than the medium-aromatic, low-naphthenic "B". The absolute differences are certainly not impressive.



Organic phase: 35 g/l reagent (as c.p.) in diluent
Aqueous phase: 2 g/l Cu as sulphate, pH = 2.0
Stirring : organic continuous

Fig. 7

Rate of extraction of copper with t.p. 2-hydroxy-5-nonylacetophenone oxime in commercial diluents.

Table 3

Type analysis of commercial diluents

Type of compounds	Method of analysis	Content, %w "A"	 "B"	 "C"
Olefins		<0.1	<0.1	<0.1
Aromatics	UV	3	26	0.8
Mono-aromatics	mass spectrometry	3	25	-
Normal paraffins	mol. sieves abs.	29.4	24.9	9.2
C_nH_{2n+2} (total paraffins)	mass spectrometry	68	54	39
C_nH_{2n} (naphthenics)	mass spectrometry	19	14	33
C_nH_{2n-2} (bicyclics)	mass spectrometry	9	6	26
C_nH_{2n-4} (tricyclics)	mass spectrometry	1	1	2

The iron rejection of the system is strongly dependent on diluent character, more so than the extraction of copper. This is also illustrated in fig. 3. It must be noted that fig. 3 does not give a fair representation of iron extraction, since copper was also present. In fact, at the pH's of 2 virtually all the copper was contained in the organic layer, taking up a considerable part of the loading capacity of the reagent. It is also appropriate at this point to stress that in the higher pH range the measured points for iron actually become of doubtful value because of the precipitation of iron hydroxide. The points are rather scattered and the plots have been drawn arbitrarily with slopes equal to those of the copper extraction. From fig. 3 it can be calculated that at pH 2.0 the use of a pure saturated hydrocarbon as diluent gives a separation factor S (= D_{Cu}/D_{Fe}) of about 1000, whereas the use of a pure aromatic diluent improves this separation factor. In other words, the selectivity of copper extraction can be improved by using a more aromatic diluent.

Kinetics of extraction and stripping

Again the general trend is that the higher the solvency of the diluent, the worse the performance of the extractant. Figs. 5 and 6 clearly show this effect. The "suitability order" of the various diluents in the extraction of copper with 2-hydroxy-5-tert-octylacetophenone oxime (c.p) is:

iso-octane $\gg$ n-heptane $>$ methylcyclohexane $>$ toluene

In the stripping circuit the differences are somewhat obscured. Here the order is:

methylcyclohexane $=$ iso-octane $>$ n-heptane $>$ toluene

Loading capacity

The loading capacity of 2-hydroxy-5-nonylacetophenone oxime as a function of the diluent is given in table 4.

Table 4

Loading capacity of t.p. 2-hydroxy-5-nonylacetophenone oxime

Reagent concentration : 23 g per litre in diluent (calculated on pure reagent content)
Aqueous copper concentration : 50 g Cu per litre (as copper sulphate)
Apparatus : see Experimental Section
Phase ratio : org./Aqueous = 1/10
Continuous phase : Aqueous
Time of equilibration : 30 minutes
Final pH : $\geqslant 2.7$[*]

Diluent	g per litre of Cu loaded
Toluene	2.04
Methyl cyclohexane	2.18
n-Heptane	2.20
iso-octane	2.36
"A"	2.33
"B"	2.33

[x] Since, when measured against a massive excess of copper, the maximum loading capacity of 2-hydroxy-5-nonylacetophenone oxime is reached at pH values slightly below 2, it suffices to ensure that the final pH of the solution is well above 2.

Although aromatics and naphthenics especially are expected to adversely affect the loading capacity, in practice both commercial diluents investigated gave the same loadings, which were slightly higher than expected. Obviously the influence of iso-paraffins outweighs that of the other compounds.

Discussion

In the preceding sections "primary" extractant properties (pH functionality, selectivity, rates of extraction and stripping, and loading capacity) could be related reasonably well to the character of the diluent, although the relations were indicative rather than explanatory. It is felt that a more theoretical approach, comprising e.g. kinetic measurements in systems of pure reagent plus pure diluent (see e.g. ref. 5) could lead to a better understanding of the reasons underlying the relationships found. It seems however that this would not be of much practical value, as it is hardly possible for general rules to adequately cover all possibilities.

In a general sense it can be concluded that an excessive amount of aromatics could adversely affect the overall "primary" performance. To some extent this has been confirmed in practice. However, it is felt that consideration of the aromatics content should not be given too much weight when finally the diluent is chosen. The most economic hydrocarbon diluents available will almost invariably have an aromatic content between 0-3 and 25 %. From the figures it can be concluded that within this range no dramatic differences in primary performance are to be expected. In fact, performances that can be rated as "comparable" can quite easily be achieved with diluents of very different compositions.

An even more important reason for tempering our appraisal of the type composition of the diluent lies in the "secondary" performance aspects. For instance, phase disengagement characteristics, third-phase formation, sensitivity to crud formation and entrainment are of the utmost importance to the plant manager of a solvent extraction plant, and probably have a greater bearing on the results of the operation as a whole. To date it has not been possible to relate these properties reliably to the gross composition of a hydrocarbon mixture. Although minute amounts of impurities in the diluent that normally escape a type analysis might be partly responsible for an unsatisfactory performance, real difficulties will probably arise only in actual field testing, and then only when a particular combination of extractant solution, leach solution and operating conditions does not work out favourably. It is felt therefore that a close contact between the "man in the field" and the supplier of the diluent is indispensible.

Tailormaking of a hydrocarbon diluent could be envisaged. It would involve isolating pure-type products form feedstocks, or manufacturing them in a chemical plant, and optionally mixing them again in the ratio required to obtain a special purpose diluent. However, it can be seen from the result given in the paper that in this way properties of the extractant systems can only be varied within rather narrow limits. Furthermore, this tailormaking would render the products so expensive that in our opinion it is not a practical proposition.

CONCLUSIONS

The data provided in the second part of this paper indicates rather than explains the relationships between the character of a diluent and the "primary" performance of an extraction system, i.e. its "efficiency". It was found that small but measurable changes in the copper-chelating properties of the system can be brought about by changing the character of the diluent. In general, aromatics have a slightly adverse influence as compared with paraffinic, isoparaffinic and naphthenic compounds.

In practice, the "primary" performance aspects of a system are thought to be of less importance than the "secondary" ones, concerned with the "handlability" of the system. So far it has not been possible to relate phase separation properties to diluent composition; however they highly influence the feasibility of a system as a whole.

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B 2. HYDROCARBON SOLVENT DILUENTS IN HYDROXY-OXIME SOLVENT EXTRACTION PROCESSES

S. Dobson and A.J. van der Zeeuw.

Chem. & Ind. 1976, 175

(Only the part written by the present author has been reproduced)

EXPERIMENTAL RESULTS AND DISCUSSION

In the eyes of a team of reagent designers the extractant has "primary" and "secondary" properties. This refers only to the stage at which these properties are being investigated: the "secondary" ones follow when the "primary" ones are found acceptable. A possible division is as follows:

PRIMARY PROPERTIES

Equilibrium
- log D/pH
- loading capacity
- selectivity

Dynamic
- kinetics

SECONDARY PROPERTIES

Phase disengagement
- third-phase formation
- entrainment levels

Of course such a scheme is not limitative, and several other factors could have been included.

Equilibrium properties

Since the measurements needed mainly concern concentrations in a static situation, determination of equilibrium properties is relatively easy. However, the fundamental information that can be gained is comparatively scant.

1. Log D/pH

Log D/pH plots of oxime type reagents, be they measured in practical systems[1] or in ideal ones (highly diluted, constant ionic background, and so on)[2], have slopes between 1.5 and 1.8. Although admittedly the use of slope analysis has some disadvantages and one should not rely too heavily upon it, the consistent deviation from 2.0 is too important to be neglected completely. Computer analysis of the data suggests that there may be some (but only some) indication of dimeric complexes of the form $(CuR_2)_2$.x HR. Maximum loading experiments give the impression that complexes containing extra liganding reagent may be formed: CuR_2 together with CuR_2.HR, CuR_2.2 HR, and so on. This bears a strong analogy with what Spink and Okuhara[3] found for the Kelex/Cu system.

It is also assumed that for the oxime systems the ratio between the various complexes is dependent on, among other things, the structure of the reagent and the character of the diluent. The question of whether diluent molecules are actually taking part in the complexing cannot be answered along these lines.

In practice the influence of log D/pH plots of the compounds constituting hydrocarbon solvents can be stated as: paraffins, isoparaffins and naphthenes are equal, and all better than aromatics (fig.1).
In principle therefore one would expect a considerable improvement in the pH functionality if one changed from a highly or medium aromatic commercial diluent to a non-aromatic one in a practical system. The effect turns out to be only marginal, as can be seen from the following table and also from ref.1.

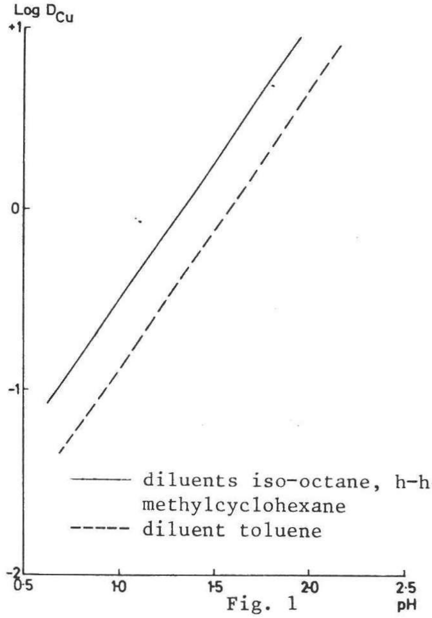


Fig. 1

Extraction of Cu with chemically pure 2-hydroxy-5-nonylacetophenone oxime in model hydrocarbons.
Organic: 0.1 M reagent.
Aqueous: 0.02 M $CuSO_4$, 0.5 M Na_2SO_4

Table 1

pH_{50} values of chemically pure 2-hydroxy-5-nonylacetophenone oxime in hydrocarbon diluents.

Organic: 0.02 M reagent in diluent

Aqueous: 0.002 M $CuSO_4$, 0.5 M Na_2SO_4

Diluent	pH_{50}
toluene	2.14
n-heptane	1.68
methylcyclohexane	1.70
Shell diluent MSB 210 (2 % arom.)	1.70
Escaid 100 (approx. 20 % arom.)	1.70

2. Loading capacity.[x]

The loading capacity of hydroxy-oximes of the 5-alkyl-2-hydroxyphenyl alkyl ketoxime type is influenced by the character of the hydrocarbon diluents in the same way as log D/pH functions, as can be seen from table 2.

Table 2

Loading capacity of 5 % w/v solutions of SME 529[xx]

Diluent	g/l of Cu loaded
toluene	2.04
n-heptane	2.20
methylcyclohexane	2.18
iso-octane	2.36
Shell diluent MSB 210	2.33
Escaid 100	2.33

And again the net adverse effect of aromatics up to the 20-25 per cent level is hardly perceptible. In fact the very high loading capacity of both commercial diluents is obviously caused by the preponderant influence of isoparaffins.

---

[x] Defined as the amount of copper in g/l that 1 part of a 2½ % w/v solution of the pure oxime will take up from 10 parts of an aqueous solution of 197 g/l of $CuSO_4.5\ H_2O$, the pH of which has been adjusted before equilibration to 4.0.

[xx] SME 529 contains 50 % w/w of 2-hydroxy-5-nonylacetophenone oxime as the active component, in a hydrocarbon diluent (in principle MSB 210).

Determination of loading capacities both of various chemically pure model 5-alkyl-2-hydroxyphenyl alkyl ketoximes and of commercial products (including SME 529, LIX 65 N and P-17) have demonstrated that it is virtually impossible to achieve the theoretical loading of 1 copper to 2 oxime in the acid region. The loadings actually obtained range between 1 : 2.2 and 1 : 2.4, and are influenced by the oxime structure and the diluent. This provides further backing for the view that assigning the composition CuR_2 to the complexes is an oversimplification.

3. Selectivity.

Selectivity in separating copper from ferric iron is probably the only primary property of a reagent system of the kind discussed here for which an improvement is observed when one used an aromatic model hydrocarbon instead of a non-aromatic one[1]. In commercial diluents with aromatic contents up to 25 %, however, the difference is again negligible (table 3).

Table 3

Selectivity for copper of chemically pure 2-hydroxy-5-nonylacetophenone oxime in various diluents.

Organic: 0.1 M in diluent.

Aqueous: 0.02 M Cu^{2+}, 0.02 M Fe^{3+}, 0.5 M Na_2SO_4

pH of aqueous phase after equilibration 2.0

Diluent	log D_{Cu}	log D_{Fe}	log S
n-heptane	1.1	-2.0	3.1
toluene	0.7	-3.2	3.9
MSB 210	1.0	-2.1	3.1
Escaid 100	0.85	-2.3	3.2

Dynamic properties (kinetics of extraction and stripping).

Reliable and relevant kinetic measurements are considerably more difficult to carry out, but the information obtained is correspondingly more elucidating since it is related to the processes actually going on during the extraction.

Recently[1] one of the present authors gave some information on rates of extraction and stripping in model hydrocarbon diluents, in the form of percentage extraction or stripping versus time plots, from which it was evident that in a practical system a high aromatics content in the diluent could lead to a slower rate of achieving equilibrium. This was actually borne out in a comparison between two commercial diluents, a low and a medium aromatic one.

The measurements give little information about the pure kinetic differences, however, for the following reasons:

1. During the reaction pH changes continuously. It has been known for a long time that rates are lower at lower pH, all other conditions being equal. This has recently been substantiated by Flett et al.[2]
2. The interfacial surface area was not known.
3. Phase continuity was found to have a great influence on the shape of the curve.

The differences were found to be sufficiently important, however, to make it worthwhile to try and tackle the kinetic problem in a more fundamental way. In an initial attempt the approach of Flett, Okuhara and Spink[2] was followed, the reasoning being that a few changes in the set-up might be introduced that would particularly suit our purpose, i.e. use of a type of apparatus in which the interfacial surface area was known with some degree of accuracy, and use of chemically pure reagents and diluents.

The apparatus used consisted of a standard shape double walled glass vessel (height/diameter ratio 1, contents 250 ml), provided with four baffles (width 0.1 of vessel diameter) and a turbine stirrer (diameter 0.3 of vessel diameter) with six blades (width 0.1 of vessel diameter). In the experiments the organic layer was always taken continuous, which was achieved by putting this layer in the vessel first, starting stirring with the impeller halfway down the phase, and then adding the aqueous phase. Completion of addition of the latter marked time zero. Addition plus homogeneous dispersion did not take more than five seconds.

The actual experiments consisted in contacting aqueous and organic layers (phase ratio 1) to equilibrium, separating them, adding tracer copper to the aqueous layer, recontacting the layers and measuring the distribution of the tracer copper between the layers. The temperature was maintained at 25° C, the stirring rate used was 2000 rev/min.

From Van Heuven and Beek[4] we assumed that in the system the interfacial surface area can approximately be given as

$$S \quad \alpha \quad \frac{1}{d_{32}} \quad \alpha \quad \left(\frac{\sigma_i}{\rho}\right)^{0.6}$$

in which d_{32} is the Sauter mean diameter of the droplets, σ_i is the interfacial tension in the system, and ρ is the density of the dispersion.

Fig. 2 gives the results for a pure oxime in various diluents.

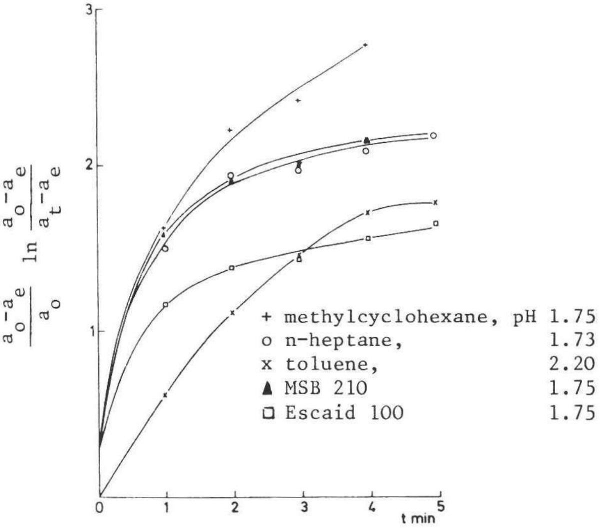


Fig. 2

Kinetics of forward reaction under equilibrium conditions. Data treated according to Flett et al.[2]

Organic: 0.02 M chemically pure 2-hydroxy-5-t-octylacetophenone oxime in diluent.

Aqueous: 0.002 M $CuSO_4$, 0.5 M Na_2SO_4

On the basis of the above formula one may safely assume that in the first approximation the interfacial surfaces were equal. Obviously this first attempt was not very successful, in that it did not produce the straight lines hoped for; clearly the interfacial surface areas generated were so large that the first points measured are already close to the limit of the region in which reliable kinetic measurements can be done. For example, the first measured point of the Escaid 100 curve already represents 89 % of equilibrium in the distribution of tracer copper. A better and more clearly defined experimental set-up is deemed necessary. Nevertheless the experiments indicate two important things. Firstly, the rate constants differ by factors rather than by order(s) of magnitude, and therefore it is not necessary to reject aromatic diluents for doing kinetic measurements. Secondly, the differences in type composition between commercial diluents will probably show up in kinetics in a measurable way.

We feel that one may be confident that kinetic measurements will give much valuable information as to the relation between reaction rates and composition of the diluent. They do not, however, bring us any closer to solving the problem of the nature of these relations.

In recent years it has quite frequently been observed in discussions, papers and so on, that surface or interfacial phenomena are bound to play an important role in liquid/liquid extraction, and there are indications that various groups working in this field are currently trying to find a quantitative basis for these considerations.
Price[5] showed for one oxime (2-hydroxy-5-nonylbenzophenone oxime) that, going from a highly aromatic through a medium aromatic to a non-aromatic diluent, the extraction rate of copper increases. At the same time he showed that in this sequence the interfacial population density of the oxime also increased. The suggestion that there might be a direct relation between interfacial population density and rate of extraction is self-evident.

Flett[6] has tentatively attributed the observed differences in copper extraction rate for SME 529, Acorga P-17 and LIX 65 N to different degrees of difficulty the reagent molecules have in packing at the interface, explainable on the basis of molecular size and shape.

Both suggestions appear logical and are quite appealing and promising, since relatively simple physical measurements might give a quantitative basis to the reasoning. Current work at the Koninklijke/Shell Laboratorium is aimed at elucidating the relations between extraction rates, interfacial population densities, oxime structure and diluent properties. We find ourselves in the relatively good position of having access to many chemically pure oximes belonging to the proprietary Shell class of 5-alkyl-2-hydroxyphenyl alkyl ketoximes, which are chemically sufficiently akin to warrant comparison. Although our work is still in the initial stages, the first results are surprising enough to make early publication worthwhile.

When a pure oxime, e.g. 2-hydroxy-5-tert-octylacetophenone oxime, is dissolved in a hydrocarbon diluent the decrease in surface tension in relation to air as a function of concentration is negligible up to 0.5 M: one tends to find more or less the value for the pure diluent. When one measures interfacial tensions with an aqueous layer, however, these are found to decrease strongly with increasing concentration of the oxime. This is of course caused by an orientation of the oxime molecules at the interface, which in itself would not be surprising.

Measurements of interfacial tensions can be used to calculate the interfacial population density of the oximes by applying the Gibbs formula in the form[7,8]

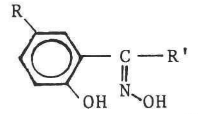
$$\Gamma_{2,1} = -\frac{1}{RT}\cdot\frac{d\sigma_i}{d\ \ln C} = -\frac{0.43}{RT}\cdot\frac{d\sigma_i}{d\ \log C}$$

in which σ_i is the interfacial tension ($mN.m^{-1}$), C is the bulk concentration of the oxime, and $\Gamma_{2,1}$ is the excess interfacial population density (EIPD). From the latter the interfacial population density (IPD) can be calculated by adding the cross-section population density (CSPD), that is the population density of the oxime in a random cross-section of the bulk phase.

The oximes used so far in our investigation are summarized in Table 4.

Table 4

Oximes of general formula



used

No of oxime	R	R'	m.p., °C
I	t-C_4H_9	CH_3	138-9
II	t-C_8H_{17}	CH_3	83.5-85
III	t-C_9H_{19}	CH_3 (SME 529)	--
IV	t-C_8H_{17}	n-C_7H_{15}	69-70
V	CH_3	n-C_7H_{15}	88.5-89.5

All compounds were purified, no III by distillation of the ketone, the others by recrystallization of the oximes.

An example of a plot of interfacial tension as a function of concentration of oxime II in two different diluents is given in fig. 3. Even a superficial study of these curves provides some very interesting information.

Firstly, there appears to be a 'threshold concentration', above which the oxime molecules tend to collect at the interface. This'threshold concentration' is considerably higher in toluene than in heptane (about 0.005 M compared to < 0.0001 M in the case of oxime II), and this was consistently found for all oximes. This fact illustrates the better solvent properties of the aromatic diluent.

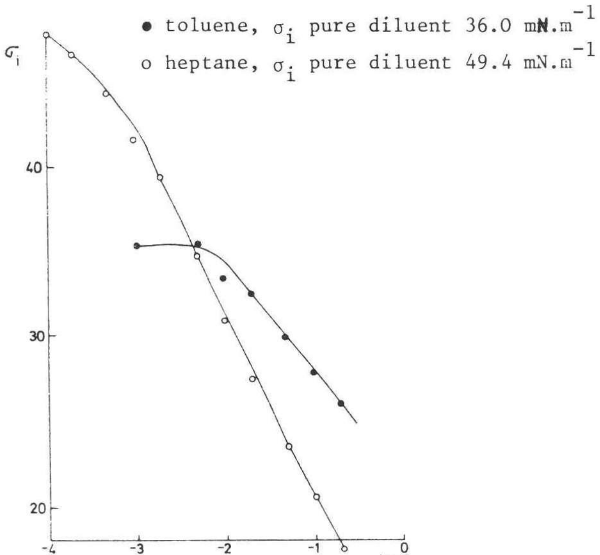


fig. 3

Interfacial tension of oxime II in heptane and toluene against 0.5 M Na_2SO_4, pH 2.0, T = 25° C

Secondly, soon after the 'threshold concentration'is exceeded the interface is densely populated, and the EIPD (as expressed by the slope of the σ_i vs. log C plot) is rather constant. This is not uncommon, and is paralleled by, for instance, the behaviour of aqueous solutions of higher aliphatic alcohols[9]. The real IPD increases only slowly, therefore, because the only increasing factor is the changing contribution of the CSPD. Table 5 gives some numerical values of IPD's for oxime II.

