Detergency in Liquid CO_2

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Cover: Washing test results for clay on wool (CW) and sebum on wool (SW) in liquid CO_2 with and without the addition of surfactants. Designed by Rodrigo Gárate.

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To my Husband
Ignacio

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Prologue

In this dissertation we study Detergency in liquid Carbon Dioxide. Detergency is the cleaning performance of additives, surfactants in particular, in washing fluids. Liquid CO_2 is under consideration, for environmental and toxicological reasons, to replace perchloro-ethylene as the solvent in textile dry-cleaning technology. Inherent problems of such a transition were confronted with the methodology of chemical engineering design. The Basic Cycle of Design (BCD) approach was used as a pathway for designing a detergent. The BCD also establishes the structural framework of the thesis, which can, therefore, be read as records from a successful product engineering project, in which an effective detergent has been designed for a new dry-cleaning solvent .

Chapter 1 reviews the technology of washing and dry-cleaning, including the types of soils encountered in such processes, the mechanisms for their removal and the surfactant action on the washing. Criteria for the selection of liquid CO_2 as the solvent are also exposed.

In Chapter 2, existing models for understanding detergency are evaluated and some inconsistencies in the theory are exposed. The results and conclusions of previous research, which led to the formulation of the Dynamic Detergency Model (DDM), are also analyzed. This DDM model succeeds to explain the role of surfactants in the washing operation. It is, therefore, used as a rational starting point for the design of a detergent in liquid CO_2.

Chapter 3 begins with a short review of the BCD methodology for designing a chemical product. The target criteria are specified for a surfactant which should act as a detergent in liquid CO_2 . Such a surfactant must be: sparingly soluble in the solvent, surface-active and able to form micelles in the solution. Given an almost complete lack of experimental solubility data in this novel solvent, we needed an approach to estimate these values. Several parameters were analyzed that allow the estimation of individual group contributions of separate carbophobic and carbophilic moieties to the solubility parameters of an amphiphilic surfactant molecule, dissolved in liquefied carbon dioxide. With these "theoretical" insights, and using an imaginary building up procedure, we put together a surfactant molecule with the desired solution properties according to the DDM. The result of these considerations was, that members of the homologous polyoxyethylene/alkane series, generally described by the shorthand formula C_iE_j, were selected as the most plausible candidates in the Basis of the Design (BOD) for the desired product.

The experiments in Chapter 4 establish which of the molecules in the BOD were indeed, as predicted, soluble in carbon dioxide under the specified conditions of pressure and temperature for the dry-cleaning process. Cailletet and light scattering experiments showed the solubilities of C_iE_j-molecules in the solvent. Differences in polydispersity between laboratory- and industrial samples of the surfactants were considered in this analysis. However, for the specified conditions, an optimum chain length of the carbophilic moiety (C_i) as well as for the carbophobic moiety (E_j) was found.

In Chapter 5 we designed experiments to verify that the selected molecules would indeed behave as surfactants (surface-active and able to form micelles in solution). Measurements at the water/liquid CO_2 interface have shown that the adsorption of sparingly soluble C_iE_j-compounds does effectively reduce the interfacial tension. The molecules will, therefore, also be surface-active at the textile/liquid CO_2 interface. Dye dissolution experiments, monitored by light scattering and UV-Vis absorption spectrometry, showed the concentrations where these molecules begin to form micelles in the solution. Polar compounds, which are highly insoluble in liquid CO_2, can be solubilized in the interior of such micelles. Considering solubility and commercial availability as selection criteria, the surfactants C_8E_3 and $C_{12}E_4$ were proposed as the most suitable candidates for a technical evaluation.

In Chapter 6, the technical evaluation of the detergent is carried out. This is the essential step in every product design. It is at this stage that the value of the design result is tested, by comparing the real performance of the product with the target specifications. To this effect, quantitative washing tests had to be developed. This included: the selection of the monitors (woollen fabrics reproducibly soiled with clay particles and with a sebum/carbon black paste), the colorimetric method for the quantitative evaluation of dry cleaning results, the equipment and the methods for laundering experiments in high pressure autoclaves with the possibility to include controlled mechanical action and a rinsing step after the washing. A short introduction to colorimetry is given, which elucidates the origins and the physical meaning of the indexes for evaluation of laundering tests. The results of the experiments showed, as predicted by the DDM, that high washing performance can be obtained with C_iE_j detergents, both for a purely particulate soil (clay) and for more complex stains, like sebum (fat) with carbon black (soot) dispersed in it. As is emphasized by the Dynamic Detergency Model, the mechanical action in the liquid (flow) turns out to be a key factor in the washing performance of a detergent. Redeposition was identified as a major problem in dry-cleaning with liquid carbon dioxide as the solvent. But this problem can be solved by using formulations which contain polar cosolvents. In semi-pilot scale experiments we could, once more, obtain high washing performances. The results of these tests did show that the designed detergents, in formulations that had not been optimized any further, can reach the specified washing performances. They are, indeed, as good for dry-cleaning textiles as the present perchloro-ethylene (Perc) technology.

In Chapter 7, the laundering observations presented in this dissertation are reviewed and further analyzed. Technical as well as formulation proposals are deduced, oriented towards improved dry-cleaning processes. And at the end, as has become the custom in dissertations from our Delft Laboratory of Physical Chemistry, we have summarized our scientific conclusions on detergency in four final theses.

Chapter 1

Laundering and Dry-Cleaning

Laundering and Dry-Cleaning

Laundering is one of the most common activities in man's life. Its objectives and methods have basically remained unchanged for ages. The machinery for textile cleaning has gradually developed but the basic principles of the technology remain the same. Although water has mostly been chosen as the solvent, the use of other solvents was introduced two centuries ago in commercial laundering of delicate fabrics. Nowadays, delicate garments made of textile fibres such as wool, which are sensitive to wrinkling and shrinking, are preferentially laundered in these other solvents. That process is known as *dry-cleaning*. Dry-Cleaning originated by accident, around the middle of the 19^{th} century in Paris, when Jean Baptiste Jolly's maid overturned a kerosene lamp on a table cloth and he noticed that it became cleaner. Some years later, he began to offer a new cleaning service, which he called *dry-cleaning* [1].

The main advantage of dry-cleaning is that the organic solvents do not soften fibres as water does. Wrinkling, shrinkage, pilling and bleeding of dyestuffs, which are caused by the properties of water as a solvent, can be avoided. As an economic advantage in commercial laundering operations, the subsequent, labor intensive pressing step for numerous garments is greatly facilitated in dry-cleaning, compared with washing with water [2].

During the 19^{th} century, low boiling naphthas and benzenes were the most popular dry-cleaning solvents. However, at the beginning of the 20^{th} century those solvents were replaced by gasoline. Later on, around 1920 in Germany, chlorinated hydrocarbons were introduced in the industry. After World War II tetrachloroethylene, better known as perchloroethylene or Perc, became the overwhelming choice as a solvent for industrial dry-cleaning. Not only was this non-flammable solvent safer and faster, but it also did a much better job of cleaning and required less massive equipment and floor space. When Perc was introduced, dry-cleaning could be installed in retail locations (the so called pappa-mamma stores) offering excellent quality one-hour dry-cleaning service. Nowadays, the majority of clothes all over the world are dry-cleaned with Perc.