Table 5

Interfacial population densities (IPD) of oxime II in heptane and toluene as a function of concentration.

Concnentration, M	IPD in 10^{13} molecules.cm^{-2}	
	n-heptane	toluene
0.001	12.1	0.07
0.01	12.3	7.2
0.1	13.6	8.2
0.2		9.1

Thirdly, the IPD in toluene is lower over the whole concentration range than in heptane (although the difference is in fact surprisingly small). This again was consistently found for all oximes tested.

To see whether there is any indication that a quantitative relation could exist between the IPD of an oxime, the character of the diluent and the extraction rate we have collected values of EIPD's (representing the slopes of the σ_i/log C plots) for our various oximes, covering the concentration range between about 0.001 and 0.1 M and put them together in table 6.

Table 6

Excess interfacial population densities (EIPD) for oximes from table 4 in heptane and toluene.

Oxime No.	EIPD in 10^{13} molecules.cm^{-2} n-heptane	toluene
I	14.6	
II	12.1	7.2
III	12.8	
IV	17.1	9.5
V	10.9	6.8

A study of the above data with the aid of our background knowledge on relative extraction rates for these oximes revealed two interesting things.

Firstly, the biggest molecule is by far the slowest of the series: oxime IV is at least 20 times slower than II, and at least 15 times slower than III. However, its EIPD (and therefore also its IPD) is by far the highest. Obviously, there is no indication whatsoever of the existence of packing difficulties in direct relation to the size of the molecule. (This, incidentally, is also paralleled in the behaviour of higher aliphatic alcohols in aqueous solution[9]. In the range hexanol through decanol the IPD was found to be constant).

Secondly, as expected, the EIPD of oxime V is markedly lower in toluene than in heptane. However, this oxime happens to work faster in toluene (although by all standards it is a slow reagent). So the existence of a relation between IPD and extraction rate is also highly questionable.

We realise that the above data probably generate more problems than they solve. It might well be, for example, that the apparently 'simple' process of mass transfer into and from the organic phase has to be split up into various steps, each of which can, in a particular case or for a specific oxime, be rate determining, e.g.:

1. reaction of copper with the reagent molecule(s) at the interface;
2. migration of the loaded extractant from the interface into the organic bulk layer;
3. filling of the open sites at the interface.

CONCLUSIONS AND LINES FOR FUTURE INVESTIGATION

As will be obvious from the preceding sections, the conclusions are different for equilibrium and non-equilibrium properties.

When using model hydrocarbons, one will usually measure appreciable differences in the equilibrium properties of a system. In all respects except as regards Cu/Fe selectivity the aromatic model hydrocarbons show up worse than the non-aromatic ones. In practice however, when composite mixtures of hydrocarbons containing anything between 0 and 25 % aromatics are used, the effects are found to be marginal, or even hardly measurable. It follows, and it has also been argued before[1], that the differences do not warrant acceptance or rejection of a diluent on this basis alone.

In kinetics the differences between solutions in aromatic and non-aromatic model hydrocarbons are more obvious, and could in a preliminary way be quantified as rate 'constants'. The differences also show up in a measurable way between two commercial hydrocarbon mixtures, the higher aromatic one being slightly worse than the low aromatic.

The attempt to correlate extraction rates, interfacial population densities, molecular size, and diluent characterwas not successful. The following conclusions could be drawn from the present work:

1. No direct relation exists between interfacial population density and molecular size, or between interfacial population density and extraction rates.
2. Within the homologous series of oximes tested the smaller molecules were found to extract faster.
3. The fact that aromatic diluents are better solvents for the oximes could be more or less quantified in terms of higher 'threshold concentration' and lower interfacial population densities.

The problem of connecting the observed rates of extraction with a mechanism for this extraction is most probably of a greater complexity than has been realized previously.

No experimental results are included of the 'secondary' effects such as phase disengagement, third-layer formation, and so on. The influence of the diluent on heterogeneous equilibria associated with individual systems is obviously of considerable importance, yet so far no satisfactory relationship can be shown between these effects and the type composition of the diluent.[1,10] Attention is being given to the possibility of the influence of impurities in the diluent (for example olefins or S-containing compounds) which are known in other use areas to influence interfacial properties. Temperature is an important factor to be considered in relation to third-phase formation. Real difficulties associated with 'secondary' effects are often only first revealed in commercial practice, and then only under a particular combination of leach solution, extractant solution and operating conditions.

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B 3. ORGANIC AND PHYSICO-CHEMICAL ASPECTS OF PROPERTIES OF HYDROXY-OXIME EXTRACTANTS

A.J. van der Zeeuw.

Paper presented at the Distinguished Seminar, University of Waterloo, Ont., Canada, 19th February 1976.

INTRODUCTION

Following the announcement and subsequent commercialization of selective hydroxy-oxime extractants for copper the literature on studies of the properties of these reagents has been growing rapidly in volume. Much of this concerns performance characteristics, but increasing attention is now being paid to the more fundamental study of kinetics and chemistry, in other words to the question how the reagents actually work.

It is felt that these studies are still in their very early stages, and as yet one is a long way from a complete understanding of the process. A major obstacle for most investigators so far has been the lack of availability of chemically pure compounds similar enough for comparison of their properties to be meaningful. However, various interesting suggestions have been made in recent literature which warrant further investigation.

This paper describes the kinetic and chemical studies of hydroxy-oxime extractants conducted to date at the Shell Laboratory in Amsterdam indicating the lines along which we are thinking.

The nature of further work required in this field is, of necessity, rather academic. Our feeling is therefore that sooner or later our investigations will have to come to an end, and will have to be summed up to provide those institutions that are by nature more geared to this type of work with a useful set of ideas, results, etc. We feel that our contribution will be of value here since we have access to a class of oximes, many individual members of which can be prepared in a very pure state.

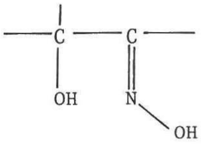
PART I

ORGANIC CHEMISTRY OF HYDROXY OXIME EXTRACTANTS

Structure of reagents

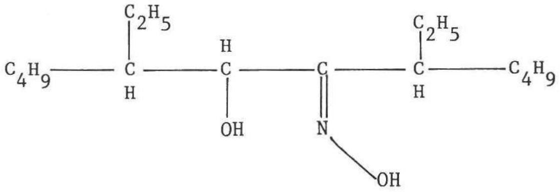
The hydroxy-oxime reagents which we know to exist so far can be divided in two categories. Both types have an OH group and a C═N—OH group in close proximity, enabling them to join with a metal (copper) ion to form a five- or six-membered ring (chelate).

The LIX 63-type of molecule is characterized by the presence of the group:



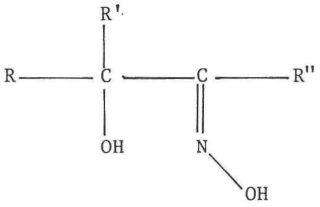
As far as we know only two products with this structural group, both from General Mill Chemicals Inc. (GMCI), have become available.

LIX 63



was the first hydroxy-oxime to be announced, and it was initially marketed with the explicit aim of large-scale solvent extraction of copper (and nickel). Currently it is mainly of importance as a kinetic accelerator for LIX 65 N (see below).

Some time ago General Mills announced the potential availability of a new reagent, tentatively called X18A. Analysis showed it to have the following structure:

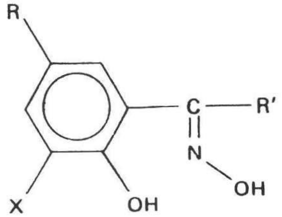


All substituents are very likely to be straight-chain aliphatic groups. From NMR the following combinations were possible:

	R	R'	R''
I	C_4H_9	C_4H_9	C_6H_{13}
II	C_4H_9	C_6H_{13}	C_4H_9
III	C_8H_{17}	C_2H_5	C_4H_9

Although the stucture could not be elucidated fully, the logic of organic synthesis strongly favours structure II. We have not heard very much about this reagent recently, and do not know whether GMCI are still pursuing its commercialization.

The second category might be seen as similar to LIX 65 N, i.e. all compounds in this category have in common the presence of a phenolic OH group in the vicinity of an oxime group. The structure of this group of compounds can be given as:



The following products belonging to this class are currently on the market, or have been announced.

R	X	R'	Name	Supplier
C_9H_{19}	H	phenyl	LIX 65 N	GMCI
do	Cl	do	LIX 70	GMCI
do	H	methyl	SME 529	Shell
do	H	benzyl	P-17[x]	Acorga-ICI
do	H	H	P-50[xx]	Acorga-ICI

[x] Taken from the market soon after this paper was written.

[xx] Now, under its new name P-5000, the basis of the P-5000 range of products.

LIX 64 N, as is by now widely known, is essentially LIX 65 N to which a small amount of LIX 63 is added as an accelerator for the extraction and stripping kinetics. Commercial LIX 70 may also contain some LIX 63 as accelerator, although this is not certain. LIX 71 is a mixture of LIX 70 and LIX 65 N, and LIX 73 is LIX 71 with some LIX 63 as accelerator.

Structure and performance

There are two main differences between the two categories of extractants (the LIX 63 and the LIX 65 N types). The first category (at least LIX 63 itself) can be characterized as a fast extractant, with a rather poor pH functionality. This means that for example it extracts copper at a high rate, but starts to do so only at relatively high pH values ($\geqslant 3$). The LIX 65 N type can be described as rather slow, but with good to excellent pH functionality.

As yet there is no adequate explanation for the rate differences between the two classes, although useful working hypotheses on this have recently led to the development of active accelerators by Shell. The difference in pH functionality, however, is clearly due to the acidity of the phenolic OH group, which increases both the tendency to complex with the metal and the stability of the chelate.

Differences in extraction rates and pH functionality can also be distinguished within the class of "LIX 65 N type". The rates of copper extraction of the various key compounds can be compared as follows:

P 50 > SME 529 > P 17 > LIX 65 N = LIX 70

The reasons for this are not at all clear. Some aspects of various theories will be discussed later. The pH functionalities can be rated as follows:

LIX 70 ⩾ P 50 > SME 529 ⩾ P 17 > LIX 65 N

The very good pH functionality of LIX 70 is quite clearly due to the increased acidity of the phenolic OH group, caused by the ortho-substitution with a chlorine atom.

The sequence LIX 65 N < P 17 ⩽ SME 529 can easily be explained on the basis of inductive effects: the phenyl substituent of the molecule of LIX 65 N has a - I effect, thus diminishing the electron density on the nitrogen of the oxime group, and the complex is therefore slightly destabilized. The methyl substituent in SME 529 has a (slight) + I effect, which in principle results in stabilization of the complex. P 17 (with a benzyl substituent) takes an intermediate position. If there is any steric influence, it is certainly very slight, as can be seen from the table below, which compares extractive properties of "SME type" reagents with different substituents, expressed as pH_{50} (pH at which 50 % of the copper is extracted).

pH_{50} values for Shell Oximes,
0.1 M in toluene, against 0.02 M $CuSO_4$

R	R'	pH_{50}
C_9H_{19}	CH_3	1.57
n-C_8H_{17}	CH_3	1.53
CH_3	n-C_7H_{15}	1.56

The odd one out in the sequence now is P 50, which has a very good pH functionality. On the basis of inductive effects alone it would be expected to be very similar to SME 529 and P 17 in performance, the inductive effect of H being by definition zero. It might well be that the extremely small size of the "substituent" (H) in P 50 allows the complexes of the latter to assume a more ideal structure, leading to increased stability. Molecular models give some support to this assumption.

Syn-anti isomerism

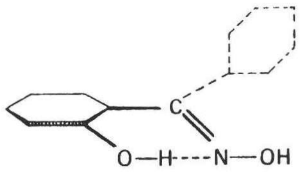
In principle asymmetric oximes may exist in two isomeric forms, normally called syn and anti. In the case of 2-hydroxybenzophenone oxime the presence of two isomers was demonstrated a long time ago[1,2], and in fact this oxime has played a key role in the elucidation of this isomerism.

LIX 65 N only differs from 2-hydroxybenzophenone oxime in having an alkyl substituent in the 5 position. It is therefore not surprising that this molecule also shows the syn-anti isomerism. This was first noted by Atwood and Miller[3] and the former later elaborated the theme in his thesis[4]. In an excellent piece of work, mainly based on skilfully used chromatographic, infra-red and ultraviolet techniques, Ashbrook[5] identified both isomers in various LIX reagents, and determined syn/anti ratios.

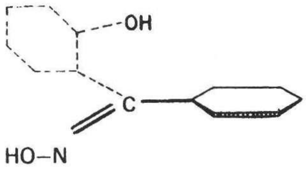
Although the anti isomer is the strongest extractant of the two, and in fact totally responsible for the extractive properties of LIX 65 N and LIX 64 N in the acidic region, the syn isomer does complex copper at high pH, e.g. in ammoniacal medium. We have found that this complexing does not take place via transformation of the syn into the anti isomer: pure syn-LIX 65 N (which can easily be prepared by refluxing LIX 65 N with a 4 N aqueous/alcoholic solution of NaOH for several hours) could be made to complex with copper, and was recovered unchanged after stripping with sulfuric acid, as was established by thin-layer chromatographic analysis.

As already stated, this syn/anti isomerism may exist in asymmetric oximes. It is therefore, at least in principle, also possible in products like P 17, P 50 and SME 529. However, in practice it has not been observed in these compounds. Simple reasoning makes clear why not.

The spatial configurations of syn- and anti-2-hydroxybenzophenone oxime can be drawn as follows:



ANTI



SYN

In anti-LIX 65 N the oxime group assumes coplanarity with the hydroxyl-substituted phenyl group in a nearly ideal way, as can also be seen from models. This configuration also involves the energetically very favourable six-membered "chelate" ring containing the bridgeing H atom.

The syn-LIX 65 N, however, cannot assume the above coplanarity, and therefore cannot make use of the six-membered ring formation. It is therefore logical that the anti isomer should be fundamentally more stable than the syn one, which is borne out by the anti/syn ratios as determined by Ashbrook[5].

The unfavourable gain in energy with syn- as compared to anti-LIX 65 N is partly compensated for by the capacity of the oxime group to become coplanar with the second (unsubstituted) phenyl group. In compounds like P 50, SME 529 and P 17 the molecule does not gain anything from this, because coplanarity with, respectively, an H atom, a methyl group and a benzyl group is of no use. Although theoretically syn/anti isomerism remains possible, the net unfavourable gain in energy with the syn isomers is so substantial that in practice these compounds contain only the anti isomers.

Hydrogen bridge formation and dimerization

On the basis of his own measurements of infra-red spectra of syn- and anti-LIX components in combination with literature data on other, somewhat similar compounds, Ashbrook[6,7] has argued that in syn-LIX 65 N intramolecular hydrogen bonding predominates, whereas in anti-LIX 65 N intermolecular H bridges are more important.

With respect to his first statement we do not have directly conflicting evidence. On the other hand, we do have some relevant data which, if pursued further, might well lead to different inferences being drawn.

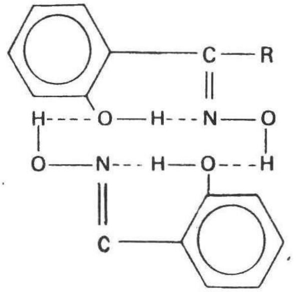
Firstly, syn- and anti-LIX 65 N can be titrated separately and in this sequence in non-aqueous medium. In this titration the stronger acid of the two, syn-LIX 65 N, behaves very much like nonylphenol. In fact nonylphenol added cannot be distinguished from the syn-LIX already present. Anti-LIX 65 N, however, as Ashbrook correctly states, is a much weaker acid. This could point to a much stronger H-bridge in the latter.

Secondly, the behaviour of syn-LIX 65 N in thin-layer chromatography as a strongly polar, slow-running compound (more strongly polar than nonylphenol) could mean that there is no strong hydrogen bridge formation, and that therefore the polar groups (OH groups) are hardly blocked.

Thirdly, it is not very likely that seven-membered "chelate" rings involving H bridges (as appear in most of Ashbrook's possibilities) would be very stable. In this respect it is interesting to note that 4-oximinoundecanoic acid (prepared in our laboratory several years ago for testing as a chelating agent) did not differ at all from a normal carboxylic acid in its behaviour towards Cu, Ni, Co and Fe. It did not show selectivity for copper, had no improved pH functionality, and gave a normal extraction sequence ($Fe^{3+} >$ Cu > Ni, Co). Obviously the seven-membered chelates are not very favoured.

Last but not least a rather strong theoretical argument against both aspects of Ashbrook's view is the well-known fact of the relatively high melting points of intermolecular bonded molecules as compared to those of intramolecular bonded ones. A striking example, not completely outside the present context, is that of isomeric hydroxy methyl acetophenones: 4-hydroxy-2-methylacetophenone melts at 128° C, and 2-hydroxy-4-methylacetophenone at 21° C. The first can only be intermolecularly H-bonded, whereas the second is without any doubt only intramolecularly H-bonded. Completely in line with this reasoning are the melting points of the syn-LIX compounds as reported by Ashbrook. They are in fact extremely high for compounds which are in themselves mixtures of at least 10-15 structural isomers, owing to the nature of the nonyl chain.

Ashbrook's view that in anti-LIX 65 N intermolecular bonding prevails is directly contradicted by Laskorin[8], who convincingly showed (in a case in which only the anti-isomer could exist, i.e. in SME 529-type oximes) that both intermolecular and strong intramolecular hydrogen bonding are present. He also gave evidence that in not too diluted solutions these oximes might be present as dimers, and he proposed a structure of the type:



Using chemically pure 5-alkyl-2-hydroxyphenyl alkyl ketoximes we obtained the following apparent molecular weights, which also point in the direction of dimerization in the bulk phase.

R	R'	apparent molecular weight in toluene	iso-octane	theory
t-C_8H_{17}	CH_3	301	372	263
t-C_8H_{17}	n-C_7H_{15}	398	486	347
CH_3	n-C_7H_{15}	281	340	249

As can be seen, the apparent molecular weight in iso-octane is about 1.4 times the real MW, whereas the apparent MW in toluene is only about 1.15 times the real one. This illustrates the better solvency properties of toluene, i.e. its higher polarity.

PART II

PHYSICO-CHEMICAL CONSIDERATIONS WITH RESPECT TO THE EXTRACTION REACTION

In which phase does the reaction take place ?

In principle the reaction may occur in three phases: the aqueous, the organic, and in something which is rather vaguely described as "interface". (More difficult concepts, like reaction in more than one phase, are omitted from consideration).

The most unreasonable proposition is reaction in the organic phase: it is difficult to imagine that the strongly solvated Cu^{2+} ions would show any tendency to migrate into the organic phase. Moreover, such a mechanism would probably result in the rate of extraction being independent of pH until precipitation of copper hydroxide occurs, whereas it is known that the extraction rate is strongly pH dependent.[9]

The two other possibilities are more acceptable. At this moment experiments have not yet brought the final solution. Neelameggham[10] has proposed a mechanism based upon aqueous-phase reaction. Important objections to his mechanism are that it assumes involvement of ionized oxime in the aqueous phase, and that the presence of LIX 63 in the experiments (which were done with LIX 64 N) is neglected. It can be calculated[9,11] that the ionized oxime can hardly be present at reasonable concentrations in the aqueous phase.

Flett et al.[9] and Ashbrook[11] have proposed mechanisms based upon interfacial reaction, which are essentially the reverse of each other. For the time being we have to accept that both aqueous and interfacial reaction remain possible in the light of current knowledge. Intuitively the chemist would give some preference to the interfacial mechanism, and this view (though, as indicated above, as yet without final proof) has now been widely accepted.

Kinetics of the extraction

Assuming first-order kinetics with respect to copper, Flett et al.[9] analysed the extraction of copper by LIX reagents under non-mass-transfer conditions, i.e. at equilibrium. They derived a formula for the rate constant:

$$k't = \frac{a_o - a_e}{a_o} \ln \frac{a_o - a_e}{a_t - a_e}$$

in which k' and t are the observed rate constant and the time, respectively, and a_o, a_t and a_e stand for aqueous copper concentration at time zero, time t, and equilibrium.

In Flett's work two main disadvantages can be found. Firstly, the whole set-up was to measure the kinetic performance of a commercial, rather composite mixture, and to explain those kinetics in terms of a mechanism. Secondly, the work was performed in the AKUFVE apparatus, which does not guarantee that the interfacial surface area (of prime importance in a supposedly interfacial mechanism) would be well-defined, or even equal in duplicate experiments.

In an attempt to repeat Flett's work in our context we tried to offset both disadvantages as much as possible. We were able to use chemically pure oximes of well-defined structure. In addition, we did our experiments in a baffled, turbine-stirred apparatus, which we assumed would give us equal, and hopefully measurable or calculable, interfacial surface areas throughout.[x]

Fig. 1 shows the rather disappointing results obtained with three chemically pure oximes in toluene. Clearly, the Flett treatment can only be used with some success on the slowest of the three, 2-hydroxy-5-tert-octylphenyl n-heptyl ketoxime. The others very soon started to show a distinct curvature. From the experimental data from which the curves were composed it can easily be calculated that in the latter two cases the reaction had already proceeded to over 80 % towards equilibrium, i.e. to well outside the region in which reliable calculation can be carried out, when the first measurement was taken (after 1 minute).

Influence of oxime and diluent character on kinetics

It has been accepted for some time that the nature of the diluent has an influence upon the performance of the reagent. It in fact affects all performance characteristics, pH functionality, loading capacity, selectivity etc., but we shall restrict ourselves here to its effect on the kinetics.

It can be stated quite briefly, that reaction rates become lower with increasing aromaticity of the diluent[12,13]. Without explicitly mentioning it, Flett et al.[9] applied this principle in choosing toluene as the most suitable diluent for their kinetic work.

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[x] In later internal discussions it became clear that this principle was open to doubt, so we did not use it in the numerical treatment of our data.

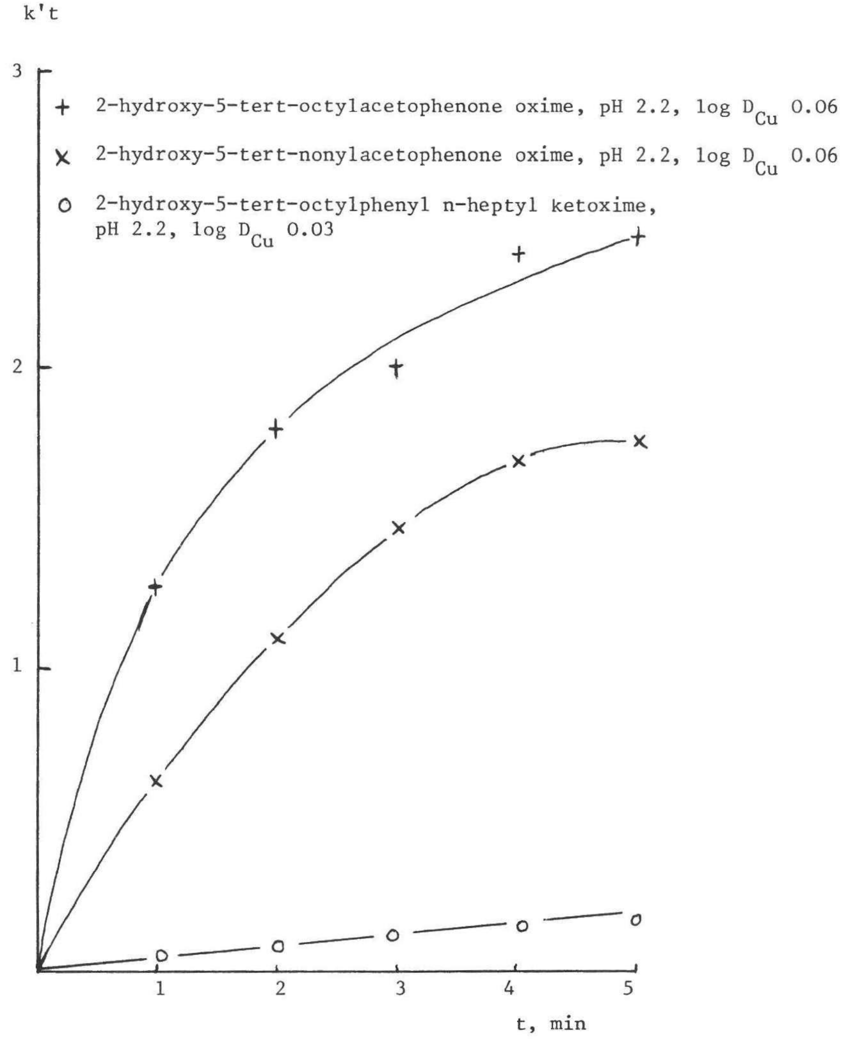


Fig. 1

Flett treatment of extraction kinetics of three chemically pure oximes in toluene. Oxime concentrations: 0.02 M. Aqueous: 0.002 M $CuSO_4$ in 0.5 M Na_2SO_4.

In fig.2 the kinetic treatment according to Flett et al. is used in plotting the results obtained with one oxime in various diluents. Again the rather disappointing behaviour of the results is clear, but the qualitative confirmation of the principles used[12] is obvious.

The potential influence of the nature of the oxime on reaction rates has also been recognized for some time. Price[13] has noted the difference in extraction rates for the Acorga reagents P 50 and P 17, and the present author, on the same occasion[12], presented a qualitative characterization for the kinetics of extraction of various oximes from the Shell proprietary class. The kinetic data presented now, although not suitable for quantitative treatment, confirm earlier reports.

Interfacial population densities of oximes in relation to structure and diluent (see also the section on comments on papers)

Naturally phenomena like those mentioned above having been observed, people start thinking about the reasons behind them. Flett[14] has argued that the rate differences found between three commercial reagents, i.e. SME 529 $\gg$ P 17 $>$ LIX 65 N, could be due to "packing difficulties" at the interface, due to increase in this order. Price[13], comparing the behaviour of one oxime in diluents of varying character, supposed that the interfacial population density in aromatic diluents was lower, causing the extraction rates to be lower as well.

These principles are very appealing because of their simplicity: if found correct, only a relatively simple physical measurement would be required to explain the differences found.

We started a rather extensive programme on this basis, measuring interfacial tensions as a function of concentration for a number of oximes, with n-heptane and toluene as model diluents.

Measurements of interfacial tensions can be used to calculate interfacial population densities by applying the Gibbs formula in the form[15,16]:

$$\Gamma_{2,1} = -\frac{1}{R\,T}\,\frac{d\sigma_i}{d\ln C} = -\frac{0.43}{R\,T}\,\frac{d\sigma_i}{d\log C}$$

in which σ_i is the interfacial tension ($mN.m^{-1}$), C is the bulk concentration of the oxime, and $\Gamma_{2,1}$ is the excess interfacial population density (EIPD). From the latter the interfacial population density (IPD) can be calculated by adding the cross-section population density (CSPD), that is, the population density of the oxime in a random cross-section of the bulk phase.

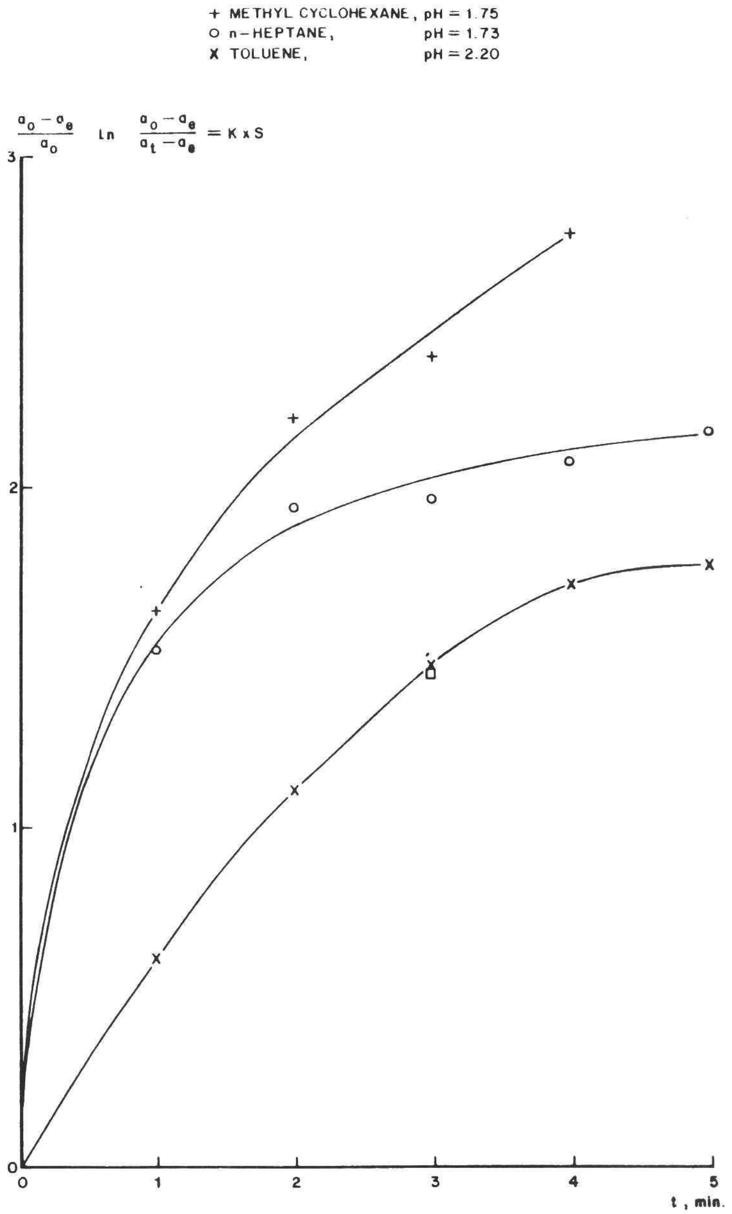


Fig. 2

Flett treatment of extraction kinetics for chemically pure 2-hydroxy-5-tert-octylacetophenone oxime in various diluents.
Organic and aqueous concentrations as in fig. 1. Log D_{Cu} = 0.

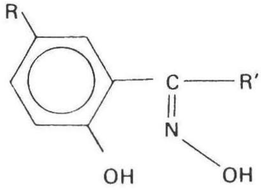
Preliminary results of our work have been presented at the Annual Group Meeting of the Solvent Extraction and Ion Exchange Group of the Society of Chemical Industry, May 1975, at Bristol, UK and will be published shortly.[17] We now present some more data, together with some conclusions.

Fig. 3 shows typical results obtained, and can be used to illustrate some general facts. It is a plot of interfacial tensions as a function of concentration of chemically pure 2-hydroxy-5-tert-octylacetophenone oxime (m.p. 83.5 - 85° C) in heptane and toluene. Two important observations can be made directly.

Firstly, there appears to be a threshold concentration above which the oxime molecules tend to collect at the interface. This threshold concentration is considerably higher in toluene than in heptane (about 0.005 M as against $\leqslant$ 0.0001 M for this specific oxime), and this was consistently found for all oximes tested. This fact illustrates the better solvent properties for the aromatic diluent (see also fig. 4).

Secondly, soon after the threshold concentration is exceeded the interface is densely populated, and the EIPD (as expressed by the slope of the σ_i/log C plot) is fairly constant. Over a wide range of concentrations the real IPD increases only slowly, the only increasing factor being the changing contribution of the CSPD.

A survey of our results with compounds of the general formula



is presented in the following table. A full series of measurements was of course done, but we confine ourselves here to the results determined for a fixed concentration of 10^{-2} M, because this concentration was well within the straight part of the plot for all oximes and both diluents.

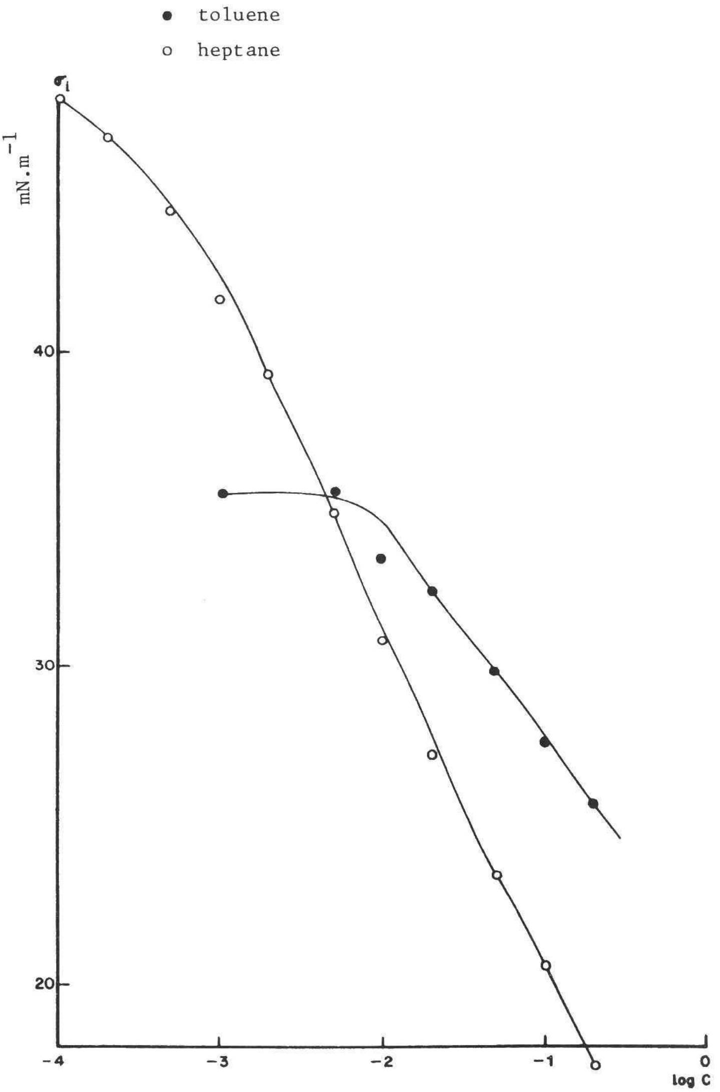


Fig. 3

Interfacial tension of 2-hydroxy-5-tert-octylacetophenone oxime in heptane and toluene against 0.5 M Na_2SO_4, pH 2.0. T = 25°C

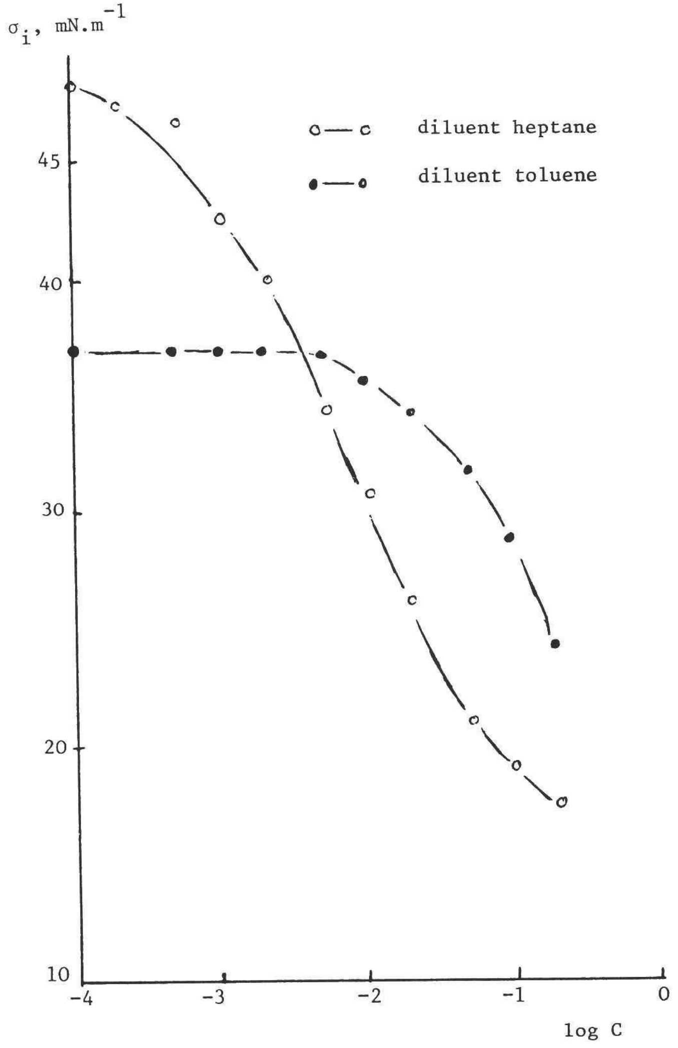


Fig. 4

Interfacial tension of 2-hydroxy-5-tert-nonylsalicylaldoxime in heptane and toluene against 0.5 M Na_2SO_4, pH 2.0. T = 25°C.

Slopes of σ_i/log C plots, EIPD's[x] and IPD's[x] for various oximes in toluene and heptane. Oxime concentrations 10^{-2} M.

OXIME			HEPTANE			TOLUENE		
No.	R	R'	SLOPE	EIPD	IPD	SLOPE	EIPD	IPD
I	t-C_4H_9	CH_3	-11.8	12.3	12.6	-11.1	11.5	11.8
II	t-C_8H_{17}	CH_3	-10.5	10.9	11.2	- 6.7	7.0	7.3
III	t-C_9H_{19}	CH_3	-10.8	11.2	11.5	- 6.2	6.4	6.7
IV	t-C_8H_{17}	n-C_7H_{15}	-16.2	16.8	17.1	- 9.2	9.4	9.7
V	CH_3	n-C_7H_{15}	- 9.9	10.3	10.6	- 6.6	6.9	7.2
VI	t-C_9H_{19}	H	-13.5	14.0	14.3	-13	13.5	13.8

If one tries to relate observed rates of extraction[xx] for these oximes:

$$\mathrm{VI} \gg \mathrm{I} > \mathrm{II} > \mathrm{III} > \mathrm{V} > \mathrm{IV}$$

to the interfacial properties measured, the remarkably high IPD's of compounds IV and VI attract attention. Oxime VI is very fast, but IV can only be described as extremely slow. This effectively proves that a high IPD does not necessarily mean a high rate of extraction, that a high molecular weight does not automatically lead to packing difficulties at the interface, and in fact that no obvious relation exists between IPD and reaction rate.[xxx]

When comparing the behaviour of heptane systems to that of toluene ones, oximes I and VI have to be omitted: both are so fast that their approach to equilibrium in both diluents is over 95 % in 15 seconds, and differences cannot be measured reliably with our method. For the other oximes (II through V) toluene was consistently found to give slower systems than heptane. (Our earlier observation[17] that oxime V was slower in heptane than in toluene was made with a sample that had been stored for a long time, and was found to be incorrect when the experiment was repeated with the purified sample that was also used for the interfacial tension measurements.)

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[x] In 10^{13} molecules/cm^2.

[xx] The rate at which barren extractant solutions extract copper from an aqueous phase. Usually expressed as % extraction vs. time.

[xxx] Reference is again made to the section on comments on papers.

In the above reasoning the measurements on systems with oxime I have been left out on purpose: since this oxime is distinctly soluble in water, both the interfacial tensions and the observed rates are influenced in an uncontrollable way.

Mechanism of the extraction reaction

It has now been widely accepted (though, as stated before, not proven beyond doubt) that the reactions discussed are interfacial by nature. Therefore a link must exist between the number of reagent molecules at that interface and the reaction rate.

However, in the light of the totality of our results discussed above that link cannot be a straightforward one. It may very well be of a complex nature, and the mechanism might have to be broken down into several steps, e.g.:

1. reaction between copper ions and reagent at the interface,
2. diffusion of the loaded reagent into the bulk organic phase,
3. refilling of the gaps left at the interface with fresh reagent.

It might be necessary to distinguish two separate steps in the first one, i.e. a stepwise reaction of Cu^{2+} firstly with one reagent molecule and then with the other. Steps 1 and 2 will certainly depend on the IPD, whereas 3 depends on the bulk concentration. Both 2 and 3 will incorporate an element of diffusivity of fresh and loaded reagent, respectively. There is some logic in assuming that the actual reaction rate at the interface will not depend on the molecular weight of the oxime as long as the compounds being studied are chemically similar, like the Shell proprietary ones. However, the molecular weights will certainly influence the diffusivities of loaded extractant into the bulk organic phase and fresh extractant towards the interface. We therefore tentatively suggest that the main reasons for rate differences between chemically similar reagents might have to be sought in steps 2 and 3, rather than in step 1.

Something can be said with respect to the actual process of reagent accumulation at the interface. As Laskorin[8] has shown, there are strong indications of oximes like those discussed here being dimeric in the bulk phase of diluents, at least at concentrations well above 10^{-3} M. It is difficult to imagine that such dimers, characterized by rather strong inter- and intramolecular hydrogen bridges, will show a very polar (hydrophilic) character of their own. It is therefore not unreasonable to assume that at the interface the dimers will be broken up because the single molecules prefer hydrogen bonding with water.

It will be clear from the above that, as a first approach, we prefer to regard the real reaction as one between the metal ion and monomeric reagent molecules rather than to support the fairly complicated mechanism proposed by Price based on reaction of the reagent in the dimeric form.[13]

Proposals for future work

Our scheme for the reaction presented above is obviously a tentative one, although we feel that many of our data at least support the basic principle. Much work will be needed to clarify the whole process. Although our company has so far been most accomodating in allowing us to carry out work of the kind described, we obviously cannot continue it for ever, as it will not be of any benefit to the company in financial terms. Moreover, we feel that, since these studies are time-consuming and are becoming increasingly academic, the time is coming for them to be taken over by universities.

In the following few paragraphs we indicate fields that are in our opinion very interesting for further investigation. As our group of workers is certainly not yet leaving the scene, we have deliberately kept the wording rather vague in some instances in order to keep our own options open.

Firstly, the concentration range in which no accumulation of the reagents at the interface is apparent (particularly in toluene) would seem to be a very interesting one for kinetic investigations, since through it one might be able to find the real rate constant of the reaction proper. We would strongly recommend this as a promising field or research to any interested party.

Secondly, measurements of the diffusivity of oximes of different molecular weights may throw some light upon the relative importance of the various processes indicated above.

Thirdly, the different explanations given by Flett and by Ashbrook for the action of accelerators make clear that this question cannot yet be considered answered.

Lastly, the presence of syn-LIX 65 N in the commercial mixture might influence a number of process characteristics, including the rate of the reaction.

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B 4. KINETICS AND MECHANISM OF COPPER EXTRACTION WITH 5-ALKYL-2-HYDROXYPHENYL ALKYL KETOXIMES

A.J. van der Zeeuw and R. Kok.

Proc. Int. Solvent Extr. Conf. 1977, Toronto.
CIM Special Volume 21, 210 (1979).

ABSTRACT

The paper involves work done to elucidate the kinetics and mechanism of the copper-chelating reaction with hydroxy-oximes. The kinetics of the forward and backward reaction were measured independently; from the results, together with theoretical considerations, it is concluded that the mechanism very likely involves the dimer of the reagent. The work shows that both accelerators and retardants can be classified as compounds showing a higher degree of interfacial activity than the reagents proper. The actual involvement of the accelerators in the mechanism still remains unclear. Some fresh views are put forward on the influence of diluents and modifiers.

EXPERIMENTAL

KINETIC MEASUREMENTS

SOLUTIONS, PREPARATION OF CHEMICALS

The aqueous solutions were made up from analytically pure chemicals and contained an ionic background of 0.5 M Na_2SO_4.

The organic solutions were made up in analytically pure diluents. Oximes of the (5-alkyl-2-hydroxyphenyl)-n-alkyl ketoxime type were prepared by subjecting the 4-alkylphenyl esters to a Fries rearrangement, distilling the ketones formed, oximating them, and recrystallizing the oximes various times, in most cases from pentane or heptane.

Syn-2-hydroxy-5-nonylbenzophenone oxime (syn-HNBPO) was prepared by boiling diluent-free commercial LIX^R 65 N with 4N aqueous/alcoholic NaOH for 12 hours. After working-up and isolation, the syn-HNBPO had a melting point of 114-115° C.