The Variation in Soils Substances

In laundering of textiles we generally have to deal with simultaneous removal of a wide variety of soils. They must be addressed according to their behavior in the cleaning process and can be classified accordingly:

1. Substances that may dissolve as molecules, which can be sub-divided in water-soluble (hydrophilic) and oily-grease (lipophilic or hydrophobic) soils.
2. Oxidizable or Bleachable soils.
3. Proteins and other adsorbing macromolecules.
4. Particulate soils, which are disperse insoluble materials like soot, clay particles and metal (oxides) fines.

Whether substances that are soluble as molecules may or may not become an issue in the laundering operation depends on the solvent. Water-soluble soils like salts and sugar are easily removed by cold water and they are of no concern for the laundering of textiles in water. However, these hydrophilic (*water loving*) materials become an issue in the technology for dry-cleaning when non-polar solvents are used. The same applies, vice versa, for the oily-grease soils. They easily dissolve in non-polar, lipophilic (*fat loving*) solvents but represent a problem in a water-laundering operation. The general terminology is to call a substance lyophilic when it will easily dissolve in a solvent and lyophobic when it will not. Specifically, a soiling substance, which does dissolve in water but not in liquid CO_2, is a hydrophilic but also a carbophobic material. A non polar organic substance, however, which mixes in all proportions with aliphatic hydrocarbons as well as with liquid CO_2, is considered both oleophilic and carbophilic. The same terminology applies for textiles: cotton is more hydrophilic than wool, because it is more easily wetted with water, but the lack of specific interactions of the fibers surfaces with liquid CO_2 makes both materials relatively carbophobic.

Oxidizable and bleachable soils like wine, blood, fruit juices, grass, tea, coffee, etc. owe their color to conjugated double bonds in porphyrinic and other aromatic structures. These molecules will often contain color enhancing (auxochromic) groups which can be oxidized by hypochlorite, hydrogen peroxide, or peracids. This treatment shifts the absorption spectrum to invisible wavelengths, leading to colorless substances. For laundering purposes that is sufficient. The molecules may not be removed during the laundering, but the stains are not longer visible and that is often the desired result.

Proteins and starch, which are polymeric materials, resist conventional cleaning. They adsorb on textiles fibers and get attached to the solid surface by multiple specific interactions between chemical groups in both materials. To weaken these bonds, they must be displaced by adsorption of other, more strongly bound but smaller molecules (like a monomer of the same macromolecules)[3].

At the interface macromolecules can act as a glue for other soils or solubilize these in their macromolecular structures, making the cleaning more difficult. In modern laundering, enzymes are applied to attack macromolecular soils. Enzymes can decompose the macromolecular chain molecules. Reducing the effective size of the macromolecules in this way, they simplify the washing strategy for such substances to the removal of (low) molecular soil.

Particulate soils consist of insoluble particles, either liquid (like oil drops in water), or solid. Particles are mainly deposited on textiles from suspensions in air (aerosols). Solid soot, dust and clay particles usually have large surface areas, on which oil and grease absorb very strongly. This property interferes with the laundering by making the removal of oily and greasy soils more difficult.

Since particles are not soluble, neither in water nor in non-polar solvents, particulate dirt does not disintegrate in the laundering process. It can redeposit on the surfaces of textile fibers after the washing. Therefore, particulate soils must not only be dispersed as colloids in the washing fluid, but also stabilized as a suspension in the solvent by well chosen additives.

Mechanisms of Soil Removal

Molecular Soils

Molecular soils are soils which can dissolve as separate molecules in the washing liquid or in some other phase which is dispersed into it as additive. Lyophobic soils are those which are not soluble in the laundering solvent itself. But then it helps when surfactants are added. They adsorb strongly at all the available interface (solvent/substrate as well solvent/soil). This has a number of consequences. In the first place, the adsorption lowers the interfacial tension at these surfaces, allowing complete wetting of the fabric in all its pores by capillary effects. The adsorption must be completed before any further detergency can take place. Sometimes, surfactants molecules can act as "displacers" on other substances, like polymers and other tenacious soils. After that, depending on the structure of the adsorbed layer and of surfactant micelles in the solution, a soil can dissolve and become solubilized by the surfactant, in the inner core of these micelles or even in the lyophobic inside of the adsorbed surfactant layer itself.

Solubilization of oily substances can occur when oil drops come into contact with aqueous surfactant solutions. Upon colliding with an oil drop a micelle will disintegrate and spread its molecules over the interface. If the rate of spreading exceeds the rate of desorption, the interface will become supersaturated. In order to reestablish the equilibrium new micelles must form somewhere in the interface. When these micelles leave and disjoin from the O/W interface, they carry some oil molecules with them into the aqueous laundering solution [4, 5]. But in the absence of convection the complete solubilization of free oil drops by this mechanism can take hours. This is not fast enough for effective laundering in practical applications, especially if we consider that in this process soils are not loosely dispersed but attached to textile fibers.

A particular laundering strategy for molecular soils is "prespotting". In prespotting, the textile is first impregnated locally with a concentrated surfactant solution end then flushed with water. Local desorption of surfactant by the flushing creates gradients of surface tension and, therefore, Marangoni flows at the interface. These can sometimes help and will eventually remove difficult stains. However, in normal laundering the detergent is added into the medium and not directly onto the soiled spot [4].

Particulate Soils

Particulate soils consist of solid and of liquid particles. To disperse the latter as colloids would be a form of emulsification. Emulsification is when a liquid is dispersed as small droplets into another, continuous, liquid in which it is essentially insoluble. We can distinguish two types of emulsification. The best known and most common emulsification process is the dispersion of a liquid by adding emulsifiers and shearing the coarse two-phase mixtures. The other method is spontaneous emulsification (like in microemulsions). In the latter case highly concentrated surfactant and cosurfactant solutions are required in specific proportions, which is a much too specific condition for application in a realistic laundering process. For dispersion by shear one normally requires a high input of mechanical action in order to reach the colloidal domain of particle sizes. Bancroft's empirical rule about emulsification states that as an emulsifier a surfactant is needed in the process, which is more soluble in the continuous phase than in the emulsion droplets. And even then a good emulsion needs to be stabilized against drop coalescence by added surfactants. In many textbooks a mechanism called "roll up" is considered important for removing oil from a solid surface with the help of water and surfactants. Roll up would be effected because surfactant adsorption alters the relative magnitude of the S/L and L/L surface tensions. As a consequence of Young's law, the contact area between the liquid soil and the substrate will also change. Sometimes it shrinks and eventually an oil drop could detach and carry its volume into the liquid as an emulsion drop.

Somebody must have had a dream, of such mechanism. It will not be effective in realistic laundering conditions because the residual stain remains in place. Hydrodynamics should play a key role in roll up since drop deformation implies the motion of fluids. On irregular substrates like porous textile fabrics, the effects of the advancing and receding interplay between capillary forces is difficult to predict. Spontaneous roll up mechanisms present serious theoretical difficulties as an explanation for detergency.

Solid particles, even when not caught and carried between the yarns of the clothes, will adhere to textile fibers by London van der Waals dispersion forces. With colloidal dimensions of the particles, like in soot and other particulate soils, these adhesion forces are relatively large and difficult to overcome [6]. Direct repeptization by adding a solvent to aggregated colloidals will be the exception rather than the rule. But in laundering the addition of surfactants seems to help, even though spontaneous redispersion of coagulated colloids by adding surfactants has never been successful with submicron particles.

Surfactants will sometimes reduce the adhesion of the particles on the substrate and they will stabilize the colloid after the particles have been detached. The latter is certainly important to prevent redeposition. Surfactants, and also polymers like carboxy-methylcellulose (CMC), will reduce the probability that a particle re-attaches somewhere else on the fabric by heterocoagulation from the washing fluid. Particulate soils often occur in combination with other substances such as oil and grease, which are wetting the particles. This combination contributes the extra effect of liquid bridges to the toughness of the soil deposit [7]. Its strength is then determined by

(Laplace) capillary forces. This capillary type of cohesion in a paste is much stronger than any mechanical forces which can directly be applied to submicron particles. The best way to clean such stains away is by adding a surfactant solution, which dissolves the oil and grease in micelles. This facilitate the subsequent removal of the particles by the mechanical action of the friction forces, which are exerted on the textile by the flow of the washing liquid.

Detergent Action

It is clear from centuries of experience that surfactants enhance the laundering process. This effect of additives on the washing process is known as *detergency.* There are several mechanisms, which could give detergent properties to a surfactant solution. Surfactants lower the surface tension of the washing liquid and improve the wetting of the textile material. Adsorbed surfactants can displace substances, which adhere to a solid surface. And, by forming micelles, they can solubilize the substances which have difficulty to dissolve in the washing medium itself. A polar liquid like water is not a good solvent for fatty substances, whereas it will dissolve the ions of salts easily. In solvents like hexane or heptane this situation is inverted. In fact, the only possibility for insoluble molecules to be taken away by the washing fluid is when they become solubilized in the inside of surfactants micelles, which have been added for improved detergency. And furthermore, the removal of insoluble particulate soils like carbon black or silica does also require the addition of specific additives. Surfactants are used for this purpose too.

Water, Perc, conventional non-polar liquids like hexane and unconventional solvents like liquid CO_2 have all different characteristics. But each of these solvents can be used as a laundering liquid. Of course, the objective of the laundering, removal of soil from the textile, is always the same. And, *mutatis mutandis*, many of the problems which must be solved are also similar with all those solvents. Many of these problems are addressed chemically, in the formulation of a detergent for a specific solvent medium. The removal of lyophobic soils, which are the water-soluble soils for non-polar solvents and the oily and greasy substances for water, must be made possible by adding surfactants to the chosen solvent. The function of detergency, which is the effect of additives, is to allow the required degree of soil removal in combination with acceptable levels for other process conditions. Excessive stirring and mechanical action, for example, could easily cause unacceptable damage to the textiles that must be laundered.

Classes of Surfactants

In the ubiquitous context of aqueous media, surfactants are classified according to the charge on the molecules at neutral pH. One could then distinguish:

1. Anionic Surfactants
2. Cationic Surfactants
3. Amphoteric or Zwitterionic Surfactants

But in a different solvent than water, the ionization of surface active molecules is no longer a good criterion for the characterization.

A more general description is obtained when the molecules of a surfactant are considered as "amphiphilic". This means that they consist of two distinctly different moieties, one polar or hydrophilic and the other apolar or hydrophobic. The polar part of the molecule is soluble in water and the apolar part is insoluble. And *vice versa*, when the solvent itself is apolar in nature.

Depending on the chemical nature and the size of two moieties, one could think of the hydrophobic and hydrophilic properties of the complete molecule being built up by additive contributions. In this way the "HLB"-value of an amphiphilic substance has been defined. It represents the ratio of the hydrophilic (H) and the lipophilic (L) contributions to the solubility and the surface activity of such a molecule in the solvent. In this HLB value the ionisable (head) group in surfactants contributes, obviously, to the hydrophilic side. Long aliphatic tails are an example of the moieties with a lipophilic nature. But this same formalism can also classify the important group of non-ionic surfactants, in which a polar oligomer (e.g. consisting of some carbohydrate, a number of vinyl-alcohol groups or a water-soluble polyether chain of ethylene oxide and/or propyleneoxide monomers) is combined with an aliphatic (lipophilic) alkane into one non-ionic surfactant molecule [8].

Surfactants can always be described as some rather soluble substance (the solving loving moiety), which has, step by step, been made more insoluble by the bonding to it of more and more lyophobic groups in the other half of the molecule. Most surfactants are, indeed, sparingly soluble substances in any solvent liquid. But their function demands adequate solubility in many technological applications. In selecting a surfactant for a particular application, the HLB-value and the concentration of the surfactant must be specified. In order to make such decision, it is useful to understand their temperature-concentration phase diagram. For some applications, e.g. under near critical conditions, the pressure effect has also to be included. The most commonly used surfactants are anionic and nonionic. Information about their phase diagrams in aqueous solution is available.

The consequence of their amphiphilic structure is a peculiar phase behavior of surfactant solutions. In Fig. 1.1 [9] we see a typical (T,X) phase diagram for some ionic surfactants in water, which is a key for some interesting properties.

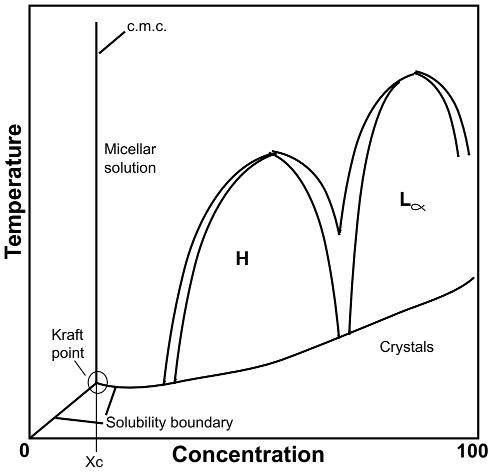


Figure 1.1: Typical phase diagram of ionic surfactants in water.

Above some rather low concentration X_c, which is known as the critical micellar concentration or c.m.c, the solution appears to become saturated with the surfactant and separate into two different phases. The new, as yet disperse, phase contains all the surfactant molecules in excess of the c.m.c. It consists of very small association colloids of the amphiphilic molecules, which are called surfactant micelles (see Fig. 1.2). The

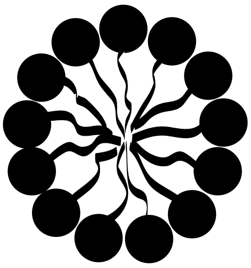


Figure 1.2: Cartoon of a micelle.

lyophobic parts of the molecules are ordered in the inside of each micelle. Their lyophilic parts in the outside shell of the structure interact with the ambient solvent in the surface of the particle.

Depending on the molecular structure and the concentration of the surfactant, micelles can be spherical or cylindrical. Normally, as the concentration X increases, there is a transition from small spherical micelles with an association number below 100 surfactant molecules to cylindrical micelles. These oblong structures can separate out of the solution as a new "lyotropic" liquid crystalline phase. In more concentrated solutions rather complicated anisotropic liquid crystalline phases can appear. The first is often a hexagonal (nematic) phase and later, at still higher concentrations, a lamellar (smectic) phase will form. Those ordered phases melt at elevated temperatures. The presence of additives like electrolytes has a strong effect in the phase behavior: solubility, location of the c.m.c and other phase transitions are affected by it.

The phase behavior of a nonionic surfactant is presented in Fig. 1.3 [10]. At low temperatures (T≤ 20 °C) the sequence of phases resembles that of ionic surfactants (see Fig.1.1). However, at more elevated temperatures the phase diagram is dramatically different.