Anti-HNBPO was prepared by separating the isomers of diluent-free commercial LIX^R 65 N through column chromatography on activated silica. Thin-layer chromatographic analysis showed that each of the isomers was free of the other.

Diluent-free 5,8-diethyl-6-hydroxy-7-oximinododecane (DEHOD) was prepared by dissolving commercial LIX^R 63 in methanol, adding slowly under stirring a methanol solution of $Cu(CH_3COO)_2.H_2O$, filtering off the olivegreen crystalline precipitate, washing the latter repeatedly with acetone, and drying it in the air. Then the crystalline copper complex was dissolved in heptane and treated three times with excess of 2N H_2SO_4. Because even then some copper remained in the organic layer, the latter was washed once more with 0.5 N HNO_3. The colourless organic layer was then dried over Na_2SO_4 and the diluent evaporated to leave a white crystalline material with melting point 40-41^o C.

APPARATUS, OPERATING CONDITIONS, PROCEDURE AND RELIABILITY

A cylindrical double-walled glass vessel (capacity 250 ml, internal diameter 70 mm) was used, equipped with four baffles (width 7 mm), a bottom sampling cock (no dead space), a quickfit flange lid with the necessary inlet and outlet tubes, and a six-bladed turbine stirrer (tip-to-tip diameter 28 mm). In all experiments the position of the stirrer was 5 mm below the interface.

In all experiments the organic phase was held as the continuous phase. The organic/aqueous (O/A) phase ratio was 1/1, 100 ml of each phase being present at the start of each experiment. The stirrer speed throughout was 2000 $\pm$ 20 rev/min. The temperature was maintained at 25 $\pm$ 0.2^o C by means of a thermostat bath connected to the double wall of the vessel.

The kinetic experiments were carried out using the relaxation technique[1]. A survey of all experiments done under these conditions is given in Table 1. After equilibration of the phases with respect to copper distribution and temperature, the layers were separated and one of the phases was seeded with radio-active copper. The actual experiment was then started by rapidly adding the aqueous phase to the organic phase under stirring. This was timed to take 3 seconds. End of addition was set as time zero. Dispersion time in this reactor is less than 1 second.

Sampling was done from the bottom cock. The absence of dead space meant that homogeneous sampling was ensured. The size of the samples was $\pm$ 6 ml. After phase disengagement, which took 7 seconds, the layers were separated and analysed.

The fact that mixing and disengagement of the phases normally take time might be a reason to question the reliability of the method used. However the total uncertainty (approx. 11 s.) was only 6 % on the fastest run reported, and less than 3 % on most. We therefore neglected the time effect. The good reproducibility of the data shows that this was correct.

TABLE I

SURVEY OF KINETIC EXPERIMENTS UNDER RELAXATION CONDITIONS

Experiments reported in this table were done in toluene unless stated otherwise. All concentrations are in mmoles/l.

1. Experiments with 2-hydroxy-5-tert-octylphenylheptyl ketoxime (HOPHO)

Exp.	Initial conditions		Equilibrium conditions				
	$[\overline{RH}]_{o,a}$	[Cu]	$[\overline{RH}]_{f,a}$	$[\overline{Cu}]$	[Cu]	D_{Cu}	pH
A	20	11.7	17.8	1.1	10.6	0.106	1.53
B	20	2.2	18	1.0	1.2	0.83	2.00
C	20	1.18	18	1.05	0.12	8.86	2.52
D	20	0.99	18	0.97	0.02	43.9	2.98
E	20	11.1	18.1	0.93	10.2	0.091	1.50
F	20	1.9	18.4	0.79	1.13	0.69	1.92
G	20	1.6	17.3	1.35	0.20	6.82	2.51
H	6	3.6	5.9	0.25	3.37	0.075	2.00
I	10	2.3	9.3	0.38	1.89	0.20	2.00
K	60	3.4	53	3.0	0.47	6.23	2.00
L	= H						
M	= B	but with tracer copper added to the organic phase instead of the aqueous phase					
N	= K						

2. Experiments with anti-2-hydroxy-5-nonylbenzophenone oxime (anti-HNBPO)

P	20	2.0	18.2	0.80	1.20	0.67	2.00

3. Experiments with HOPHO in heptane

Q	20	1.85	18.0	0.98	0.88	1.11	1.50
R	20	1.06	18.1	0.96	0.09	10.2	2.00
S	= Q	but with tracer copper added to the organic phase instead of the aqueous phase					
T	= R						

THE KINETICS OF THE FORWARD AND BACKWARD REACTIONS

In its simplest form, the reaction between a copper ion and a single chelating reagent can be presented as:

$$Cu^{2+} \quad + \quad 2\ RH \quad \rightleftharpoons \quad CuR_2 \quad + \quad 2\ H^+ \qquad (1)$$

This equation, which fully disregards any aspects of mechanism, polymerization of the reagent, etc. indicates which dependencies one has to establish in order to devise a suitable rate equation.

The forward reaction will at least be dependent on the Cu^{2+} concentration at the site of the reaction, and on a free (i.e. not copper-bound) reagent concentration. Other factors, like hydrogen ion concentration, or complex concentration, might be reflected in the rate of the forward reaction if they play a role in the mechanism. The backward reaction will show dependencies on hydrogen ion concentration and complex concentration, and again on any factors that might creep into the mechanism.

Under conditions of equilibrium, Flett et al.[1] have carried out tracer experiments and interpreted the results on the basis of

$$k_f^{\prime} t \quad = \quad \frac{[Cu]_o - [Cu]_{eq}}{[Cu]_o} \ \ln \frac{[Cu]_o - [Cu]_{eq}}{[Cu]_t - [Cu]_{eq}} \qquad (2)$$

Let us consider the differentiated rate equation of a process as in equation (1) and also take into account possible complications as indicated. The rate of disappearance of Cu^{2+} from the aqueous phase will be given by:

$$-\frac{dCu}{dt} = k_f[\overline{RH}]_{free}^{w}[X]^x[Y]^y[Z]^z[Cu] - k_r[P]^p[Q]^q[R]^r[H^+]^m[\overline{CuR_2}] \qquad (3)$$

provided the reactions are first order in copper ions and in complex. $[X]^x$, $[Y]^y$ etc. indicate any additional factors that might influence the kinetics apart from the obvious ones. It can easily be seen that when one looks for the dependency on copper concentration and all other factors are constant (that is, at conditions of equilibrium as in Flett's tracer studies) this equation reduces to:

$$-\frac{dCu}{dt} = k_f^{\prime}[Cu] - k_r^{\prime}[\overline{CuR_2}] \qquad (4)$$

Simple mathematical treatment easily leads to equation (2), as illustrated in Ref. 2.

The fact that this relation produces a straight line with the experimental data through a considerable range of conversions supports the hypothesis of a first-order dependence on aqueous and organic copper concentrations.

1. The influence of the hydrogen ion concentration

Flett et al. have found that in the extraction of Cu^{2+} with LIX 64 N the rate of disappearance of Cu^{2+} from the aqueous phase is inversely proportional to the hydrogen ion concentration, all other factors being kept constant. Thus, in the symbols of equation (2):

$$k'_f = k''_f \, [H^+]^{-1} \qquad (5)$$

Mil·ler and Atwood[2] however argued that in fact the apparent inverse first-order relation found resulted from a direct first-order relation between the rate of the backward reaction and the hydrogen ion concentration, or, in terms of equation (4):

$$k'_r = k''_r \, [H^+]^{+1} \qquad (6)$$

One may put the conditions given in equations (5) and (6) in a more general form, and assume that the forward rate depends on the m^{th} power of the hydrogen ion concentration and the reverse on the n^{th} power of that same concentration. Or in formulae:

$$k'_f = k''_f \, [H^+]^{m} \qquad (5')$$

$$k'_r = k''_r \, [H^+]^{n} \qquad (6')$$

Now the following reasoning can be set up:

At equilibrium:

$$k'_r = k'_f \frac{[Cu]_{eq}}{[\overline{Cu}]_{eq}} \qquad (7)$$

Substitution of (5') and (6') into (7) then yields:

$$k''_r \, [H^+]^{n} = k''_f \, [H^+]^{m} \frac{[Cu]_{eq}}{[\overline{Cu}]_{eq}}$$

$$\text{or} \quad k''_f = k''_r \, [H^+]^{n-m} \frac{[\overline{Cu}]_{eq}}{[Cu]_{eq}} \qquad (8)$$

Now the equilibrium constant K_{eq} derived from equation (1) is :

$$K_{eq} = \frac{[\overline{CuR_2}] \, [H^+]^2}{[Cu] \, [\overline{RH}]^2} \qquad (9)$$

$$\text{or} \quad \frac{[\overline{\mathrm{Cu}}]_{eq}}{[\mathrm{Cu}]_{eq}} = K_{eq} \frac{[\overline{\mathrm{RH}}]^2}{[\mathrm{H}^+]^2} \tag{10}$$

By combining (8) and (10) it follows that

$$k''_f = k''_r K_{eq} [\overline{\mathrm{RH}}]^2 [\mathrm{H}^+]^{n-m-2} \tag{11}$$

and, since k''_f is now by definition no longer a function of $[\mathrm{H}^+]$:

$$n - m - 2 = 0 \tag{12}$$

The experimental results of Flett et al.[1] being that m = - 1, it follows of necessity that n must be + 1. If, as Miller and Atwood[2] suggest, m = 0, the consequence is that n must be 2.

Figures 1-4 present the results of a series of experiments with chemically pure (2-hydroxy-5-tert-octylphenyl)-n-heptyl ketoxime (HOPHO) in toluene as a function of pH. The rates were followed under relaxation conditions with tracer copper distribution. Care was taken that both the free organic reagent concentration and the copper complex concentration were kept equal in all experiments, so that the property under investigation could be properly isolated.

The rate of the forward reaction was followed by adding tracer copper to the aqueous phase (fig.1) and that of the backward reaction by adding tracer copper to the organic phase (fig. 2).

Figure 3 shows the relation between the forward rate constant and pH . Both the constants measured directly from fig. 1 and those derived from the measured values from fig. 2 via formula (7) are given. Similarly, fig. 4 gives the relation between the backward rate constant and pH. The slopes of the plots are 0.94 and - 0.90, respectively, close enough to unity to substantiate the view that in equation (12) n = 1 and m = - 1. In other words, the forward reaction is inversely proportional and the backward reaction directly proportional to the hydrogen ion concentration.

2. The influence of the free reagent concentration

A reasoning similar to that given for the pH dependence leads to the conclusion that, in terms of equation (3):

$$w - p - 2 = 0 \tag{13}$$

if P is the free monomeric reagent concentration influencing the backward reaction and p its exponent in the rate equation.

In interpreting the results of experiments designed to find the relation between rate and reagent concentration one faces a fundamental problem: to decide whether the reagent concentration should be expressed in terms of free (that is not bound to copper) analytical concentration, $[\overline{RH}]_{f,a}$, free monomeric reagent, $[\overline{RH}]_{f,m}$, or free dimeric reagent, $[(\overline{RH})_2]_f$.

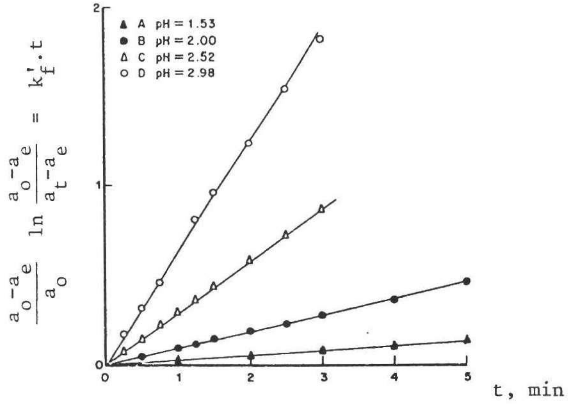

Fig. 1

The rate expression as a function of time at different pH. Forward reaction, HOPHO in toluene. Tracer copper added to the aqueous phase.

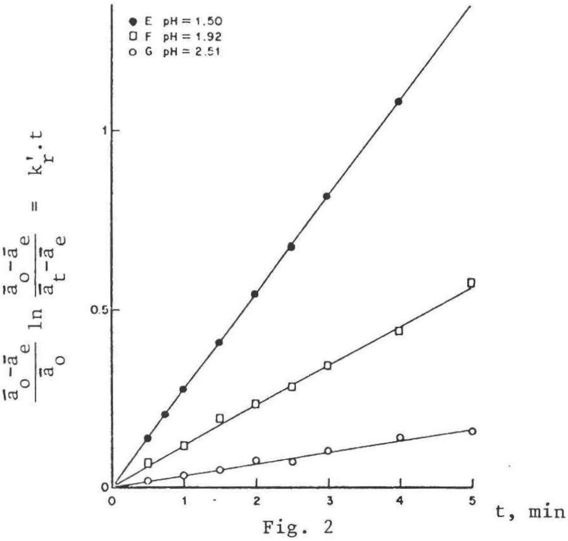

Fig. 2

The rate expression as a function of time at different pH. Backward reaction, HOPHO in toluene. Tracer copper added to the organic phase.

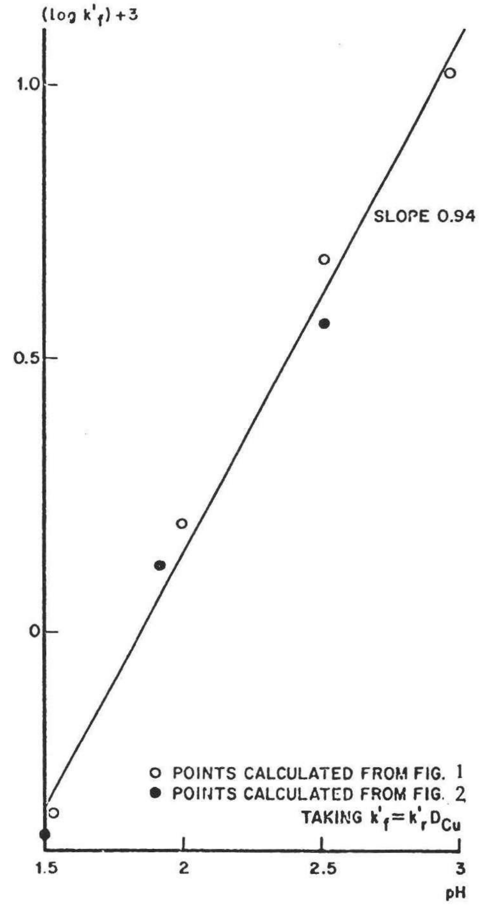

FIG. 3

Relation between k'_f and pH, HOPHO in toluene.

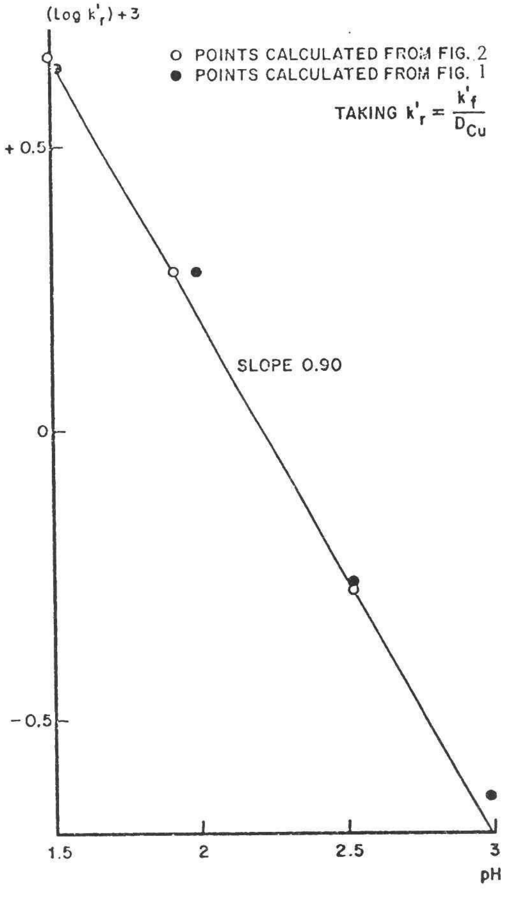

FIG. 4

Relation between k_r' and pH. HOPHO in toluene.

In the context of the paper we shall (for reasons which will become clear) express the relation to be found in terms of both free monomeric reagent, $[\overline{RH}]_{f,m}$ and free dimeric reagent $[(\overline{RH})_2]_f$.

It is now generally accepted that the reaction between copper and the chelating reagent is an interfacial one. Our work concerning interfacial tensions and interfacial population densities of hydroxy-oximes[3] leads us to believe that the reagent will collect at the interface predominantly as a monomer. On the other hand it has been suggested[4,5] that in the bulk phase hydroxy-oximes occur at least partly as dimers. Table 2 presents a few data on apparent molecular weights, degree of dimerization α and equilibrium constants K_{eq} for the reaction

$$2\,\overline{RH} \rightleftarrows (\overline{RH})_2$$

for some chemically pure oximes in toluene and isooctane.

TABLE 2

DATA ON DIMERIZATION OF SOME OXIMES IN 0.01 - 0.04 M SOLUTIONS IN TOLUENE AND ISOOCTANE

Oxime	Toluene				Isooctane		
	MW	MW_{app}	α^*	K_{eq}^*	MW_{app}	α^*	K_{eq}^*
2-Hydroxy-5-tert-octyl acetophenoxime	263	301	0.25	8.9	372	0.59	70
HOPHO	347	378	0.17	5.0	486	0.57	62
2-Hydroxy-5-methylphenyl-n-heptyl ketoxime	248	281	0.23	7.8	340	0.54	51
anti-HMBPO	339	368	0.16	4.5	439	0.46	32
syn-HMBPO	339	385	0.24	8.3	insoluble		
DEHOD	271	304			374		

*These values for α and K_{eq} were calculated using 0.025 as the average concentration in the range measured.

In the interpretation of our experiments carried out with HOPHO in toluene we calculated $[\overline{RH}]_{f,m}$ from the free stoichiometric reagent concentration using the value 5.0 for K_{eq} and assuming 2/1 complexation with copper.

TABLE 3

CONCENTRATION DATA

Original oxime conc. $[\overline{RH}]_{o,a}$, M	Free oxime conc. $[\overline{RH}]_{f,a}$, M	Free monomer conc. $[\overline{RH}]_{f,m}$, M	Free dimer conc. $[(\overline{RH})_2]_f$, M
0.006	0.0058	0.00552	0.00014
0.01	0.0093	0.00863	0.00034
0.02	0.018	0.0158	0.001
0.06	0.053	0.039	0.007
0.1	0.088	0.058	0.015

The values for $[\overline{RH}]_{f,m}$ and $[(\overline{RH})_2]_f$ used in Figures 5 and 6 and some other useful data are presented in Table 3. It can be seen that especially in the higher concentration range a considerable part of the oxime will be in the dimeric state.

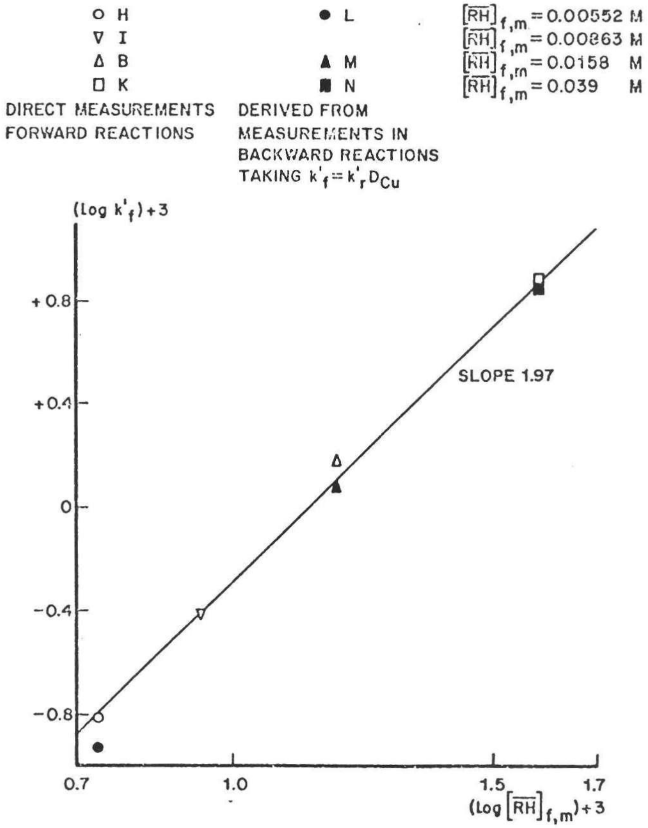

FIG. 5

Relation between k'_f and the free monomeric reagent concentration at pH 2.00. HOPHO in toluene.

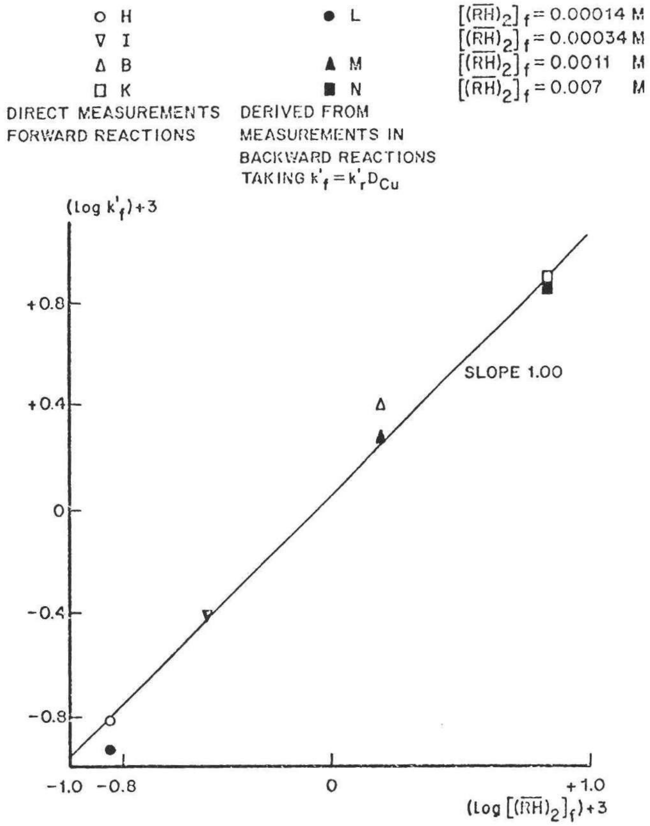

FIG. 6

Relation between k'_f and the free dimeric reagent concentration at pH 2.00. HOPHO in toluene.