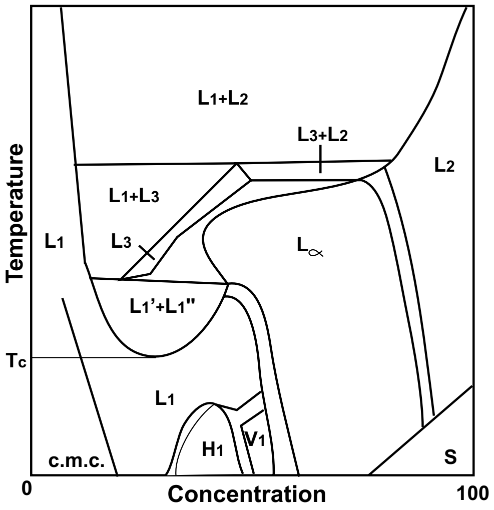


Figure 1.3: Typical phase diagram of nonionic surfactants in water. L_1 and L_2 denote normal and reverse micellar solution. L_1' and L_1" are the lean and rich micellar phases respectively. H_1 is a hexagonal, V_1 a cubic and L_α a lamellar liquid crystal. L_3 is an isotropic solution containing bilayers.

The solubility of the nonionic lyophilic moieties in water is relatively low already compared to anionic and cationic chemical groups, and it decreases as the temperatures increases. At some critical temperature the homogeneous liquid phase separates into a surfactant rich and lean phase. This temperature is known as the "Cloud Point" of the solution because the two-phase system is turbid and scatters light. This point can be visually determined. In many cases these surfactant rich phases are also liquid-crystalline and birefringent. The location of the Cloud Point depends on the molecular weight and the structure of the nonionic surfactant. More complicated phase diagrams (see Fig. 1.3) occur with the appearance of new structured phases like the L_3. Isotropic solutions containing bilayers can be observed for some of them [9, 11].

Dense CO_2 as a Versatile Solvent for Dry- Cleaning

Some decades ago, concerns have been expressed about the use of Perc in the dry-cleaning industry. Studies indicate that Perc could be harmful for the environment [12]. As a result of the legislation, especially in developed countries, companies (large and small) must replace toxic solvents in their operation and look for more environmentally friendly alternatives. Solvents like the traditional hydrocarbons, but also silicone oils and even liquid CO_2 have been proposed as attractive and competitive alternatives to chlorinated compounds like Perc. The issue of an economically competitive alternative is important and pressing, because of the present structure of the dry-cleaning industry. A high level of investment would force many small dry-cleaning shops out of the business and completely alter the logistics of the dry-cleaning service as it is known today.

Dense CO_2 –liquid or supercritical– (see Fig. 1.4) is one of the proposed alternatives as a solvent in the dry-cleaning industry. It has a number of interesting properties. It is a nontoxic, nonflammable and inexpensive solvent. It is liquid at room temperature and, industrially speaking, moderate pressures, with a lower critical temperature ($T_c = 304\,\mathrm{K}$) and pressure ($P_c = 73.1\,\mathrm{bar}$) than other solvents.

Near these critical conditions the density and the characteristics of the liquid as a solvent can be varied by changing the pressure. This makes dense CO_2 an attractive solvent for the successive extraction of various substances in process industries, like decaffeinating coffee beans. Different substances can be removed from a complicated substrate with only one solvent (which is, of course, what a dry-cleaner wants to do). All those aspects make dense, near critical CO_2 an intriguing solvent for various applications like extraction of natural products, spray painting, polymerization and

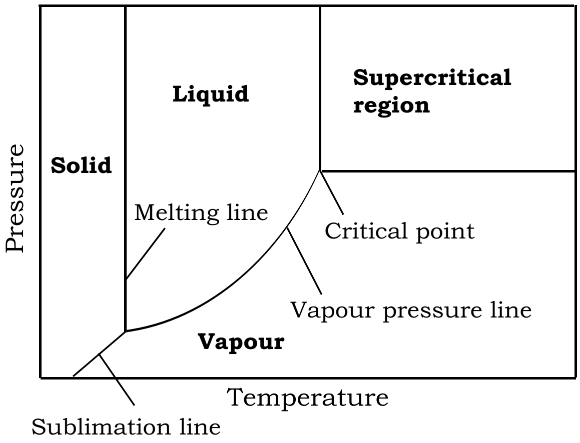


Figure 1.4: Phase diagram of CO_2.

polymer processing, purification and crystallization of pharmaceuticals or the dyeing of fibres and textiles [13]. And, maybe, also for dry-cleaning.

Worldwide, there are a number of projects investigating the use of dense CO_2 as a versatile solvent in the dry-cleaning industry. The research, which is described in this thesis, was done in the context of one of these projects, managed by TNO-RT and funded by the Dutch Government EET program. From what we know about dry-cleaning it will not be sufficient to just select a new solvent for the laundering process. The chosen liquid alone, pure CO_2, is not capable to remove stains from textile fabrics on its own. It is an extremely apolar medium, which can only cope with all the more polar kinds of textiles, stains and soils with the help of a detergent.

Within this project the first problem was to find an effective detergent. This was quite urgent: nothing else was known about detergency in liquid CO_2 but that the pure liquid does not wash at all. Worldwide, no useful detergents for this application have been developed yet, and no theory was available to relate detergency with surface activity in media like liquid CO_2.

In the Delft Laboratory of Physical Chemistry we had developed the Dynamic Detergency Model (DDM). In principle that DDM-model might help to find such a detergent. But the DDM concept had only recently been developed, in the experimental context of "wet", water borne textile laundering [4]. The chemical generalization of the DDM-model had yet to be extended to other media and the odds were small indeed that it would work without adaptations in a weird solvent like dense CO_2 as the washing liquid.

So, as chemical engineers do, we have chosen to design a detergent for liquid CO_2 as our first research objective. The design would involve a physico-chemical generalization of the DDM-model. The compounds for a designed product would then have to be prepared or purchased before they could be formulated as a detergent. Only after that, the applicability of our designed detergent for dry-cleaning could be put to the test in the technology that would be developed during the course of the TNO-EET project.

Chapter 2

Models for Detergency

Surface Active Chemicals as Effective Detergents

The most important additive to a laundering solvent is the detergent. It changes an extraction medium into a washing fluid. The detergent introduces a broad spectrum of solvent capabilities into the solution, in particular because surfactants, which are added for detergency purposes, do form micellar structures. The core material of a surfactant micelle is essentially different from the solvent around the particle. It is insoluble in that medium itself, but offers a haven for many substances which could be equally insoluble in the original solvent. They do, exactly for that reason, dissolve readily in the inner parts of the micelle.

A generally accepted definition of detergency is: *"The relative ease by which unwanted foreign matter (soil) is removed from a substrate* [14]. The better the detergency of the washing fluid is, the easier becomes the laundering of textiles or the cleaning of solid surfaces. Despite the apparent simplicity of this definition, and the many books and reviews on the subject, the fundamentals of detergency are far from understood. One reason for that is the number of factors involved in the process and their interplay. Detergent action of an additive (the *detergent*) in a medium is one factor, but its effect can only be isolated when the other conditions are reproducibly standardized. Detergency is not a property of a solution that can be measured in a chemical laboratory. It must be determined under the realistic conditions of some laundering technology. With the proposed solvent (liquid CO_2), detergent development is only possible by concurrent chemical engineering of the product and the equipment for dry-cleaning. As it emerges on the drawing board and in the research laboratory.

Sinner Factors

Innumerable experimental aspects of laundering have been identified, which affect the effectiveness of textile washing. They can be grouped in four categories known as the *Sinner Factors* [15]. The four Sinner Factors are Chemistry (C), Mechanical Action (M), Temperature (T) and Time (t).