A series of experiments with chemically pure HOPHO in toluene at pH 2.0 under relaxation conditions (tracer copper added to the aqueous system) gave the relation between k'_f and the free monomeric reagent concentration illustrated in fig. 5. It may be concluded that the dependency is close to a second-order one. Alternatively, the figures may be plotted against $[(\overline{RH})_2]_f$, in which case a neat first-order plot is obtained (fig. 6). When one plots the forward rate constants against the free analytical reagent concentration, the slope is 1.76, which deviates considerably from 2. In retrospect this may be seen as a justification for not choosing the free analytical reagent concentration as the variable in plotting.

The results for the stripping reaction presented in figs. 7 and 8 are less easy to interpret. In the low concentration range the dependency of k'_r on both the free monomeric and dimeric reagent concentrations is obviously zero order. At higher concentrations the picture becomes somewhat complicated because the plot acquires a slope. The slope is however slight, and might easily be caused by increasing deviation of the organic phase from the ideal state. This would undoubtedly come out more strongly in the stripping reaction than in the extraction, since in the former one has to consider the behaviour of the copper complex. It would appear justified to describe the back reaction as basically zero order in free reagent concentration.

3. The influence of the diluent

In general terms the change from an aromatic to an aliphatic diluent is known to result in better pH functionality of the reagent and higher extraction rates.

In experiments using n-heptane as the diluent a serious difficulty is the limited time available. The useful period for measurements in toluene can easily be 10 minutes or longer, whereas the reactions in heptane are over within 2-3 minutes. In our experimental process this causes problems in timing of samples; it also means that the time needed for combining the phases and for phase disengagement after sampling can no longer be neglected. Keeping in mind the above reservations, the measurements carried out and shown in fig. 9 and 10 appear very reasonable.

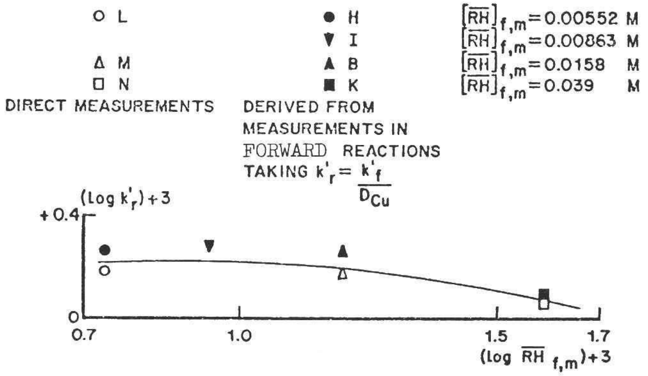

FIG. 7

Relation between k_r' and free monomeric reagent concentration at pH 2.00. HOPHO in toluene.

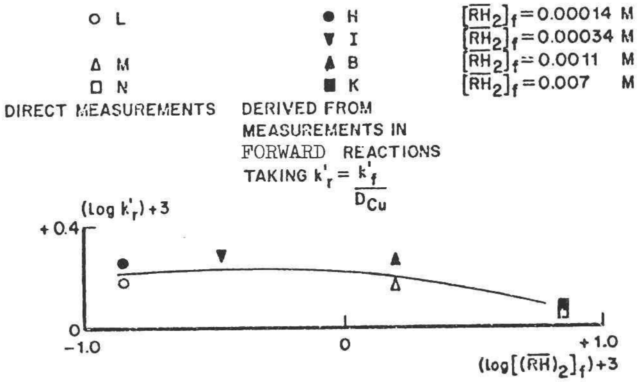

FIG. 8

Relation between k_r' and free dimeric reagent concentration at pH 2.00. HOPHO in toluene.

Table 4 compares the rate constants shown in figs. 9 and 10 with those measured in toluene under comparable conditions.

Table 4

REACTION RATE CONSTANTS OF COPPER EXTRACTION AND STRIPPING WITH HOPHO IN TOLUENE AND HEPTANE AT 25 °C

Initial concentration 0.02 M

pH		Heptane	Toluene*	Ratio	Heptane	D_{Cu} toluene*
1.50	k'_f	14.6×10^{-3}	0.46×10^{-3}	31.7	1.15	0.1
	k'_r	12.7×10^{-3}	4.70×10^{-3}	2.7		
2.00	k'_f	40.8×10^{-3}	1.41×10^{-3}	28.9	10.2	0.82
	k'_r	4.0×10^{-3}	1.58×10^{-3}	2.5		

*Values extracted from Figs. 3 and 4.

Two conclusions can be drawn from above data. Firstly, as in the case of toluene, the dependencies of k'_f and k'_r on $[H^+]$ are again minus first and first order, respectively. Secondly, both the forward and the backward reactions are faster in heptane than in toluene, but the difference is much greater for the forward reaction. The net result is in practice found in the form of the known better pH functionality (higher distribution coefficient at equal pH) for the aliphatic diluent.

4. The rate equation and a possible mechanism

From sections 1 and 2 it can now be concluded that the rate equation for the reaction of copper ions with HOPHO in toluene may have either of the following forms:

$$-\frac{dCu}{dt} = k'_f\,[\overline{RH}]^2_{f,m}\,[H^+]^{-1}\,[Cu] - k'_r\,[H^+]\,[\overline{Cu}] \tag{15a}$$

$$-\frac{dCu}{dt} = k'_f\,[(\overline{RH})_2]_f\,[H^+]^{-1}\,[Cu] - k'_r\,[H^+]\,[\overline{Cu}] \tag{15b}$$

In attempts to find a mechanism fitting these equations one has to take into consideration that at least the initial reaction is assumed to take place at the interface. In the concentration range studied the interfacial population density of "an" oxime species in HOPHO/toluene solutions is virtually constant, as can be seen from the slope of the σ_i/log C plot in fig. 11. Although these measurements refer to a static system, it is reasonable that the conclusion also holds for a dynamic

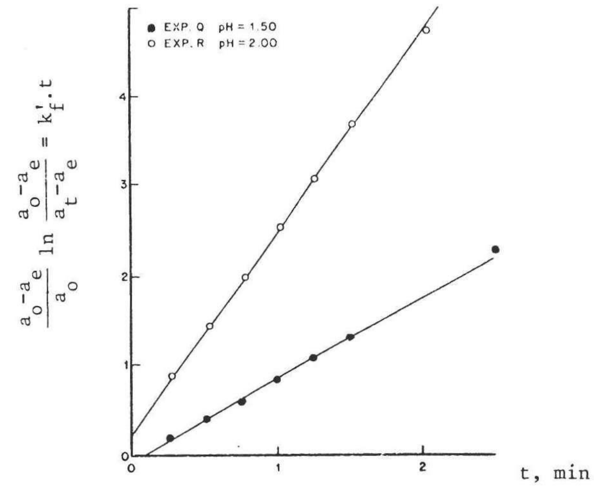

Fig. 9

The rate expression as a function of time at different pH. Forward reaction, HOPHO in heptane. Tracer copper added to the aqueous phase.

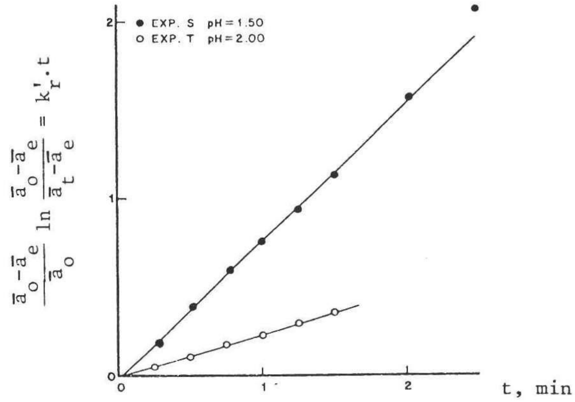

Fig. 10

The rate expression as a function of time at different pH. Backward reaction, HOPHO in heptane. Tracer copper added to the organic phase.

(extracting) one: because of the high rate of diffusion of fresh reagent molecules to the interface, the latter will still maintain a constant population density. This in fact means that, if the species populating the interface creeps into the mechanism, its concentration will disappear in the rate constant(s). The consequence now is that, if one accepts that one of the species $(HOPHO)_2$ or HOPHO collects at the interface, rate equations (15a) and (15b) must result from the influence of "the other one".

It has been argued in section 2 that the species collecting at the interface will probably be the monomer, HOPHO. Because of the high degree of satisfaction of its need for hydrogen bridging[5] the dimer, $(HOPHO)_2$, is likely to behave neutrally towards the interface, or it might show a slight preference for the bulk organic. In formula:

$$[(\overline{RH})_2]_i = a[(\overline{RH})_2] \qquad (16)$$

$$a \leqslant 1$$

We now propose the following mechanism:

$$Cu^{2+} + (RH)_{2\,i} \rightleftharpoons CuR_2H^+_i + H^+ \qquad (17)$$

$$CuR_2H^+_i \rightleftharpoons CuR_{2\,i} + H^+ \qquad (18)$$

$$CuR_{2\,i} \rightleftharpoons \overline{CuR_2} \qquad (19)$$

Equations (16) through (19) lead to rate equation (15b) if (18) is rate determining. Because of the fixed relation through the dimerization constant between $[(\overline{RH})_2]_f$ and $[\overline{RH}]_{f,m}$ equation (15a) will also hold. It should be stated that, by splitting equation (17) into two parts, one obtains a mechanism similar to that proposed by Price and Tumilty[4], e.g.:

$$Cu^{2+} + (RH)_{2\,i} \rightleftharpoons CuR_2H_2{}^{2+}{}_i \qquad (17a)$$

$$CuR_2H_2{}^{2+}{}_i \rightleftharpoons CuR_2H^+_i + H^+ \qquad (17b)$$

The only difference is that the present authors suggest a two-step dissociation of the complex $CuR_2H_2^{2+}$ in order to account for the rate dependencies.

Apart from fitting the rate equations, the mechanism also qualitatively explains the difference in behaviour found between toluene and heptane as diluents. In the more polar toluene the dimer concentration is lower, which leads to a decrease in the overall forward rate constant. The influence on the backward rate constant (which is independent of the reagent concentration) is much less pronounced. In the extreme case of solutions in ethers or ketones one would estimate that there was very little dimer present. Ether solutions of hydroxy-oximes do not extract copper from acidic medium, only from ammoniacal medium.

Side by side with the effect of diluents on dimer concentration goes their influence on interfacial concentration (or concentration close to the interface) of any reagent species. The mutual imponderability of these effects is still an obstacle to a more quantitative explanation.

In some cases modifiers are added to a chelating reagent, usually to improve the general level of its performance or handlability. The modifiers are often oxygen-containing polar compounds, like higher phenols or alcohols, or tributyl phosphate. They are usually added in considerable quantities, e.g. 10-40 % on total diluent volume, and sometimes more, and one frequently finds that the "modified" reagent has a lesser pH functionality than the pure one[6]. As stated in section 3, such a decreased pH functionality does in fact mean that k'_f is more strongly negatively influenced that k'_r. It might well be that this effect of modifiers belongs to the same category as the diluent effect.

5. The influence of accelerators and retardants

The role of accelerators in the extraction of copper with hydroxy-oxime extractants is far from clear. With respect to the one case which has been investigated to some depth, i.e. the combination LIX^R 65 N + LIX^R 63, it has been found[1] that the latter appears in the rate equation of the forward reaction to an approximate 0.5 order, and a mechanism was proposed to account for that dependency.

On the basis of the same work[1] however, other authors[2-7] proposed mechanisms that differed markedly from the first one, as well as from each other, and it was rightly stated[7] that the role of the accelerator is still unknown.

When adopting the view that the primary reaction between copper ions and the chelating reagent takes place at the interface, a possible mental step is to assume that the accelerator interferes with the mechanism at that

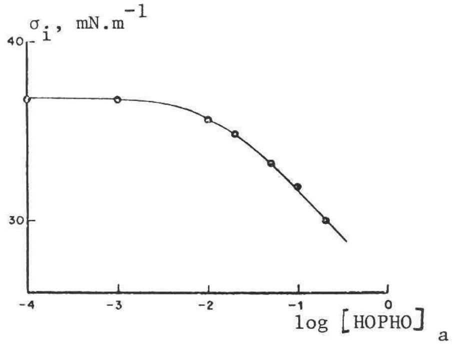

Fig. 11

Interfacial tension of HOPHO in toluene at 25° C against 0.5 M Na_2SO_4 at pH 2.0.

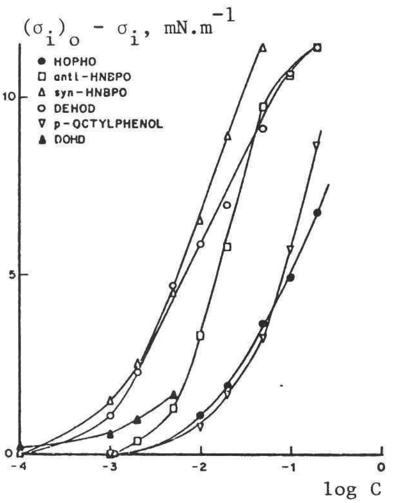

Fig. 12

Interfacial pressures of extractants, accelerators and retardants in toluene at 25° C against 0.5 M Na_2SO_4 at pH 2.0.

same interface[7]. A consequence of that idea would be that a category of retardants can also exist: strongly polar, non-chelating compounds that may successfully compete with the extractant for space at the interface. Ultimately one may then conceive that the accelerator may exert one or both of the following functions:

1. act as an accelerator proper, because of its assumed high rate of reaction with copper, or (and)
2. compete with retardants for space at the interface.

Table 5 shows the influence of some accelerating and retarding compounds on the forward reaction rate of two oximes with copper ions, measured under relaxation conditions. The initial and equilibrium conditions of the standard (blank) experiments are given in table 1 under letter B for HOPHO and P for anti-HNBPO.

Table 5
THE INFLUENCE OF ACCELERATORS AND RETARDANTS ON k_f'

Oxime	Standard exp.	Compound added	mmole/l	mole % on oxime	$k_f' \times 10^{-3}$, s^{-1}
HOPHO	B	--	--	--	1.55
	B	DEHOD	0.20	1.00	1.38
	B	DEHOD	0.27	1.35	1.13
	B	DEHOD	0.68	3.4	2.53
	B	DEHOD	2.0	10.0	3.58
	B	tert-octylphenol	2.0	10.0	1.52
	B	tert-octylphenol	4.0	20.0	1.46
anti-HNBPO	P	--	--	--	10.2
	P	DEHOD	0.68	3.4	4.1
	P	syn-HNBPO	2.0	10.0	4.9

The highly surprising conclusion to be drawn from table 5 is that DEHOD, a well-known accelerating molecule, starts to work as an accelerator only at quite a high concentration, and that below that it is even a retardant.

A very marked retarding effect is also shown by syn-HNBPO.The latter starts to display extracting action at high pH values, and to all intents and purposes may be considered here to be non-chelating. Tert-octylphenol shows little activity as a retardant, and it is only expected to influence reaction rates strongly at high concentrations, which is in line with literature findings[6]

The interfacial population density of a solute in a two-phase system can be calculated from the slope of a plot of the interfacial tension σ_i against the logarithm of the concentration of that solute[3]. The numerical value obtained, however, is indicative of the space a molecule needs at the interface, rather than of the tendency for such a molecule to collect at the interface.

This tendency is expressed more appropriately in the solute concentration at which a decrease in the interfacial tension becomes observable. A direct visualization of this tendency is obtained when the interface pressure, $(\sigma_i)_o - \sigma_i$ (in which $(\sigma_i)_o$ is the interfacial tension of the pure diluent in the system), is plotted against the logarithm of the solute, log C. This has been done in fig. 12 for a few extractants, accelerators and retardants.

In comparing the curves of HOPHO and p-octylphenol one sees that neither of the two shows a marked preference over the other to collect at the interface. This would explain why the phenol at low to moderate concentrations hardly influences the rate of the reaction: behaving almost as HOPHO, it barely decreases the concentration of $(HOPHO)_2$ at or close to the interface. Of course at higher concentrations the phenol starts to act as a modifier.

Syn-HNBPO, DEHOD and 8,9-dioximinohexadecane (DOHD) display a more pronounced tendency towards interface orientation than anti-HNBPO and HOPHO. Syn-HNBPO is a distinct retardant for anti-HNBPO. It seems possible that in its obviously very effective competition for space at the interface it suppresses the interfacial concentration of the dimers of the active component; in other words the syn-HNBPO decreases the factor a in equation (16). The net effect is a decrease in reaction rate.

Qualitatively the effect of the accelerators DEHOD and DOHD also finds a basis in their clear preference for the interface. Attempts to find a reasonable mechanism for the accelerated reactions (in which of course by definition the accelerators have to play a role) are however seriously impeded by the peculiar retarding action of DEHOD at low concentrations. At present we are inclined to believe that the DEHOD (isolated from a commercial product) might contain one or more impurities that could act as powerful retardants. Only relatively large amounts of DEHOD may then be able to overcome this initial unfavourable influence. Work is going on to clarify this point.

NOTATION

Concentration

$[X]$	Concentration of X in the aqueous phase
$[\overline{X}]$	Concentration of X in the organic phase

Subscripts

a	Analytical
eq	Equilibrium
f	Free
i	At the interface
m	Monomeric
o	Initial
t	At time t

General

A	Aqueous
a.t.e.	Approach to equilibrium
D	Distribution coefficients
DEHOD	5,8-Diethyl-6-hydroxy-7-oximinododecane
DOHD	8,9-Dioximinohexadecane
HNBPO	2-Hydroxy-5-nonylbenzophenone oxime (syn and anti)
HOPHO	2-Hydroxy-5-tert-octylphenylheptyl ketoxime
K_{eq}	Equilibrium constants
k'_f, k'_r	Forward and backward reaction rate constant, in s^{-1}
MW	Molecular weight
O	Organic
Stg. eff.	Stage efficiency
α	Degree of dimerization
σ_i	Interfacial tension

Subscripts

app	Apparent
aq	Aqueous
eq	Equilibrated
i	At the interface
org	Organic

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C 1. IDEAS AND PRACTICE IN THE DESIGN OF SOLVENT EXTRACTION REAGENTS

A.J. van der Zeeuw and R. Kok.

Proc. Int. Solvent Extr. Conf. 1977, Toronto.
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INTRODUCTION

The rapid advance of the practical application of solvent extraction of metals to maturity, especially in the case of the chelating extraction of copper, has not been accompanied by an equally fast increase in the level of our knowledge of the reactions and mechanisms involved.

The present authors and their colleagues have always felt that obtaining theoretical information on kinetics, mechanisms, etc. should go side by side with reagent design in order for the maximum progress to be achieved in both.

The active cooperation of all colleagues in this rather broad field has resulted in considerable progress in improving the kinetics of copper extraction with hydroxy-oximes. In addition, promising leads have been found that hopefully will result in the design of an attractive nickel extractant for acidic media.

The present paper is devoted to work done in the field of design of copper extraction accelerators and selective nickel extractants. A paper on mechanistic and kinetic aspects will be published elsewhere.

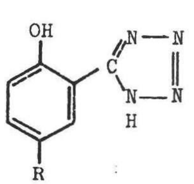
PRACTICAL APPROACHES TO THE PROBLEM OF ACCELERATOR AND REAGENT DESIGN

SURVEY OF CURRENTLY KNOWN TYPES OF ACCELERATORS

At a meeting of the Solvent Extraction and Ion Exchange Group of the Society of Chemical Industry in London, May 1976, Dr. Dalton (ICI) revealed that his colleagues and he had identified basically five types of accelerators for the extraction of copper with 2-hydroxyphenyl ketoxime extractants. Together with two types found in our work, the list of known accelerator types looks as follows:

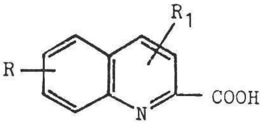
a. aliphatic α-hydroxy-oximes

b. hydroxyaryl tetrazoles



c. alkylated hydroxyquinolines

d. alkylquinaldic acid



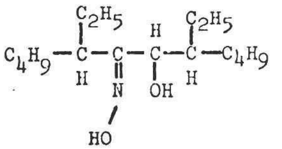
- e. alkylphosphoric acids
- f. sulfonic acids
- g. carboxylic acids

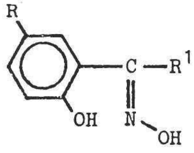
WORKING HYPOTHESIS WITH RESPECT TO THE MODE OF ACTION OF ACCELERATORS

The property common to classes a, b and c is their chelating power: they are copper-chelating reagents in their own right. Categories e, f and g are essentially acids, forming more or less normal salts. Class d probably takes a position intermediate to the others, combining chelating and salt-forming properties.

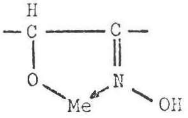
The action of categories e through g is probably quite easy to explain: in the appropriate pH range they may form copper salts through a fast (ionic) mechanism, and in the organic phase the copper is transferred to the much stronger chelating agent. The above reasoning is backed by the behaviour of VERSATIC. At pH 3 and higher, small amounts of VERSATIC have a spectacular accelerating effect on copper extraction with 2-hydroxyphenyl ketoximes. However, at pH 2 and lower (the important range for copper extraction), amounts of up to 40 % molar on oxime have no effect at all, except for ruining the iron rejection; at that pH the ability of VERSATIC to form copper salts has virtually disappeared. It would be interesting to know whether alkylphosphoric and sulfonic acids show similar behaviour below the pH at which they are able to form copper salts.

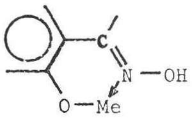
More intriguing, and also more useful from a practical point of view, would be to try and find a basic concept to define the action of chelating accelerators. To simplify the picture one might consider the only commercial one known so far, LIX^{R} 63, and compare it with the compound whose action it accelerates, the phenolic ketoximes



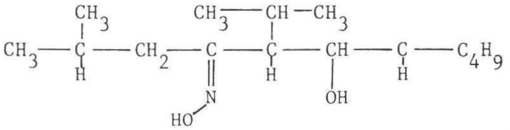


One striking difference between the accelerator and the accelerated compound is that the former will form a five-membered ring when chelating copper, whereas the accelerated compound forms a six-membered ring with the metal, e.g.:





Since the competition for copper between the above accelerator and the accelerated compounds will thermodynamically go in favour of the latter, the obvious working hypothesis was that kinetically the formation of the five-membered ring with the accelerator is favoured. In this connection the behaviour of 7-ethyl-2-methyl-5-isopropyl-6-hydroxy-4-oximinoundecane



is interesting: the compound exerts no accelerating action at all. Copper-chelating capacity is totally absent. The high rate of reaction between e.g. copper ions and the hydroxyquinoline reagents (Kelex^{R} 100 etx.) might also be explicable along these lines.