1. **Chemistry, C**. Refers to the variable composition of the washing fluid. It can include chemicals like surfactants, electrolytes, complexants, bleaches and other additives in a chosen solvent. These are combined to an optimum formulation for detergency.
2. **Mechanical Energy, M**. Refers to mechanical energy "M" spent in the laundering by stirring, stretching and agitation of the textiles and of the washing fluid in which they are soaked.
3. **Temperature, T**. Refers to the effect of temperature on rates of processes like cleaning and sterilization of goods during the laundering process.
4. **Time, t**. Which is the discriminating variable for the effectiveness of a washing process. An optimum process for industrial laundering will require that acceptable laundering results are delivered in the shortest possible time.

The optimum detergency efficiency for different operations is always a specific compromise with set values of these four Sinner factors.

An aspect of adding detergents is that they do not just facilitate the removal of soils from the textile. They also seem capable to considerably **speed up** the washing process. This effect of detergents on the rate of laundering is, obviously, of great economical importance, but the point has remained out of the scientific focus for a long time (see, e.g., van Roosmalen [16]). Recent studies of laundering kinetics have given some understandings about the rates of laundering *processes*. A new role for the detergents has been discovered by Timmerman [4]. They speed up the washing process considerably. This result is described in the *Dynamic Detergency Model*.

Detergency Mechanisms

Textile laundering is the separation of the soil from a solid surface (of the dirty textile yarns) and mass transfer to the washing fluid. The separation step depends on the soil ingredients. It can be dissolution in the medium, either directly or into the core of detergent micelles, repeptization of solid particles or the emulsification of oily stains. But if one of these mechanisms does work spontaneously it is fast enough: a matter of seconds. The transfer of these soils into the ambient washing fluid will nearly always be rate limited by diffusion. The mass transfer occurs through the stagnant liquid in the boundary layers which fill the pores of the textile with washing liquid. A well-known engineering method to calculate the rate of this mass transfer process is the concept of the diffusion boundary layer. It is assumed, on the basis of hydrodynamic theory, that close to a solid surface (like in the pores of the textile) there is no free flow of a liquid solvent. Without flow, there is no convection transport of solutes either and the Peclet number remains low. Any soil ingredient passes into the bulk of the washing fluid by diffusion through this almost stagnant boundary layer. The soil itself may be a colloidal particle, an emulsion droplet or a dissolved molecule in the medium or inside a detergent micelle.

In this film model of mass transfer, diffusion through the stagnant boundary is faster than convection. But diffusion, especially of particulate dirt, is a relatively slow process. It becomes rate limiting for a laundry process, regardless of the way in which the soil was originally separated from the solid surface.

The Equilibrium Approach

Laundering starts with a clean washing fluid and a dirty fabric. The washing fluid has to separate the dirt from the solid material in the yarns. "Repeptization" of the dirt particles and dissolution of soil substances, i.e. the separation step, has long been considered the most difficult aspect of detergency. Adsorbed substances cling to the textile surface with the strength of their adsorption energy. To remove them, their molecules must be extracted from the fibrous material. The success of that extraction will depend on the quality of the washing liquid as a solvent for the adsorbed molecules.

As we have already observed, no fluid can be a good solvent for every soil substance. But it helps considerably if the washing fluid contains a surfactant. Surfactants have a large tendency to adsorb at the interface with the textile and to form association colloids (micelles) in the solution. Textbooks identify two special detergent functions for surfactants as additives in the Sinner Factor C, the chemical composition of the washing fluid. As a good detergent the surfactant must diminish the adhesion of the soil by lowering the interfacial tension of the textile. And the micelles must solubilize dirt molecules to strengthen the soils carrying power of the washing fluid. Both effects promote the separation of the soils. That is a prerequisite for eventually reaching the final goal of the process: the soil substances being carried away in the washing liquid and the textiles clean and ready for re-use.

All this is very interesting in terms of releasing the dirt. But this approach focuses on adsorption equilibria at S/L interfaces and has no bearing on the rate of the mass transfer, which has a decisive role in detergency.

Due to the amphiphilic structure, individual molecules of a surfactant have a very limited solubility in any solvent. They tend to accumulate at the interface between two non miscible phases like between a polar and a non polar liquid, a liquid-vapor or liquid-solid interface. This adsorption gives a large surface excess Γ_s of the surfactant at the interfaces, which carries the dirt. In equilibrium, according to Gibb's equation,

$$\left(\frac{\partial \gamma}{\partial c}\right)_T = -\frac{RT\Gamma_s}{c}, \tag{2.1}$$

the surface tension γ (i.e. the excess free energy per unit surface in the system) is also lowered by the adsorption. This improves the wettability of the solid surface. Surfactant molecules are very effective in displacing other adsorbed substances from an interface because of their extremely large adsorption free energy.

Surfactant Micelles

Their name tells that surfactants are surface active. They are also known to form micelles in solution. These two properties of surfactants are related consequences of their molecular structure. At low concentration the amphiphilic molecules of a surfactant will dissolve like any other sparingly soluble substance. But as the concentration increases above the solubility limit, the material must begin to precipitate somehow. Surfactant molecules have their self-organization in micellar structures as an alternative way out, which is specific for amphiphiles. Amphiphilic molecules can associate into micelles and self-organize in such a way, that their lyophobic parts form the core of a particle. The lyophilic parts of the molecules are concentrated in the micelle's interface with the solvent.

There is one concentration of a surfactant solution where the chemical activity is the same for single dissolved molecules ("monomers'), for the adsorbed molecules at the surface of the solution (a_s) and for the molecules in a micelle. That concentration is the critical micellar concentration or c.m.c for the surfactant in the solvent. Above the c.m.c the activity in the solution, in the adsorbed layer and in the micelles is independent of the weighed in amount of surfactant. The surplus separates out in the form of more micelles, increasing their number when more surfactant is added.

This leads to a constant monomer concentration in the solution, a constant surface coverage Γ_s at the interfaces, and thus, according to Gibb's equation (2.1) also to a constant value of the surface tension γ.

Micellization occurs at a fairly precisely defined concentration. A plot of the surface tension as a function of the surfactant concentration, like many other plots for properties of the solution (such as conductivity, turbidity and osmotic pressure) undergoes a sharp change in slope. Therefore, by measuring any of these plots (see Fig. 2.1), it is possible to estimate the c.m.c

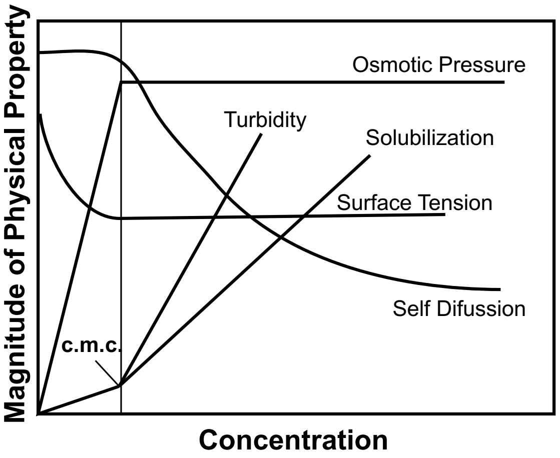


Figure 2.1: Change of solution properties at the c.m.c.

Temperature is a key factor in the aggregation. For an amphiphilic system to self-organize as a micelle, its moieties must be sufficiently flexible to undergo contortions demanded by the micelle shape. The temperatures must be high enough for the molecules to remain liquid inside the concentrated association colloid, so that (hydrogen) bonds are not aligned rigidly in an infinite crystalline precipitate.

Like in any solution of a sparingly soluble compound there is a small concentration of surfactant monomers in equilibrium with the sparingly soluble crystals of the compound. This is a normal situation, up to a temperature T_k, which is known as the Krafft point of the solution (see Fig. 2.2). Above the Krafft point the solubility appears to increase dramatically [17]. This is because for $T > T_k$ the micelles coexist with the monomers at overall concentrations higher than the c.m.c. The Krafft point is the temperature where the curves for the solubility and for the c.m.c intersect. At higher temperatures the number of micellar association colloids, and sometimes the

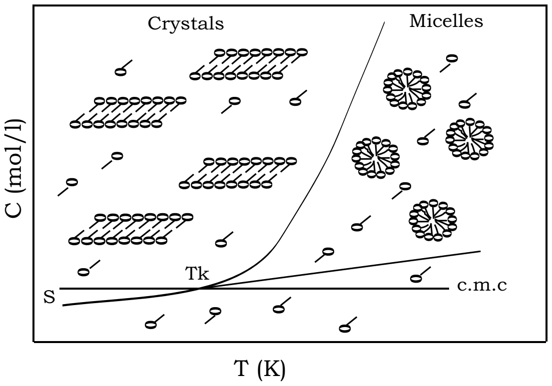


Figure 2.2: Diagram showing the Krafft point.

number of molecules in a micelle, increases with the weighed in amount of the surfactant. This is one of the reasons why the Sinner Factor T (temperature) is important in detergency. Below T_k a surfactant solution has no micelles. And because the micelles are essential for detergency, e.g. for the solubilization of lyophobic substances, the detergency in such a solution will, of course, remain small. A good washing fluid must have a concentration above the c.m.c and a temperature $T > T_k$.

Thermodynamics of Micellization

Micellization is a spontaneous process. The Gibb's free energy of micellization ΔG_m, which is

$$\Delta G_m = \Delta H_m - T\Delta S_m, \tag{2.2}$$

should be negative. It can be calculated from the c.m.c as

$$\Delta G_m = RT \ln c.m.c. \tag{2.3}$$

The contribution of the enthalpy of micellization ΔH_m in equation (2.2) cannot be generalized. For some surfactant systems negative values of ΔH_m have been measured [18], whereas for other systems both positive and negative contributions have been reported [19]. That could indicate the temperature dependence of ΔH_m, which can be derived using the Gibb's-Helmholtz relation

$$\left\{ \frac{\partial(\Delta G_m/T)}{\partial(T^{-1})} \right\}_p = \Delta H_m, \tag{2.4}$$

as an important aspect of micellization.

ΔH_m changes sign for a certain value $T = T^*$. For $T < T^*$ the enthalpy change $\Delta H_m > 0$ and micelle formation becomes endothermic. ΔH_m must be negative for temperatures above T^*, and micelle formation is then exothermic. For aqueous systems at room temperature $T\Delta S_m$ exceeds the enthalpy contribution. Since ΔG_m is negative and ΔH_m can be either positive or negative, the micellization entropy ΔS_m must be positive. Therefore, although micellization could sometimes be enthalpy driven, it is an entropy driven process in water. For apolar media, on the contrary, some authors state that micelle formation must be primarily determined by the enthalpy [20]. In these cases ΔH_m, which represents the attractive interaction energy of the lyophobic moieties in the micellar core, summed with the interaction of the ambient medium with the more lyophilic parts of the molecule in the surface (interacting among themselves and with the medium) is driving the micellization process.

Positive values of ΔS_m indicate an increase of the randomness in the system upon incorporation of a dissolved monomer in a micelle. The micelles themselves appear as ordered structures of low entropy. But the positive entropy of micellization arises from an increase in entropy of the solvent. Incorporating the lyophobic parts of the surfactant molecules in the core of a micelle places them outside the solvent. This frees a number of solvent molecules from their unfavorable interaction with lyophobic groups and allows them to relax into a higher state of entropy as part of the solvent liquid. At the same time, the lyophobic moieties will experience higher degrees of freedom inside the core of the micelles than individually solvated by the solvent. Both effects contribute to the positive value of ΔS_m [21]. In aqueous solution this phenomenon is called *hydrophobic interaction*.

The formation of micelles occurs under these thermodynamic rules. It has been analyzed in detail by considering the specifics of interactions among molecules in solution, aqueous and non-aqueous. As a rule of thumb micelles in aqueous surfactant solutions are large and of uniform size. The "inverse" micelles in apolar solvents tend to be smallish associates of surfactant molecules and have a wider size distribution.

The Traditional Model for Laundering

With surfactants displacing adsorbed soils at the interface and solubilizing lyophobic substances in the inner parts of their micelles; with enzymes cutting up unwanted adsorbed polymers; with oxidants added for the bleaching and other formulation ingredients for improving the washing results, we seem to have obtained a rather good insight in separation of soils and the detergency, to which added substances could contribute in the washing process.

If these are the responsible effects it would now seem possible to calculate the detergency. The fabric, of course, is a porous structure with narrow pores between the textile yarns and even finer porosity inside the woollen or cotton material. In these small pores there will be little liquid flow when the washing medium sloshes around in a washing machine.

Inside the fabric the dimensionless Peclet number (i.e. the ratio between convective and diffusion transport in the medium) is small. The mode of mass transfer in the laundering operation is diffusion of the soil out of the fabric. We can obtain diffusion rates for all kinds of soil substances separately from Fick's law. After successful separation to clean textile fibers, the lowest mass transfer rate will be rate determining for stain removal. Normally, colloidal materials, like clay particles, soot or metal fines will be difficult to flush out of the fabric because of their low diffusivity. Molecular soils will tend to cling strongly to the textile surface because of the molecular adsorption energy. But once they have been extracted from them, they will remain dissolved in the detergent solution.

Describing the laundering process we find two detergency mechanisms in series: detaching the dirt from the textile and carrying it away by diffusion through a stagnant boundary layer. The soaking of the fabric in the washing fluid must allow enough time for the diffusion. After that, the soils can be rinsed off the textiles by the sloshing of the washing liquid in the rotating drum of the machine.

Introducing a typical diffusion constant of $D = 3 * 10^{-10}\,\mathrm{m}^2/\mathrm{s}$ for small particles like clay, graphite, iron oxides and carbon black, we calculate the typical time needed for laundering clothes under normal washing conditions. The outcome of that kind of engineering calculation [22] is a nasty surprise. The laundering time for obtaining acceptable cleanliness, i.e. the Sinner Factor "t", would have to be several hours long!!.

Obviously, this is a completely absurd result. We are, day by day, confronted with the reality that laundering does take minutes rather than hours. A typical timescale of hours for normal textile cleaning can only be seriously wrong. It differs from the practical value by many orders of magnitude. But still, this was a perfectly sound engineering model for the calculation of mass transfers rates. It may not work at all for washing, but normally it gives correct results for chemical engineering design.