Another characteristic of the accelerator structure shown above is that the active groups are located in the middle of the chain. Experience with Shell copper extractants suggests[1] that this is not the most favourable position for good kinetics, and the logic of moving the active groups in the molecules to better (more exposed) locations was obvious.

Since in the open-chain accelerators of the hydroxy-oxime type all single bonds, including the C—C bond between the active groups, are in principle freely rotating, at any moment in time only a part of all accelerator molecules might be in the right position to complex copper. This leads to a thermodynamically unfavourable influence on the equilibrium constant, and therefore to decreased copper/accelerator complex concentrations. Blocking the free rotation of the critical bond might therefore result in improved performance of the accelerator.

The three working hypotheses used as leads in our work may now be summarized as follows: in a search for new accelerating compounds one should look for copper chelating reagents proper, possessing one or more of these properties:

a. ability to form five-membered rings with copper,

b. active groups in easily accessible positions,

c. fixation of the active groups in a favourable configuration.

NEW ACCELERATOR CATEGORIES AND USEFUL VARIATIONS OF KNOWN TYPES

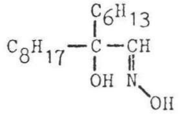
The leads indicated above were successfully applied to the development of a previously unknown class of accelerators (vicinal dioximes) and to the design of new representatives of the already known hydroxy-oxime class of accelerators.

Table 1 gives a survey of a number of these accelerators.

TABLE 1

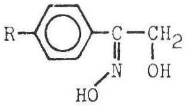
STRUCTURES OF NEW HYDROXY OXIME AND DIOXIME ACCELERATORS

I



$C_8H_{17}-C(OH)(C_6H_{13})-CH=N-OH$

II



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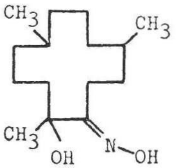
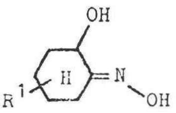
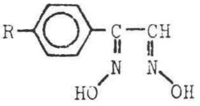


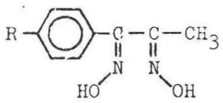
IV



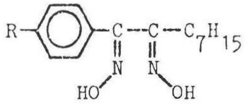
V



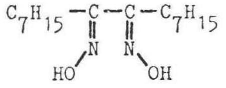
VI



VII

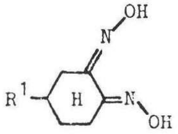


VIII



$C_7H_{15}-C(=N-OH)-C(=N-OH)-C_7H_{15}$

IX



In table 2 the effect of the above accelerators on the kinetic performance of a commercial sample of SME 529 is given, and compared with 5,8-diethyl-6-hydroxy-7-oximinododecane (DEHOD). The experiments were all done under the same set of standard conditions, which is comparable to that present in actual mixer/settler practice.

From this table the accelerators tested can be ranked as follows: V = VI > VII > VIII > IX > II > I = III = DEHOD ≫ IV. It follows that the asymmetric open-chain hydroxy-oximes from table 1 have about the same activity as the known DEHOD, with the exception of compound II, which is clearly superior.

TABLE 2

ABSOLUTE AND RELATIVE EFFECTS OF ACCELERATORS FROM TABLE I ON COMMERCIAL SME 529

Accelerator added	Quantity*, % mole on active matter in SME	Extraction in % a.t.e. after 30 s	60 s	Relative molar amounts of accelerators needed to achieve same performance
blank	--	43	65	--
DEHOD	5	67	82	
	10	82	92	1 (standard)
I	5		81	
	10		90	1
II	5		90	
	10		97	0.5
III	5		80	
	10		90	1
IV**	10		86	⩾ 1
V***	0.5	84	94	0.05
VI****	0.1	65	80	
	0.5	84	94	
	1.0	86	97	0.05
VII***	0.5		81	0.1
VIII	0.5	62	79	
	2.0	85	95	0.2
IX*	2.0	66	82	0.4

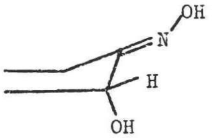
* In cases where isomers are possible, the amount is quantity of active component needed

** Side chain R = tert-nonyl, derived from propylene trimer

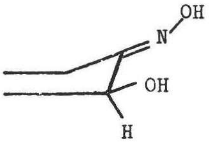
*** Side chain R = C_{10-14} alkyl

**** Side chain R = C_{15-18} alkyl

The performance of the hydroxycyclohexanone oxime IV is in fact surprisingly bad. Model studies show that in the reagent as such steric hindrance between the hydroxy and oximino groups is least when the former takes an axial position (a). On the other hand conditions for complex formation are better when the OH is in the equatorial position (b).



a



b

The situations are interchangeable through the boat <–> chair transformation of the cyclohexane ring. The energy barrier will be at least of the same order as the rotational barrier in the open-chain hydroxy-oximes, and possibly higher. It is therefore understandable that the performance of the hydroxycyclohexanone derivative is not impressive. Nevertheless, the fixation of active groups as a lead to more active reagents still has its value, as will be demonstrated later.

The open-chain vic. dioximes are extremely powerful accelerators. Theoretically they may exist in four configurations, an anti, a syn and two amphi structures. (In symmetrical dioximes the two amphi structures are identical) It was found that the anti configuration is by far the most active as an accelerator. (In addition, at least one of the other structures displays activity as a copper extractant proper, though on a lower level than the anti.) This backs our working hypothesis that the formation of a five-membered ring in the chelate is very important, if not essential, for the compound to act as an accelerator.

The cyclohexane dioxime IX is only moderately active. The anti form is an extremely potent copper extractant, able to extract copper from 2N H_2SO_4 at a very high rate. It is likely that for this reason the copper transfer equilibrium between the accelerator and SME 529 lies in favour of the former. Such a situation would also explain the low accelerating action of Kelex^R 100 on hydroxy-oxime extractants. Only the relative abundance of the SME 529 over the accelerator remains to balance the net situation quantitatively in favour of the SME/copper complex.

PERFORMANCE OF A DIOXIME ACCELERATOR IN PRACTICE

To test the practical importance of the new category of dioxime accelerators, the performance of a standard batch of SME 529 with and without a dioxime was compared. The accelerator chosen was No. VI from table I, and it was added in an amount of 0.5 mole % (active anti-component on active reagent content) to an SME 529 solution in Shell diluent MSB 210 containing 35 g/l of SME (as supplied).

The (synthetic) leach solution contained approximately 1.65 g/l Cu^{2+} and 0.6 g/l Fe^{3+}, both added as sulfates, and had a pH of 2.14. The strip solution contained 44.4 g/l Cu^{2+} and 106 g/l H_2SO_4.

The apparatus was a 2/2 stage Davy Powergas mixer/settler (one-litre mixers). In all experiments the O/A phase ratio aimed at was 1/1 in extraction and 5/1 in the strip. In the strip mixers a local O/A of 1/1 was maintained by internal recycling. The experimental temperature was 25° C.

The aim was to test the extractant as severely as possible so that the accelerator would show the maximum influence. Therefore a) the amount of aqueous copper offered slightly exceeded the loading capacity of the reagent, and b) in the second set of experiments the throughput rate was the maximum our experimental set-up would allow.

☐ E_1, E_2: EXPERIMENTAL VALUES
○ E_1, E_2: EQUILIBRATED VALUES

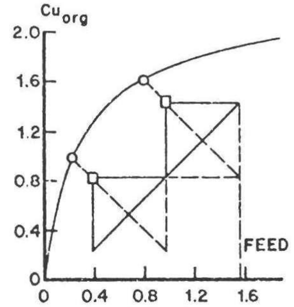


FIG. 1a

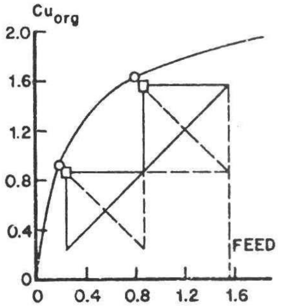


FIG. 1b

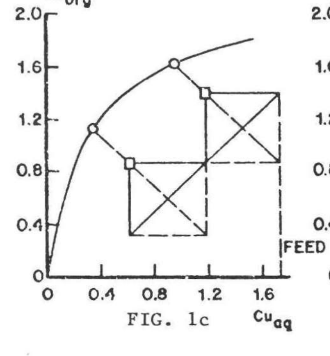


FIG. 1c

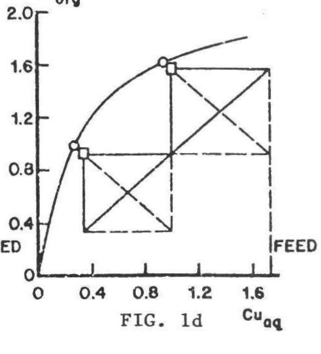


FIG. 1d

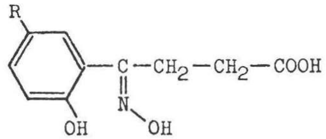
In the first set of experiments a residence time of 3 minutes in the mixers was applied. The results of the non-accelerated experiment are given in Table 3a and Figure 1a, those of the accelerated one in Table 3b and Figure 1b. In the second set of trials the throughput was pushed by applying a residence time of 1.5 minutes. Results are presented in Table 3c and Figure 1c for the non-accelerated tests, and in Table 3d and Figure 1d for the accelerated ones. Quite clearly the accelerator improves the overall copper extraction and the stage efficiencies greatly.

In spite of certain side-effects (e.g. slightly higher entrainment of aqueous in organic phase), indicating that further optimization of the preparation of the accelerators is necessary, the promise of the new category is clear.

REAGENTS WITH BUILT-IN ACCELERATOR FUNCTIONS

A logical consequence of the effect of physically mixing an extractant and an accelerator would be a combination of their functions chemically. Some of the various compounds synthesized and tested are interesting enough to be discussed briefly.

A compound combining the characteristic group of SME 529 with a carboxyl group as accelerator is 4-(2-hydroxy-5-nonylphenyl)-4-oximinobutanoic acid:



As expected, the kinetic performance of this compound was excellent. It is about twice as fast as chemically pure 2-hydroxy-5-nonylacetophenone oxime, and twenty times as fast as 2-hydroxy-5-nonylphenyl-n-propylketone oxime, with which it can be compared with respect to chain length. However, its pH_{50} for copper was found to be about 0.7 units higher, and its pH_{50} for Fe^{3+} about 1 unit lower, so that its separation factor Cu/Fe^{3+} was only 10. Both the good kinetics and the high iron extraction stem from the carboxylic group. The latter does not take part in any chelation, which can be seen from the behaviour of 4-oximinoundecanoic acid: this acts as a normal carboxylic acid towards metal ions, and shows no selectivity towards metals that otherwise easily take part in chelate formation.

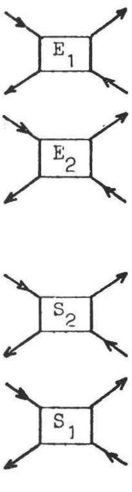
TABLE 3

INFLUENCE OF DIOXIME ACCELERATOR ON THE PERFORMANCE OF SME 529

Table 3 a

Non-accelerated test, normal residence time

Feed solution : 1.56 g/l Cu, 0.57 g/l Fe^{3+}; pH 2.14
Extractant solution : 35 g/l SME 529 in MSB 210
Strip solution : 44.4 g/l Cu, 106 g/l H_2SO_4
Residence time, mixer : 3 minutes
Specific settler area : 2.0 US gall./sq. ft./min
Temperature : 25 °C



Stg. eff., %	Metals in aqueous phase, g/l				Metals in organic phase, g/l			Stg. eff., %
	Fe	Cu_{eq}	Cu		Cu	Cu_{eq}	Fe	
			1.56		1.44	1.62	0.0035	
77				E_1				77
		0.79	0.97		0.83	0.98	0.0020	
77				E_2				80
		0.22	0.39		0.23	0.21		
			44.4					
89				S_2				88
	0.0012	45.3	45.2		0.38	0.28		
91				S_1				92
	0.0132	50.9	50.4		1.44			

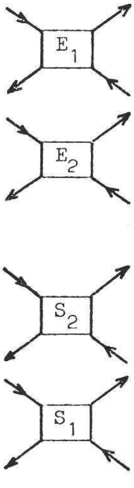
Phase ratio: A/O extraction : 1.03
A/O stripping : 0.207 (overall) (in mixers 1.0)

Cu/Fe ratio: Loaded organic : 420
Advanced electrolyte: 454

Table 3 b

Accelerated test, normal residence time

Feed solution : 1.56 g/l Cu, 0.57 g/l Fe^{3+}; pH 2.14
Extractant solution : 35 g/l SME 529 + 0.5 mole % accelerator VI in MSB 210
Strip solution : 44.4 g/l Cu, 106 g/l H_2SO_4
Residence time, mixer : 3 minutes
Specific settler area : 2.0 US gall./sq. ft./min



Stg.eff., %	Metals in aqueous phase, g/l				Metals in organic phase, g/l			Stg. eff., %
	Fe	Cu_{eq}	Cu		Cu	Cu_{eq}	Fe	
			1.56		1.57	1.63	0.0038	
93				E_1				92
		0.82	0.87		0.87	0.92		
93				E_2				93
		0.20	0.25		0.23	0.21		
			0.44					
88				S_2				87
	0.0024	45.2	45.1		0.36	0.30		
95				S_1				95
	0.014	51.4	51.1		1.57			

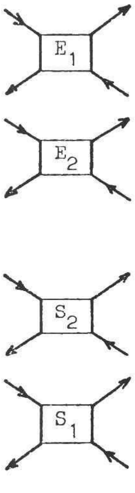
Phase ratio: A/O extraction : 1.02
A/O stripping : 0.201 (overall) (in mixers 1.0)

Cu/Fe ratio: Loaded organic : 413
Advanced electrolyte : 479

Table 3.c

Non-accelerated test, short residence time

Feed solution : 1.74 g/l Cu, 0.67 g/l Fe^{3+}, pH 2.14
Extractant solution : 35 g/l SME 529 in MSB 210
Strip solution : 48.0 g/l Cu, 106 g/l H_2SO_4
Residence time, mixer : 1.5 minute
Specific settler area : 2.0 US gall/sq. ft./min
Temperature : 25 °C



Stg. eff., %	Metals in aqueous phase, g/l Fe	Cu_{eq}	Cu		Metals in organic phase, g/l Cu	Cu_{eq}	Fe	Stg. eff., %
			1.74		1.40	1.62	0.004	
71				E_1				71
		0.96	1.19		0.86	1.12	0.002	
68				E_2				68
		0.35	0.62		0.32	0.24		
			48.0					
77				S_2				77
	0.003	49.6	49.2		0.59	0.30		
73				S_1				74
	0.015	54.1	52.8		1.40			

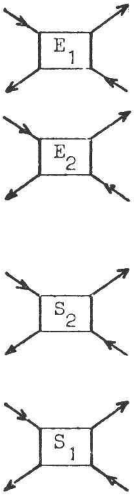
Phase ratio: A/O extraction : 0.96
A/O stripping : 0.23 (overall) (in mixers 1.0)

Cu/Fe ratio: Loaded organic : 350
Advanced electrolyte: 305

Table 3 d

Accelerated test, short residence time

Feed solution : 1.74 g/l Cu, 0.67 g/l Fe^{3+}; pH 2.14
Extractant solution : 35 g/l SME 529 + 0.5 mole % accelerator VI in MSB 210
Strip solution : 48.0 g/l Cu, 106 g/l H_2SO_4
Residence time, mixer: 1.5 minute
Specific settler area: 2.0 US gall./sq. ft./min
Temperature : 25 °C

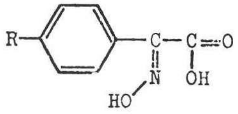


Stg. eff., %	Metals in aqueous phase, g/l				Metals in organic phase, g/l			Stg. eff., %
	Fe	Cu_{eq}	Cu		Cu	Cu_{eq}	Fe	
			1.74		1.57	1.63	0.003	
92				E_1				92
		0.95	1.01		0.92	0.98	0.002	
90				E_2				90
		0.27	0.34		0.33	0.25		
			48.0					
71				S_2				74
	0.002	49.4	49.0		0.56	0.30		
79				S_1				80
	0.013	54.7	53.5		1.57			

Phase ratio: A/O extraction : 0.88
A/O stripping : 0.23 (overall) (in mixers 1.0)

Cu/Fe ratio: Loaded organic : 523
Advanced electrolyte: 423

In compounds of the class 1-(4-alkylphenyl)-1-oximinoacetic acid:



the chelating capacities of the combination carboxyl group/oxime, the rate-enhancing properties of the carboxyl group, and the possibility of five-membered chelate formation appear together. These compounds react extremely fast, as expected. For the 4-dodecylphenyl compound, pH_{50} for copper (for a 0.1 M reagent solution against 0.01 M Cu^{2+} in 0.5 M Na_2SO_4 background) was 0.25, whereas the pH_{50} for Fe^{3+} was 1.0. Obviously this reagent is not very useful, but its behaviour backed our working hypotheses.

TRENDS IN THE DEVELOPMENTS OF EXTRACTANTS FOR OTHER METALS

Like copper, nickel is a potentially attractive metal to be won with the use of solvent extraction methods. Its price is relatively high, the quantities produced are substantial, and the future need for working ores that are less amenable to classical procedures is obvious.

The most desirable properties for a good nickel extractant are the following:

a. ability to extract nickel from moderately acidic medium,
b. selectivity for nickel over iron (ferric and ferrous),
c. rejection of associated cobalt, or alternatively the ability to release cobalt by some stripping method,
d. attractive or at least acceptable rates of extraction and stripping,
e. chemical stability under the conditions encountered in storage, extraction and stripping.

To date no reagents are known that show all these properties.

In our own research it is more or less standard to test any compound prepared as a potential extractant for copper and for nickel. The compounds belonging to the class of 1-(4-alkylphenyl)-1-oximinoacetic acids (already mentioned above) were found to have some virtues. They satisfy criteria a and d above. Cobalt is in fact co-extracted (separation factors Ni/Co 10-20), but can easily be stripped. A further disadvantage of these compounds is that, being carboxylic acids, they extract Fe^{3+} before nickel.

The most promising class of potential nickel extractants is that of the vicinal dioximes. Recently a very interesting paper[2] described the properties of a number of symmetrical vic. dioximes, and one or two promising nickel reagents were identified. Major drawbacks found were the often extremely low extraction rates and the non-strippability of cobalt.

The useful experience with the influence of chain length in copper extraction[1] led to the investigation of asymmetrical, more exposed dioximes. Compounds V and VI from Table 1 were a considerable improvement over those reported before[2] in that times of equilibration could be measured in hours instead of days. Temperatures higher than ambient could increase the rates further to a level where they start to be attractive. Extraction rate curves at 50° C for compounds V, VI and VIII (representing the state of the art[2]) are presented in Figure 2. Log D/pH plots (Figure 3) show that nickel extraction occurs in the attractive region. Iron is virtually not extracted in the pH region of interest.

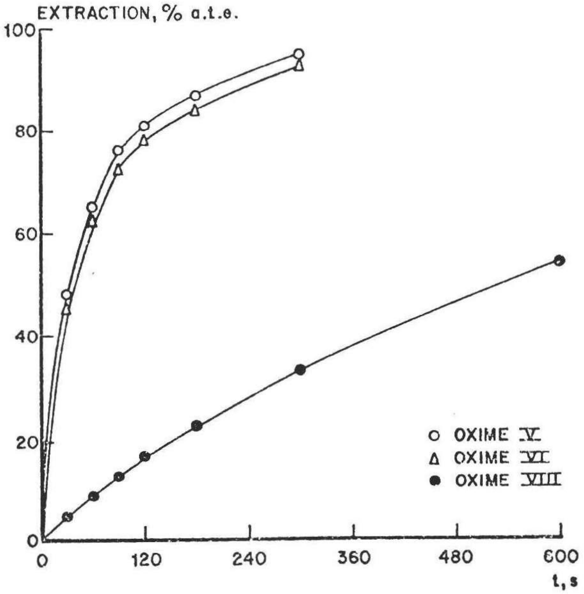


FIG. 2

Extraction rates for nickel with 0.005 M dioximes in toluene at 50° C.

Aqueous phase: 2 g/l Ni^{2+} (as sulfate). pH 3.0. O/A = 1.

Baffled, turbine-stirred reactor.

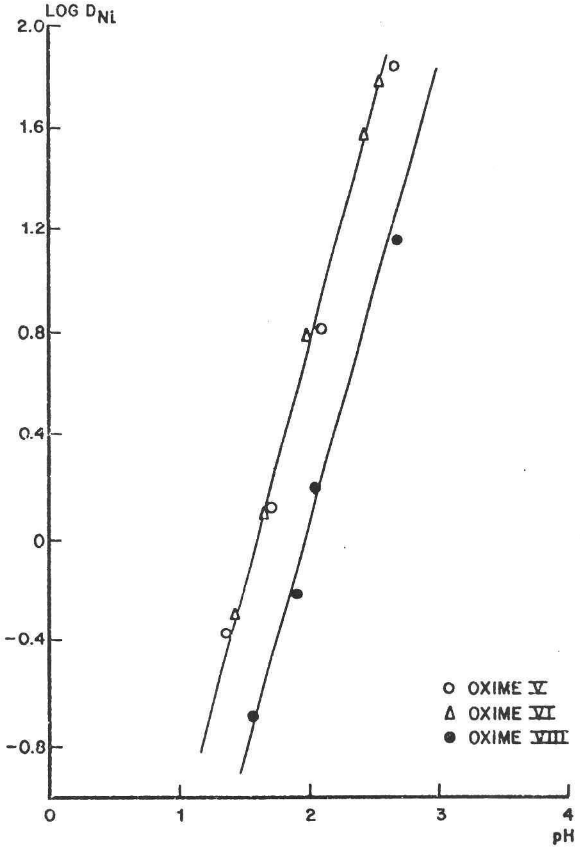
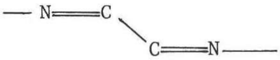


FIG. 3

Log D/pH curves for 0.005 M dioximes in toluene at 50° C.
Aqueous feed: 0.0005 M $NiSO_4$ in 0.5 M Na_2SO_4

Blytas[3] has described the use of 4-alkyl-1,2-dioximinocyclohexane as extractants for nickel and other metals. Compound IX from Table 1 quantitatively extracts nickel from 2N H_2SO_4 at ambient temperature at a very fast rate. This result proves the value of the working hypothesis about fixation of the configuration of the active groups. Open-chain vic. dioximes probably have the trans configuration in crystalline form and in solution[4]:



Molecular models show that the 4-alkyl-1,2-dioximinocyclohexanes have the oxime groups fixed in a position extremely favourable for complex formation, which lowers the extraction pH values tremendously.