The question is, why this approach fails? it fails because of the preoccupation with adsorption equilibria in the traditional approach of detergency. In the traditional model the kinetics and hydrodynamics of the process is treated as an afterthought after the soils have been separated. The physical chemistry of detergents centers around equilibrium states at interfaces: on the adsorption of surfactants, the adhesion energy of dirt particles and the wetting of the fabric by the medium. Because of that equilibrium viewpoint the theory is not aware of the special dynamic aspects of adsorbed surfactant layers during a laundering operation. Never is the rate of processes determined by the energy gain between the original and the final state. That is why the traditional equilibrium models have been, so far, unable to describe detergency in a quantitative way. **In a quantitative detergency model it must be looked into that the flow of the liquids during the process disrupts the adsorption equilibrium of the surfactants.**

Liquid Flow in Porous Media

The concept of stagnant boundary layer is responsible for the slowest step in laundering. This concept is connected with the no-slip assumption, which has been introduced by Stokes as a boundary condition for liquid flow over a solid surface. All textbooks dealing with transport phenomena or with fluid mechanics make this assumption. The no-slip condition ensures continuity of Navier-Stokes' equation across the S/L interface. However, the basis for this assumption was not physics at all. The no-slip condition is a purely mathematical expedient. In the case of laminar steady-state flow with incompressible, continuous Newtonian liquids it works very well to calculate the flow pattern at S/L boundaries.

Interesting for laundering applications, is to study slip effects in the flow of detergent solutions through nanopores [23]. The flow of a liquid in small pores is described by the Navier-Stokes' equation:

$$\rho \frac{Dv}{Dt} = -\nabla p + \eta \nabla^2 v + \rho \mathrm{g}, \tag{2.5}$$

where v is the velocity, p the pressure, g the gravity, and η the viscosity. Neglecting the gravitational forces and assuming laminar flow in the pores (because of the low Reynolds number in small ducts), a solution of equation (2.5) in cylindrical coordinates is given by

$$v\left(r\right) = \frac{P}{4\eta}\left(R^2 - r^2\right) + A \ln \frac{R}{r} + B, \tag{2.6}$$

where A and B are constants which can be determined using the appropriate boundary conditions. In the case of no-slip condition, that is

$$v\left(r\right) = 0 \qquad r = R, \tag{2.7}$$

and we find $B = 0$. Since at $r = 0$ the velocities are finite, the constant $A = 0$. This gives the typical Poiseuille velocity profile for the flow:

$$v\left(r\right)=\frac{P}{4\eta}\left(R^{2}-r^{2}\right), \tag{2.8}$$

as a consequence of the no-slip boundary condition at the pore walls.

But if we had used the more general boundary condition

$$\left.\left(\overset{\rightrightarrows}{1}-\hat{n}\hat{n}\right)\bullet\left(\overrightarrow{v}-2\lambda\,\mathrm{sym}[\overset{\rightrightarrows}{\nabla}\overrightarrow{v}]\bullet\hat{n}\right)\right|_{r=R}=0, \tag{2.9}$$

we would have found the expression

$$v\left(r\right)=\frac{P}{4\eta}\left(R^{2}-r^{2}\right)+\frac{\lambda R}{2\eta}\left(P-P_{c}\right)\Theta\left(P-P_{c}\right), \tag{2.10}$$

for the velocity profile.

Here Θ is the Heaviside function. It accounts for the possibility that slip should only be observed above certain critical applied pressure gradient P_c. Below P_c the slip length λ vanishes and therefore, there is no slip. It is important to notice that for $\lambda \ll R$ the term accounting for slip becomes negligible in macropores.

Integrating equation (2.10), we obtain for the flow rate J in the pore:

$$J=\frac{\pi R^{4}}{8\eta}P+\frac{\lambda\pi R^{3}}{2\eta}\left(P-P_{c}\right)\Theta\left(P-P_{c}\right). \tag{2.11}$$

The first term in equation (2.11) retains the pure Poiseuille character. The second term accounts for the slip contribution along the wall. It is superimposed on the velocity pattern in the form of a plug flow.

In his work, Churaev *et al.*[24] showed experimentally that slip occurs in the flow of a hydrophilic fluid over a hydrophobic wall (*et vice versa*). Timmerman [4] considered lubricated slip flow for surfactant solutions in wetted pores and derived thermodynamically that slip flow will always occur in narrow pores below some critical diameter R^* of the order of micrometers. Zhu and Granick [25] have also reported a transition to partial slip flow when fluids contain surfactants.

The Stretching of Porous Yarns

Van der Donck [26] studied the effect of elongational forces in the textile yarns on the mass transport in laundering. Measuring the release rate of soluble salts from impregnated cotton he discovered that stretching creates liquid flow inside the microporous material. The stretching reduces the diameter of the yarns and the deformation squeezes some water out of the pores. Because of the flow in the small textile pores, the mass transport of dissolved substances is not diffusion limited anymore. The applied mechanical forces on the textile fabric do act as a kind of pump and play a rate determining role in the mass transport. The periodic elongation of the yarns had an optimum frequency of the order of 1 Hz. High frequencies, which implies high frictional forces, reduce the effect and cause the rupture of the yarn. The consequences for laundering operations are straightforward. Soil transport is improved by the mechanical action which deforms the textile yarns.

The Flow of Surfactant Solutions Through Narrow Pores

Cheikh and Koper [23] experimentally showed that surfactant solution flow through nanopores follows the Poiseuille profile at low shear rates. Beyond a well defined pressure gradient the flow suddenly increases due to slip in the adsorbed surfactant layer at the pore wall. They estimated the slip length λ for sodium dodecyl sulfate solutions (SDS) as $\lambda = 20$ nm.

Those results are in accordance with observations by Timmerman [4] on the flow of SDS solutions through porous membranes. She measured the resistance while alternating between pure water and SDS concentrations in a flow through calibrated straight and narrow pores. Unexpectedly, increased resistances for the flow of pure water were found after an SDS solution had been pumped through the pores and not for SDS solutions following water. The extra resistance was attributed to the slip in the admicelle being stopped by a Marangoni force in the surfactant's concentration gradients.

Marangoni Flows

In his PhD thesis, Vincent Nierstrasz [27] studied marginal regeneration. Marginal regeneration is the most important drainage mechanism in vertical mobile soap films. The draining of liquid from the film is much faster than a Poiseuille flow between the film surfaces. Nierstrasz found that marginal regeneration is caused by surface tension gradients at the film perimeter, where it flows into the adjacent bulk liquid. It is a Marangoni effect, a liquid flow, which is driven by the gradients in the surface tension. As the film flows into the bulk its surface becomes locally supersaturated with surfactant at the perimeter and acquires a lower than equilibrium surface tension. Marangoni flows have been observed in many surfactant systems. The rate of spreading surfactant in a gradient of surface coverage is often faster than the rate of adsorption from the solution. In these systems the equilibrium between the solution and its surface is disturbed. This creates extra transport currents in the liquid and the measured (”dynamic”) surface tension is dependent on the type and the velocity of the liquid flow.

Dynamic Surface Tension in Relation to Washing Performance

Bergink-Martens [28] investigated how detergency depends on the concentrations of surfactant solutions. She related her results both to the equilibrium and the dynamic surface tension at the same concentrations. Her dynamic surface tensions were measured in the expanding surface on top of an overflowing cylinder, i.e. in a steadily expanding surface. The observations were made for many different detergent (anionic, non-ionic, cationic) solutions in water. Fig. 2.3 gives her results for fatty acid soap as the detergent. Other surfactants gave the same correlations of the washing results with the dynamic surface tensions.