Although the leads indicated above certainly open up prospects, there are a number of serious difficulties still to be overcome. Firstly, all the compounds mentioned have only limited solubility in most organic diluents. Secondly, only the anti-isomers are active nickel extractants, which necessitates optimization for anti production and, despite this, acceptance of (considerably amounts of) inactive isomers. Thirdly, in the case of the compounds of type IX, the extreme pH functionality leads to virtual non-strippability of the nickel.

Several ways of solving these problems have been found, and currently the desired structure is being optimized.

In an attempt to explain the often extremely low rates of reaction between nickel and open-chain dioximes of the type described before, it has been argued[2] that a high activation energy barrier exists between the octahedral paramagnetic and the square-planar diamagnetic configuration, as a result of which the attainment of spin-pairing necessary to form the latter is hindered. Although this certainly could play a role, it is unlikely to be the only factor. Our results prove that acceptable and even high rates of extraction are possible. Moreover, the exchange of nickel between its VERSATIC acid salt (green, octahedral[5a] and hence probably paramagnetic[5a,b]) and oxime VIII from Table 1 (an extremely slow nickel extractant) in toluene is virtually instantaneous. This would suggest that a more important problem might be "peeling off" the aquo shell of the Ni^{2+} ion.

Once in the organic solution either as an ion or as an easily ionizable species, the nickel reacts rapidly with the dioxime. The more favourable behaviour of the asymmetrical and especially of the cyclic dioximes may just be the result of the better orientation of the oxime groups.

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PART THREE

A. HISTORY OF THE AUTHOR'S INVOLVEMENT IN SX

The author started to be involved in SX work around 1969. Shell-manufactured VERSATIC acids drew attention as potential metal extractants, originally by means of work done outside Shell, notably by Fletcher et al.[1] and others. Later work at the Koninklijke/Shell Laboratorium[2] stressed the potential importance of these acids. At about this point the author joined the KSLA SX team.

A feature of VERSATIC acids is their extreme thermal and chemical stability. Burkin [3] had used this property in producing metal powders by direct hydrogenation of their VERSATIC salts. Following suggestions made at discussions between KSLA staff and Société Le Nickel the author started work on selective hydrogenation of mixtures of VERSATIC salts, notably the cobalt and nickel salts, which resulted in two patents.[4,5] Certain aspects of this work were found sufficiently interesting to warrant some fundamental work, which finally was published and will be found back in this thesis as paper A 1.

In the early seventies Shell had bought the Billiton Company, which was owner-in-part of the Kempensche Zink Industrie (now Budelco) at Budel, the Netherlands (Province North-Brabant). As is quite common in zinc manufacture, the leaching solutions obtained by dissolution of zinc calcine contained appreciable amounts of ferric iron. As an alternative to the usual precipitation processes for removal of this iron, the author started work on a solvent extraction process, resulting in a patent [6] and in paper A 2. Meanwhile Billiton had broadened their interest to metals that were not traditionally within their field, like cobalt and nickel. In this context the work published in Hydrometallurgy and reproduced in this thesis as papers A 3 and A 4 was done. The aim of this work, from the viewpoint of industry, was to obtain an idea of the behaviour of VERSATIC acid under practical conditions, considering that most of the literature work was done on almost ideal, very dilute solutions and hence was not representative. The author's added interest was to try and explain the phenomena observed in terms of complex compositions.

Already in the late sixties Shell had found the field of SX sufficiently interesting to warrant an effort also to obtain a position with other types of chemicals. As an alternative to quaternary ammonium compounds KSLA developed sulfonium compounds. [7] As extractants these were found much better, extracting the various metals at lower $[Cl^-]$. Nevertheless they could not be commercialized. Firstly, when stored they were only stable in the presence of 1 mole/mole of HCl. Moreover, in cases where the metals extracted could only be stripped from the reagent under slightly alkaline (or at least not sufficiently acidic) conditions a reaction took place which is comparable to the Hofmann degradation of ammonium compounds.

However, the climate was favourable for more specialized research into the field of SX chemicals. The idea that available chemical knowledge and technology should be used and the conception that it was best to try and find reagents for metals that were fairly valuable and were produced in large volumes led almost naturally to the investigation of hydroxy-oximes as extractants for copper, a field which had been opened by General Mills. The class of compounds of which one member was to be commercialized as SME 529 was patented in 1971.[8] Apart from the development and applicational work published elsewhere [9,10] the author and his coworkers have also paid attention to more fundamental aspects, to be found in this thesis in papers B 1 - B 4.

In due course Shell's ideas became further modified, and it was realized that the important factor to justify the research effort was in fact the profit made per unit sold times the number of units sold. This opened the way for KSLA to pay attention to metals like nickel and cobalt. Some references to this work will be found in paper C 1.

B. COMMENTS TO THE PAPERS

A 1.

As already indicated in Section A of this part of the thesis, A.R. Burkin has done pioneering work in applying direct reduction of metal salts of organic acids in kerosine solution to produce metal powders. Originally only single-metal salt solutions were involved,[3] but later an example of selective precipitation of nickel from solutions of the nickel and cobalt salts of DEHPA was claimed.[11] Slightly earlier the present author had embarked upon the programme of which the more fundamental results were presented in this paper.

In experimental practice it was found that nickel could be selectively precipitated from Ni/Co VERSATIC salt solutions. The selectivity factor, defined as

$$\frac{([Ni]/[Co])_{precipitated}}{([Ni]/[Co])_{in\ solution}}$$

was around 7, and was hardly influenced by temperatures in the range 140 - 200° C and pressures between 0 and 50 bar. Remarkably enough, the presence at the start of highly active Raney nickel (added as a catalyst) initially completely destroyed the selectivity. After the catalyst had been effectively plated with precipitated metal, selectivities were restored and again fell in the category given above.[4]

Work on a continuous process was done on the system Cu/Ni.[5] It was found that copper could be specifically precipitated from solutions in a fluidized bed of Cu granules. However, temperatures and pressures required were far higher than expected on the basis of the previous fundamental work.

Some work on continuous reduction of the copper salt of VERSATIC acid was also done at Davy-Powergas Ltd.[12]

None of the work has sofar reached a commercial status.

A 2.

Judging from the patent literature [6,13] the subject dealt with in this paper emerged almost simultaneously at various places. At KSLA the work was restricted to the use of VERSATIC acid, whereas Thorsen [13] included other organic acids as well. Both the present author and Thorsen in his original work stripped the iron from the organic extractant with mineral acid, thereby using the chemical stability of the reagent(s). It can easily be seen that an important factor in the economics of the whole process will be the question whether the mineral acid can be made reusable. One might think of thermally induced hydrolysis, e.g. of $FeCl_3$ with the Woodall-Duckham or Ruthner processes, to produce Fe_2O_3 and reproduce HCl.

In later work Thorsen and Monhemius [14] carried the process one step further, and carried out direct thermal hydrolytic decomposition of the ferric VERSATIC salt, producing Fe_2O_3 and VERSATIC acid, and meanwhile implicitly accepting the advantages of VERSATIC acid over the other acids patented by Thorsen.[13] This innovative approach is at present being tested for commercialization by Lurgi, in co-operation with Thorsen.

A 3 and A 4.

As far as the author knows his work described in these papers represents the "state of the art". No other work has been published since in which both the metal concentrations were so high and the ratio reagent concentration to metal concentration was so low.

B 1 - 4 and C 1.

1. Site of the reaction

With respect to the site of the reaction, most people working in the field assume that it takes place at the interface,[15] while some believe that at least the rate-determining step(s) occur(s) in the aqueous phase.[16] The discussion is often obscured because many workers use the commercially available impure hydroxy-oximes. The present author still believes that the reaction is basically interfacial, and that Flett's main objection against an assumed aqueous phase reaction, i.e. the very low solubility of the hydroxy-oximes,[17] stands unshattered.

If one however realizes that most workers who adhere to the "aqueous phase concept" accept that the reaction takes place in a zone close to the interface,[16] one already approaches the two-film theory of interfaces and the discussion on the actual reaction site becomes trivial. Instead, concepts of mechanisms then become more important.

2. The rate law(s)

The rate law proposed in paper B 4, with as main characteristics a second-order dependence on (free) monomeric oxime concentration (or a first-order one on (free) dimeric oxime concentration) and an inverse first-order relation between the forward reaction rate and the hydrogen ion concentration, is not always found in other work. Again however, the discussion is obscured by the frequent use of commercial products.

Very little work indeed has been reported which was done with chemically pure, structurally defined reagents. Notable exceptions are found in references 15a and b and 18. Preston and Luklinska [15a] found agreement with the present author's rate law, using a rising drop method. Danesi et al. [15b] found initial rates with a first-order dependency on bulk monomeric reagent concentration, using a strongly dispersed system. Cox et al. [18] found orders close to one both in quiescent interface and dispersed cell measurements. In contrast to Preston and Luklinska, Komasawa et al.[19] found first-order dependency on bulk monomeric reagent concentration in rising drop experiments, using purified anti-LIX 65 N.

3. The mechanism

It is very tempting to propose a mechanism for a reaction on the basis of a rate law, and in the case of hydroxy-oxime extraction of copper most authors including the present one have not been able ro resist this temptation. However, it should be realized that a rate law is nothing more than a mathematical expression, and may in principle be a reflection of various possible reaction mechanisms (perhaps even occurring simultaneously). Moreover the character of the rate law may also be influenced by diffusional transport limitations.

A major point in all discussions on mechanisms has been the question whether the monomer or the dimer of the reagent is the actual active species. Most workers favour the monomer [20] but ICI chemists believe that the dimer plays the dominant role.[21] The author's papers B 3 and B 4 illustrate that he changed his mind during his work, and in his most recent paper B 4 he proposed the dimer as the active species.

At the time, the main argument in favour of this was the assumption that the interface was populated with a constant surface concentration of monomeric reagent. Further "evidence" was drawn from the fact that attempts to correlate the rates found with the surface population of the reagents had failed.

The first attempt to find a quantitative relation of that kind for copper extraction by hydroxy-oximes was made by the present author in paper B 2. Several other papers followed.[15a,22] Paper B 3 seemingly underlines the lack of success of these efforts, by failing to reveal a relation between the Excess Interfacial Population Density (EIPD) for various model oximes and their observed rates of extraction. In the course of further work this seeming absence of such a relation was found to be due to the presence of very small amounts of impurities in one of the compounds (oxime IV in B 3). These contaminations did not show up in the form of melting point depression but strongly influenced the interfacial behaviour of the oxime. Hence recrystallization was repeated until the interfacial tension of a reagent solution against an aqueous phase remained constant.

Recalculation of the data concerned on the basis of the new measurements considerably changed the picture as presented in paper B 3. Below the relevant table from B 3 is given as it should read, and commented.

Slopes of σ_i/log C plots for various oximes in toluene and heptane, and EIPD's and IPD's[x] (both in 10^{13} molecules.cm^{-2}) at oxime concentration 10^{-2} M. Temperature 25° C.

OXIME			HEPTANE			TOLUENE		
No.	R	R'	SLOPE	EIPD	IPD	SLOPE	EIPD	IPD
I	t-C_4H_9	CH_3	-11.8	12.3	12.6	-11.1	11.5	11.8
II	t-C_8H_{17}	CH_3	-10.5	10.9	11.2	- 6.7	7.0	7.3
III	t-C_9H_{19}	CH_3	-10.8	11.2	11.5	- 6.2	6.4	6.7
IV	t-C_8H_{17}	n-C_7H_{15}	- 7.8	8.1	8.4	- 5.2	5.3	5.6
V	CH_3	n-C_7H_{15}	- 9.9	10.3	10.6	- 6.6	6.9	7.2
VI	t-C_9H_{19}	H	-13.5	14.0	14.3	-13.0	13.5	13.8

The observed relative rates of copper extraction, found in simple shake-out tests at an oxime concentration of 0.1 M, are:

$$\text{VI} \gg \text{I} > \text{II} \gg \text{III} > \text{V} > \text{IV}$$

From the above table it follows that the IPD's are related as follows:

$$\text{VI} > \text{I} > \text{III} > \text{II} > \text{V} > \text{IV}$$

Despite the fact that some doubt still exists about the purity of oximes III and VI (both are liquids, purification of which was carried out by distillation of the precursors, the ketones), it can be seen that at least a very good qualitative correspondence exists between these two sequences.

However, this is not yet fully satisfactory. At the moment paper B 3 was written the importance of the monomeric reagent concentration was not yet realized. It is reasonable to assume that the EIPD will be related to the bulk concentration of the reagent monomer, rather than the dimer. Komasawa et al.[23] give some experimental evidence to support this assumption.

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[x] The IPD (Interfacial Population Density) is calculated by adding to the EIPD the reagent concentration in a random plane in the liquid. The difference is small, and only becomes noticeable in concentrated solutions.

For oximes II, IV and V association data is available (B 4). Using this the figures in above table have been recalculated for these oximes with monomeric reagent concentration instead of bulk total concentration.

Slopes of $\sigma_i/\log C_m$ plots for various oximes in toluene and heptane, and EIPD's and IPD's (both in 10^{13} molecules.cm^{-2}) at oxime monomer concentration 0.01 M. Temperature 25° C.

OXIME			HEPTANE			TOLUENE		
No.	R	R'	SLOPE	EIPD	IPD	SLOPE	EIPD	IPD
II	$t\text{-}C_8H_{17}$	CH_3	-16.5	17.2	17.5	-9.6	9.9	10.2
IV	$t\text{-}C_8H_{17}$	$n\text{-}C_7H_{15}$	-11.4	11.8	12.1	-9.4	9.8	10.1
V	CH_3	$n\text{-}C_7H_{15}$	-16.6	17.3	17.6	-8.6	8.9	9.2

Considering the large differences found in extraction rates for these oximes (see previous page) and the small differences in IPD's it seems doubtful whether a relation between reagent structure and reaction rate can be quantified on this basis.

Preston and Luklinska,[15a] recognizing that earlier attempts to explain rate differences found between various oximes on the basis of the Gibbs isotherm had failed sofar, assumed that it could not be used in this reaction and instead applied a form of the Langmuir adsorption isotherm:

$$\frac{c}{\pi} = \frac{1}{a.b} + \frac{c}{b}$$

in which c is the organic phase concentration of the oxime, π its interfacial pressure, and a and b are constants for the system.
Basis of their discussion was that the interfacial concentration of the active reagent species was directly proportional to its bulk concentration.

Although they could this way explain a second-order dependency of the extraction rate on the bulk reagent concentration, their evidence does not justify dismissal of the Gibbs isotherm:

$$\Gamma_{2,1} = \frac{1}{R.T}\,\frac{d\,\sigma_i}{d\,\ln C} = \frac{C}{R.T}\,\frac{d\,\sigma_i}{d\,C}$$

The present author's measurements given in paper B 4 were carried out at bulk oxime concentrations of 0.006 - 0.06 M. The table below illustrates that quite possibly in the concentration range the interfacial concentration of the reagent monomer is proportional to its bulk concentration. In this table, the monomeric reagent concentrations were calculated from the total bulk reagent concentration using the association data for oxime IV from paper B 4.

Relation between bulk reagent concentration C (M), monomeric reagent concentration C_m (M) and interfacial tension σ_i ($mN.m^{-1}$) for oxime IV in toluene. Temperature 25^{o} C.

C	C_m	σ_i	
0	0	36.9	
3.0×10^{-4}	2.99×10^{-4}	36.8	
10^{-3}	0.99×10^{-3}	36.6	$\frac{d\,\sigma_i}{d\,C_m}$ = constant,
3.0×10^{-3}	2.91×10^{-3}	36.3	
10^{-2}	9.2×10^{-3}	35.7	hence $\Gamma = f(C)$
3.0×10^{-2}	2.4×10^{-2}	34.3	
10^{-1}	0.062	32.0	
3.0×10^{-1}	0.13	29.0	$\frac{d\,\sigma_i}{d\,\ln C_m}$ = constant,
5.0×10^{-1}	0.18	27.7	hence Γ = constant

This table confirms the correctness of Preston and Luklinska's basic assumption, but the use of the Langmuir isotherm instead of the Gibbs one is not necessary, provided the latter is applied in the form which is correct for the concentration range studied.

In their paper [15a] the authors present a figure (fig. 3) in which the rate of extraction by 2-hydroxy-5-methylphenyl n-heptyl ketoxime (oxime V from the present author's paper B 3) is given as a function of the bulk reagent concentration. This figure demonstrates a gradual change of slope from slightly under 2 to slightly higher than 1. Calculations based upon (admittedly not very accurate) readings from this figure, using the present author's dimerisation constant for that compound (paper B 4, table 2) rather than Preston and Luklinska's own value were carried out and the results plotted. An almost straight line was obtained for the log. of the rate vs. the log. of the monomeric reagent concentration. The slope was almost 2 over a reagent monomer concentration range 0.01 - 0.05, corresponding to total reagent bulk concentrations of 0.016 - 0.1 M. This is practically the quoted authors' whole range of measurements.

It is now no longer necessary to use the dimer concentration in the proposed mechanism. The present author's rate law remains fully valid, but the mechanism can be reformulated to give an exact agreement with that of Preston and Luklinska:

$$\overline{RH}_m \rightleftharpoons RH_i$$

$$Cu^{2+} + RH_i \rightleftharpoons CuR^+_i + H^+$$

$$CuR^+_i + RH_i \rightleftharpoons CuR_{2\,i} + H^+$$

$$CuR_{2\,i} \rightleftharpoons \overline{CuR_2}$$

The reasoning given sofar, if correct, leads to the conclusion that up till now very few measurements on pure reagents have been reported in which the bulk reagent concentration guaranteed constant interfacial population density of the active species. Cox et al.[18] briefly describe quiescent interface experiments with a pure oxime in heptane, where a constant IPD may be assumed. Their rate dependency on the log. of the total reagent concentration at pH 2.5 shows a slight curvature, with an average slope around 1. They do however neglect the very strong association of monomeric oxime, which is under their experimental conditions not permitted (see B 4, table 2). Moreover it is not clear from their paper whether the amount of oxime bound to copper was neglected, and if so, whether this was justified.

4. Conclusions

From the work which is now available on the kinetics of copper extraction with pure oximes the following conclusions can be drawn:

The reactions are almost certainly interfacial, and it is quite likely that the reagent monomer is the active species.

In conditions where the Interfacial Population Density of the reagent monomer can be described as directly proportional to its bulk concentration, the mechanism suggested above correctly describes the rate law found both in well-mixed systems (B 4) and in well-designed rising drop measurements. (ref. 15a).

It is further likely that in such conditions also the results of well-designed quiescent interface measurements could be reconciled with the same mechanism.

Not sufficient evidence is available on experiments in which the IPD of the active species could be considered constant and hence independent on bulk reagent concentration. What little there is [18] suggests that first-order dependencies might emerge between bulk (active) reagent concentration and rate.

5. Diluent effects

The influence of diluent effects on copper extraction with hydroxy-oximes has found wide attention in the literature. In paper B 4 a quantification is given in terms of forward and backward rate constants for the case of toluene vs. heptane.

Originally it was generally believed that the differences between diluents were of value, and had to be taken into account in operational design. In very pure systems the advantage of using a purely aliphatic diluent is indeed quite substantial in terms of distribution coefficients and rates of extraction and stripping.

Practical usage of this principle however is hindered by many disturbing factors in a plant, like purity of the phases, inconsistencies in the operation itself, etc. Hence in practice little difference is found between various diluents with respect to copper recovery. Gradually the emphasis has shifted from the importance of composition to that of purity, consistent quality, and flash point of the diluent.

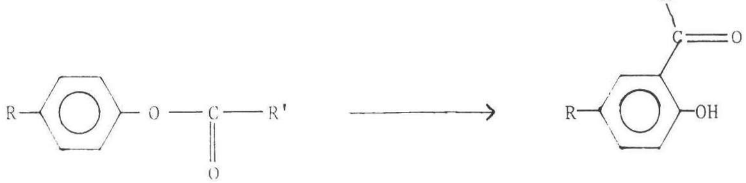
Especially sulfur- and nitrogen-containing impurities will harm, particularly with respect to the physical behaviour of the system.

At present the discussion of diluent effects has practically died out.

6. Synthesis of 5-tert-alkyl-2-hydroxyphenyl alkyl ketones

Paper B 1 contains a reference to an improved Fries rearrangement in the synthesis of 5-tert -alkyl-2-hydroxyphenyl alkyl ketones. Since this work was only published in the form of a patent[24] it appears useful to comment on it here.

Application of the Fries rearrangement with $AlCl_3$ as the catalyst to esters of p-alkylphenols should in principle after working-up yield 5-alkyl-2-hydroxyphenyl alkyl ketones:



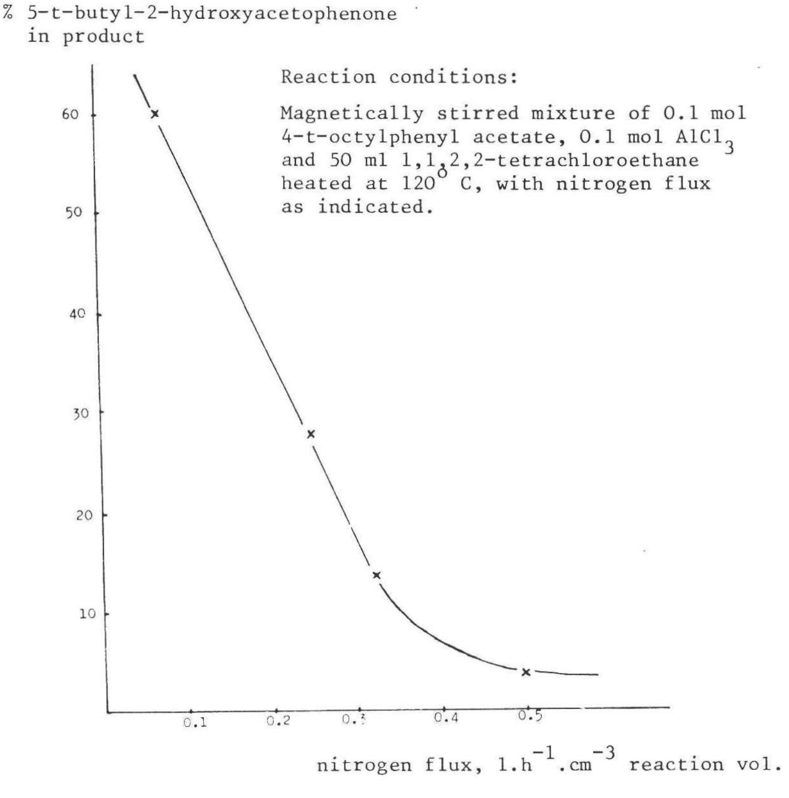
However, if the alkyl group attached to the phenol ester is of a tertiary nature, difficulties may be expected because the conditions prevailing in the Fries reaction are favourable for decomposition or even splitting-off of such chains. It has been stated in the literature [25] that de-alkylation predominates when t-alkyl substituted phenolic esters are subjected to Fries-type conditions.

Indeed our work has shown that complications do occur. A chemically well-defined compound like 4-(1',1', 3',3'-tetramethylbutyl) phenyl acetate yielded a number of products, amongst which o-hydroxyacetophenone, p-hydroxyacetophenone, 5-tert.butyl-2-hydroxyacetophenone, 5-(1',1',3',3'-tetramethylbutyl)-2-hydroxyacetophenone and 5-tert-dodecylacetophenone were identified with certainty.

Obviously not only splitting-off of the chain occurs, also partial breakdown and even elongation of the side chain happen. It became clear that these phenomena were not due to the $AlCl_3$ used in the rearrangement, but to the hydrochloric acid set free by the reaction of the phenol formed with $AlCl_3$.

It was possible to remove the HCl as it was formed by means of a flow of inert gas (nitrogen). The effect of the nitrogen flux is illustrated in the figure below. The easily identified 5-tert-butyl-2-hydroxyacetophenone was chosen as the compound to be monitored. Although a product with a minimum content of undesired compounds can thus be obtained, the method is not feasible. Over the total reaction time of 2-5 hours (depending on the specific compound) the total amount of nitrogen needed would be tremendous in a practical operation. However, it was found that the aim could also be achieved by carrying out the reaction in a boiling solvent.

Fries rearrangement of 4-(1',1',3',3'-tetramethylbutyl)-phenyl acetate.



Reaction conditions:

Magnetically stirred mixture of 0.1 mol 4-t-octylphenyl acetate, 0.1 mol $AlCl_3$ and 50 ml 1,1,2,2-tetrachloroethane heated at 120° C, with nitrogen flux as indicated.

C. THE FUTURE

At this moment (early 1983) the situation in the copper industry, which is quantitatively the biggest outlet for SX chemicals (the hydroxy-oximes), is bad. Although as already stated in Part One of this thesis SX plant in operation produces the cheapest copper, lack of capital with the copper companies has caused shelving of many projects, interrupted the building of others, and the bad copper market has even caused the closure of certain plants (e.g. Kennecott Ray).

Upon recovery of the overall economic situation in general and of the copper market in particular the interest will certainly revive. A point of future importance will be SX on chloride leaches. This is an area in which hydroxy-oximes will not be preferred reagents. These are much less stable in hydrochloric acid medium than against sulfuric acid. At least one reagent specifically designed for chloride systems is presently under development by ICI[x].

Applications of SX in the winning of other base metals are also strongly influenced by the economic situation and await its improvement. The industry is in principle interested in certain development products for cobalt extraction, but commercialization does not proceed quickly. No suitable reagent is yet available for nickel, and the author's view is that it will not be easy to develop one, because of the chemistry of the $Ni(H_2O)_6^{2+}$ and derived ions. However, if these difficulties could be overcome the potential seems excellent.

In the nuclear industry not many developments are foreseen. Although the cost factor is not so important, the reagents already available, notably tributyl phosphate, are so cheap that the chemical industry does not show much interest to develop necessarily more expensive new ones.

In the production of noble metals e.g. platinum and related ones, the influence of the overall economic recession does not seem to hit as hard as elsewhere. The cost factor of a reagent is only of secondary importance, but the potential reagent volumes are so small that the interest of the chemical industry is marginal. Much effort is being made by the metal producers themselves to try and find applications in their field for existing reagents (Matthey, Métallurgie Hoboken).

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[x] Private communication.

In a majority of its applications solvent extraction makes use of the technique of ion exchange. In this sense solid ion exchange (IX) and membrane technologies may well be compared with SX.

IX using non-functional resins impregnated with e.g. tributyl phosphate or DEHPA has already an established position in large scale uranium winning, and several continuous column designs are operational.[26,27] An advantage of IX in many cases is that the feed solutions might be less pure and especially greater amounts of solids or colloidally dissolved contaminants may be tolerated than in SX. Nevertheless attempts to use IX for copper winning have failed sofar. It is felt that the combination of diffusional resistances in the beads and a slow chemical reaction like that between copper ions and non-ionized oximes makes this kind of IX less feasible.

Chemically functionalized resins, notably those designed by Dow,[28] have sofar made no impact in the winning of base metals, probably for the reasons indicated above.

The best future possibilities for IX may be in the removal of small concentrations from large volumes, e.g. in water purification etc.

Membrane technologies have seen a fast development over the last few years. Solid membranes, either consisting of polymer films with pores permeable for certain ions or of polymer films impregnated with reagents, have been known for some time. Liquid membranes, consisting of solutions of reagents separating inorganic feed and stripping solutions, are being studied extensively. Pioneering work in this area was done by Li[29]. At a recent conference a whole session[30] was devoted to potential applications of this type of membranes. The greatest advantage of this technique is that the ions taken up at the extracting side of the membrane are continuously removed from it at the stripping side. Hence the driving force for the extraction is maximized, and one is able to extract metal ions from very dilute solutions. Application in practice is still hindered by some problems. In the case of copper extraction e.g., the stripping solution tends to lose acidity to the feed, and water from the feed is being transported to the stripping solution through the membrane. Moreover, the emulsion stabilizing the system tends to break after some time. As will be clear, the system is still in full development. Future applications would seem to be mainly in separations from dilute solutions, although a recent paper[31] suggests that also leach solutions of higher concentration may be amenable to the technique.

Fused salt extraction is under development for application in pyrometallurgy, thus providing a link between "old" and "new" processes. In principle the method encompasses contacting a molten matte (e.g. a nickel matte) with fused sodium chloride. The ability of contaminating cobalt to form chloridate complexes makes the cobalt dissolve in the fused salt, leaving the nickel behind in purified form.

As already stated in this thesis, energy costs for SX (and hence probably for related processes too) tend to be higher than for more "conventional" procedures. However, the most important driving force in favour of the newer techniques will probably be the fact that metal ores available become poorer and poorer, putting ever greater demands to the degree of sophistication of the methods used to work them. The also economically successful operation of numerous SX plants shows that SX and related methods can solve problems which are too big for older processes.

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28. Grinstead, R. et al., in: Op. Cit. 9, Chapter 52.

29. See for instance Op. Cit. 26, paper D 1.

30. Op. Cit. 26, Session D.

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NOTES added after completion of this thesis

1. Kelex 100 (p. 30)

Production of the original compound was discontinued in 1976. Later supplies appear to contain 7-[2-(5-ethylnonyl)]-8-hydroxyquinoline as the active component.

Stubina, N.M. and Distin, P.A., "Direct cobalt recovery from loaded Kelex 100 by reaction with hydrogen", CIM 21st Annual Conf. of Metallurgists, Toronto 1982.

2. LIX 860/864

After conclusion of the law suit against Henkel about the use of 5-alkyl-2-hydroxysalicylaldoximes (p. 30) in favour of the plaintiff ICI-Acorga, both companies have come to an agreement. Samples are now around of a LIX 860, which is presumably a 5-dodecyl-2-hydroxysalicylaldoxime. LIX 864, a mixture of LIX 860 and LIX 64 N or LIX 65, is presently being tested at various places.

3. Rate of copper extraction with SME 529

Miyake et al. have very recently published results of measurements in a quiescent interface cell on the extraction of copper with purified SME 529. At low reagent concentrations $[\overline{RH}]$ they found the initial rates of extraction to be a function of $[\overline{RH}]^2$, whereas at higher concentrations the dependence tended towards a first-order one.

These results can be taken to confirm the present author's third and fourth conclusions (p. 197).

Miyake, Y, Takenoshita, Y. and Teramoto, M., J. Chem. Engng. Japan 1983, 16 (3), 203.

SUMMARY

This thesis is divided in three parts.

In PART ONE a survey is given of the application of liquid/liquid extraction (further indicated as SX) in the winning of metals.

Four categories of SX can be distinguished.

1. Complexation of metal cations with anions, particularly those derived from carboxylic acids, phosphoric acid di-esters and phosphonic acid mono-esters.

2. Complexation of metal-containing anions with cations. Such metal-containing anions are e.g. chloridate complexes. Onium compounds are most widely used as cations.

3. Complexation between metal cations and chelating reagents. Appropriate cations are mostly transition metal ions. Many organic compounds are suitable as chelating agents. Most important are hydroxy-oximes, which are widely used in the copper producing industry.

4. "Real" SX, in which the non-ionizable solvent extracts a metal compound. Here the metal ion takes its own counter-ion.

Subsequently a survey is given of the application of SX in the copper winning. It is estimated that 4 - 5 % of the copper is produced using SX, but locally this figure can be much higher. SX yields the cheapest possible copper, but high capital investment hinders expansion of the application.

Lastly this part contains a survey of the composition of most chelating reagents which are or have been available commercially.

PART TWO contains the text of the author's papers in the field of SX and related areas. Papers A 1 - A 4 discuss a number of applications of VERSATIC acid (a mixture of highly branched tertiary carboxylic acids). A reaction scheme is proposed for the uncatalysed and the nickel-catalysed direct hydrogenation of VERSATIC copper salt. In two papers the average composition is discussed of some metal salts of VERSATIC acid in solution under practical conditions. Lastly the replacement of the environmentally less-acceptable jarosite and goethite precipitations in the zinc industry by an exchange extraction with VERSATIC zinc salt is discussed.

Papers B 1 - B 4 and C 1 contain the work in the area of SX with hydroxy-oximes and similar compounds. Main points are the rate laws for the forward and backward reaction of copper ions with hydroxy-oximes. It became clear that the forward reaction shows a second-order dependency on the free monomeric reagent concentration. Since it was then generally believed (also by the author) that the interfacial population density of monomeric oxime was constant, the author had to propose a reaction mechanism in which the dimeric reagent figured. Also an explanation was given for diluent effects on the basis of rate differences between forward and backward reactions in different diluents. A qualitative explanation was given for the influence of modifiers and retarding compounds on the basis of accessibility of the interface to the reagents. In paper C 1 the way of thinking of the author and his coworkers during design of SX reagents is illuminated, as are the results obtained.

PART THREE contains comments to PART TWO, as they have become necessary by the progress of science in the field. Especially it was found that the assumption given above on the constancy of interfacial population density by (monomeric) reagent molecules is incorrect in the concentration range used by the author and most other workers. It was made plausible that the Gibbs isotherm for determining interfacial population densities may be applied in the range concerned in the form

$$\Gamma = \frac{C}{R.T} \cdot \frac{d\,\sigma_i}{d\,C}$$

The way of thinking followed in the comments leads to the conclusion that it is now no longer necessary to introduce the dimeric reagent molecule as the active species. While keeping full validity of the rate law, a mechanism can be proposed using the monomeric free reagent concentration on the basis of direct proportionality between the bulk concentration and the interfacial population density in the concentration range studied.

SAMENVATTING

Dit proefschrift bestaat uit drie delen.

In DEEL EEN wordt een overzicht gegeven van de toepassing van vloeistof/vloeistof extractie (verder aan te duiden als SX) bij de metaalwinning.

Er zijn vier categorieën van SX te onderscheiden.

1. Complexvorming van metaalkationen met anionen. Onder de laatste vallen met name anionen afgeleid van carbonzuren, fosforzure di-esters en fosfonzure mono-esters.

2. Complexvorming van metaalbevattende anionen met kationen. Zulke metaalbevattende anionen zijn bij voorkeur chloridaat-complexen. Als kationen worden meest onium-verbindingen gebruikt.

3. Complexvorming tussen metaalkationen en chelaatvormende reagentia. Zulke metaalkationen zijn veelal overgangsmetaalionen. Als chelaatvormers komt een groot aantal verbindingen in aanmerking. Het belangrijkst zijn de hydroxy-oximen, die op grote schaal gebruikt worden bij de koperwinning.

4. "Echte" SX, waarbij het niet-ioniserende oplosmiddel een metaalverbinding extraheert. Hier neemt het metaalion dus zijn eigen tegen-ion mee.

Vervolgens wordt een overzicht gegeven van de toepassing van SX in de koperwinning. Naar schatting wordt 4-5 % van het koper geproduceerd met gebruikmaking van SX, maar locaal kan dit veel hoger zijn. SX levert het goedkoopst mogelijke koper, maar de hoge kapitaalinvestering werkt remmend op uitbreiding van de toepassing.

Tenslotte bevat dit deel een overzicht van de samenstelling van de meeste chelaatvormende reagentia die commerciëel verkrijgbaar zijn of geweest zijn.

DEEL TWEE bevat de tekst van de artikelen die door de auteur op het gebied van SX en verwante gebieden gepubliceerd zijn. De artikelen A 1 t/m A 4 behandelen een aantal toepassingen van VERSATIC zuur (een mengsel van sterk vertakte tertiaire carbonzuren)- Een reactieschema wordt voorgesteld voor de ongekatalyseerde en de door nikkelionen versnelde directe hydrogenering van het koperzout van dit zuur. In een tweetal artikelen wordt de gemiddelde samenstelling behandeld van enige metaalzouten van VERSATIC zuur in oplossing onder in de praktijk voorkomende condities. Tenslotte wordt de mogelijkheid besproken om de milieu-technisch minder aanvaardbare verwijdering van driewaardig ijzer uit zinkelectrolyt d.m.v. neerslaan als jarosiet of goethiet te vervangen door een uitwisselingsextractie met het zinkzout van VERSATIC;

De artikelen B 1 t/m B 4 en C 1 bevatten het werk op het gebied van de SX met hydroxy-oximen en soortgelijke verbindingen. Centraal staan hierbij de reactiesnelheidsvergelijkingen voor de heen- en teruggaande reacties bij de extractie van koperionen met hydroxy-oximen. Hierbij wordt duidelijk dat de heengaande reactie een tweede-orde afhankelijkheid vertoont van de concentratie aan monomeer, vrij reagens. Aangezien toen algemeen (ook door de auteur) werd aangenomen dat de concentratie van monomeer oxime aan het grensvlak constant was, moest de auteur een reactiemechanisme voorstellen waarbij het dimeer van het reagens een rol speelde. Verder werd een verklaring gegeven voor oplosmiddeleffecten op basis van snelheidsverschillen tussen de heen- en teruggaande reacties in verschillende oplosmiddelen. Ook werd een kwalitatieve verklaring gegeven voor de invloed van "modifiers" en van reactievertragende contaminanten, op basis van toegankelijkheid van het grensvlak voor het reagens. In het artikel C 1 wordt het denkpatroon toegelicht dat door de auteur en zijn medewerkers werd gehanteerd bij het ontwerpen van SX chemicaliën, alsmede de resultaten die daarmee geboekt werden.

DEEL DRIE bevat commentaar op DEEL TWEE, zoals dat door de vooruitgang van de wetenschap noodzakelijk werd. Met name is gebleken dat de bovenvermelde veronderstelling over een constante grensvlakbezetting door (monomere) reagensmoleculen niet juist is in de concentratiegebieden waarin de auteur en de meeste andere werkers metingen uitvoerden. Daarbij is aannemelijk gemaakt dat de Gibbs isotherm voor de bepaling van grensvlakconcentraties ook in het onderhavige gebied bruikbaar is, mits toegepast in de vorm:

$$\Gamma = \frac{C}{R.T} \cdot \frac{d\,\sigma_i}{d\,C}$$

Uit de in het commentaar gevolgde gedachtengang blijkt dat het nu niet langer noodzakelijk is het dimere reagensmolecuul ten tonele te voeren als actief deeltje. Met behoud van de volledige geldigheid van de gevonden reactiesnelheidsvergelijking kan een (in feite veel logischer) reactiemechanisme op basis van het monomere vrije reagens worden voorgesteld op basis van een rechte evenredigheid tussen de concentratie en de grensvlakconcentratie voor dit reagens in het bestudeerde concentratiegebied.

CURRICULUM VITAE

Mijn middelbare schooltijd heb ik deels doorgebracht aan de Rijks-HBS te Schiedam (1949-1952), deels aan de Zuiderpark HBS te Den Haag (vanaf 1952). Daar ontving ik in 1954 het Diploma HBS-B.

In 1954 begon ik mijn studie aan de Technische Hogeschool te Delft, waar ik in 1960 afstudeerde bij Prof. Dr. Ir. B. M. Wepster op een onderwerp uit de aryn chemie.

Na het vervullen van mijn militaire dienstplicht trad ik in 1962 in dienst van het Koninklijke/Shell Laboratorium te Amsterdam, waar ik sindsdien werkzaam ben geweest.

De eerste jaren werkte ik o.a. aan de formylering van ketonen, welk werk uitmondde in een publicatie samen met mijn toenmalige chef.[1] Later verrichtte ik o.a. werk op de gebieden oligomerisatie van olefinen, homogene hydrogenering van poly-olefinen en rubbers, en esterificatie van hogere alcoholen met ftaalzuuranhydride. Van dit laatste werk is een gedeelte eveneens gepubliceerd.[2]

Rond 1970 begon mijn bemoeienis met de vloeistof/vloeistof extractie van metalen, eerst als neventaak, later als hoofdbezigheid. Behalve in de in dit proefschrift samengebrachte artikelen heeft het werk op dit laatste gebied ook zijn weerslag gevonden in een tweetal meer toepassingsgerichte artikelen.[3,4]

1. Van der Zeeuw, A.J. en Gersmann, H.R., The formylation of ketones, Rec. Trav. Chim. 1965, 84, 1535.
2. Van der Zeeuw, A.J., Kinetics of the esterification of phthalic anhydride with model alcohols, Chem. & Ind. 1969, 978.
3. Van der Zeeuw, A.J., Liquid/liquid extraction of copper and nickel with a selective reagent, Erzmetall 1977, 30, 139.
4. Van der Zeeuw, A.J., Shell Metal Extractant 529 - a new selective extractant for copper and nickel, in: Extractive Metallurgy of Copper (eds. J.C. Yannopoulos en J.C. Agarwal), Chapter 54. AIME New York, 1976.

STELLINGEN behorende bij het proefschrift van A.J. van der Zeeuw

1. Het gebruik van de AKUFVE apparatuur voor het meten van de kinetiek van reacties die zich afspelen tussen twee onmengbare vloeibare fasen is op praktische gronden af te raden.

   Reinhardt, H. en Rydberg, J., in: Solvent Extraction Chemistry (eds. D. Dyrssen, J-O. Liljenzin en J. Rydberg), 612. North Holland Publ. Company, Amsterdam, 1967.

   Cox, M. et al., Proc. Int. Solvent Extr. Conf. Liège 1980, paper 80-118

   Hummelstedt, L. et al. Proc. 4th Int. Congress in Scand. on Chem. Engng. 1977, 123.

   Flett, D.S. et al., J. Inorg. Nucl. Chem. 1973, 35, 2471.

2. Bij hun pragmatische verklaring voor oplosmiddeleffecten op de reactiesnelheid van koperionen met hydroxy-oximen veronderstellen Komasawa et al. ten onrechte dat de monomere reagensconcentratie in heptaan hoger is dan in tolueen.

   Komasawa, I. et al., J. Chem. Engng. of Japan 1980, 13, 204.

3. Het gebruik van onzuivere reagentia is een belangrijke hinderpaal gebleken bij mechanistische studies aan de reactie tussen koperionen en hydroxy-oximen.

   Dit proefschrift.

4. De aanname van een snelheidsbepalende stap in de waterfase voor de reactie tussen koperionen en hydroxy-oximen is niet in overeenstemming te brengen met de waargenomen invloed van niet aan het mechanisme deelnemende vertragers.

   Carter, S.P. en Freiser, H., Anal. Chem. 1980, 52, 511.

   Dit proefschrift.

5. De doorzet van conventionele mixer/settler apparatuur bij de oplosmiddelextractie van metalen kan worden verbeterd door het gebruik van snellere reagentia te koppelen aan een geringere power-input in de mixers.

6. Doordat in de keten: loging - oplosmiddelextractie - (electro-)winning de oplosmiddelextractie de beste correctiemogelijkheid voor oneffenheden in de procesgang biedt is aan een zekere "overdesign" van de extractieapparatuur niet te ontkomen.

7. Het negéren van elkaars opvattingen en bevindingen door groepen die op hetzelfde wetenschappelijke gebied werkzaam zijn werkt belemmerend op de vooruitgang in dat vakgebied.

   Freiser, H., Proc. Int. Solvent Extr. Conf. Liège 1980, paper 80-II en referenties daarin.

   Nitsch, W. en Sillah, O., Ber. Bunsenges. Phys. Chemie 1973, 83, 1105.

8. Bij het ontwerpen van watergekoelde metalen automotoren wordt onvoldoende aandacht besteed aan de eisen van en aan het koelsysteem en de koelvloeistof.

9. Het schrijven van woorden, werkwoordsvormen en dergelijke volgens de uitspraak, zoals door sommigen gepropageerd wordt, lost de problemen die menigeen met de spelling heeft niet op maar verergert deze.

10. De geringe aandacht die veel leraren Nederlands tegenwoordig besteden aan een juist taalgebruik in woord en geschrift en aan een goede spelling vermindert de kansen van hun leerlingen in het maatschappelijk leven.