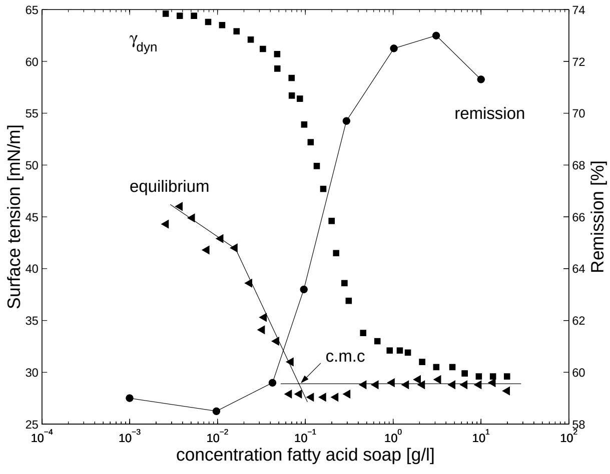


Figure 2.3: Relation between equilibrium-dynamic surface tension and washing performance for fatty acid soap.

The experiment demonstrates explicitly that detergency begins at concentrations around the c.m.c and increases with the surfactant concentration. It is the change in the dynamic surface tension, and not the equilibrium surface tension which correlates with detergency results. The best washing results are obtained where the dynamic surface tension and the equilibrium value come together. That is where the transport rate of the surfactant from the solution to the expanding surface can follow the expansion rate and keeps the surface excess of adsorbed surfactant at a steady state equilibrium value. But this is at concentrations far above the c.m.c

The transport rate in the solution increases with the surfactant concentration because there is a surplus of surfactant stored in the micellar solution. At high concentrations there are many micelles near the expanding surface. The concentration gradients are larger and the diffusion transport of surfactant to the surface becomes fast. Therefore, the values for equilibrium and dynamic surface tension converge towards the concentration where diffusion is no longer limiting the replenishing rate in the expanding surface.

Martens' results were crucial in a new understanding of detergency. They show that equilibrium phenomena, such as wetting and the lowering of equilibrium interfacial tensions are ***not*** the most important contribution of surfactants in detergency. The washing efficiency increases in the concentration range where the dynamic surface tension decreases. This observation indicates the importance of surfactant transport rates through the solution and to the interface. **It is the surfactant flow because of the disturbed equilibrium which determines the success of the laundering operation**. Along the lines of traditional (equilibrium) surface thermodynamics it is not possible to account for the dynamic aspects in a laundering operation. That is why no model could describe detergency in a quantitative way.

In order to do that it must be acknowledged that laundering is, of necessity, a dynamic process. The adsorption and micellization equilibria are disturbed by the mechanical action and the flow of washing liquid over the textile surface and restored by relaxation processes of surfactant adsorption. The local gradients in surface coverage are created by the motion and friction of the washing liquid inside the textile pores during the laundering. That is, surfactant flow opens a new mechanism of mass transfer between a solid surface and a flowing surfactant solution, that shunts out the diffusion limitation in the process.

This mechanism is described by the dynamic detergency model. It can transport substances, after they have been released from the solid surface into the solution, at a rate which is faster than diffusion by an order of magnitude. The presence of surfactants gives a better detergency because it speeds up the laundering rate to an acceptable level. The DDM-mechanism involves the disturbance of the adsorption equilibrium and a Marangoni flow in the dense, yet mobile layer of surfactant molecules at the textile/solution interface as a consequence. The disturbance in the surface is created by friction forces. Detergency is the interplay of the surfactant properties in the washing liquid with another Sinner factor: the mechanical action which stretches and bends the yarns of the textile and creates a liquid flow in the narrow pores of the solid fabric.

The Dynamic Detergency Model

The Dynamic Detergency Model (DDM) [4] postulates that soil removal is mainly due to the dynamic non-equilibrium situation at the surfactant-textile interface. From a micellar solution surfactant will adsorb as a continuous bilayer (admicelle) at all the pore surfaces in the textile. The molecules in this admicelle are mobile. Its density and viscosity depend on the surfactant and it lubricates the friction forces in the flow of the liquid which is forced through the pores. The forces, which drive this flow, are the effect of the deformations of yarns and pores by the mechanical action during the laundering.

Inside the narrow pores the adsorbed molecules of the liquid-like admicelle slip over the surface as a two dimensional flow of concentrated surfactant. This flow of surfactant carries all the material with it that has been extracted into the admicelle. Because there is slip relative to the solid surface, the transport barrier from the solid into the flowing solvent (i.e. the adsorbed surfactant of the admicelle) is reduced to one layer of surfactant molecules. Any particle that finds its way through this monomolecular layer will be carried along in the flowing admicelle and is eventually transported into the solution by micelles.

If some larger, colloidal, particle should adhere and obstruct the flow in the admicelle this will cause a concentration gradient, with smaller surface coverage downstream from the particle. The effect of this gradient is a Marangoni force on the particle. This is the extra force which can overcome the attraction between the particle and the surface. The particle is rolled away from the surface by it and carried away in the flow of the slipping liquid.

The flow of surfactant in the admicelle creates local gradients in surface coverage wherever the friction of the flow changes. Not only at obstructions but also where the channel widens. Local supersaturation of the surface with the inflowing surfactant will develop there. Relaxation to equilibrium in such a spot is by the creation of new micelles which detach from the admicelle. These are the transport vehicles which carry the soil material from the admicelle into the solution. And to repair the lower surface coverage in narrower spots, the fresh micelles of the detergent solution act as a reservoir. They replenish surfactant wherever it is needed, by demicellization and adsorption. These coupled processes must be fast enough to keep the flow in the admicelle going. Their combined effect is what is also detected in measurements of the dynamic surface tension. Such experiments reveal that the rate limitation in detergency is in the detergent solution. It could be in the slow diffusion which has already been described, but also in the rate of adsorption in the admicelle or the de- and re-micellization processes which must keep the quick mass transfer in the textile pores going. But not because of the stagnant liquid in the diffusion boundary layer.

Kinetics of De- and Re- Micellization

Micelles are a system in dynamic equilibrium where two processes of micellar relaxation can take place. The first is the exchange between micelles and the single monomers in the solution. This is a very fast equilibrium, with a relaxation time τ_1 of the order of microseconds. The other is a slower process, with a relaxation time τ_2 between milliseconds and minutes. It is associated with a micelle formation-dissolution equilibrium when the ambient surfactant concentration is suddenly altered [29, 30].

Micellar relaxation times τ_2, associated with the formation and break-up of micelles play an important role in many technological processes. Strong correlation with τ_2 has been found for foam formation, wetting time of textiles, bubble volumes, solubilization in micellar solutions and other dynamic processes which involve surfactants. In general: as extra monomers are needed to equilibrate newly created surfaces, micelles have to break-up. The additional monomers which are needed to replenish the surface must be given up by the surplus of surfactant that is stored in the micelles of the solution.

For very stable micelles, high τ_2, it will not be easy to augment the flux into a newly created surface instantaneously. As a consequence, the performance of a number of dynamic processes will be affected: less foamability is expected, higher interfacial tension in emulsification and longer textile wetting times [30].

In their paper, Patist *et al.* [30] have studied some techniques to adapt τ_2 for specific applications. They demonstrated that τ_2 for SDS in water can greatly be enhanced by adding long chain alcohols. Increasing the degree of ethoxylation leads to shorter τ_2 in aqueous solutions of nonionic surfactants. In the same line, Pandey *et al.* [31] proved that oppositely charged surface active molecules give enhanced stability of micelles by increasing the attraction energy between polar groups. They also showed that film rigidity, and thus stability, can be modulated by the chain lengths of the two oppositely charged surfactant. The highest rigidity is obtained when the two surfactants have the same length.

In our case we need detergents in a solvent other than water. It is the solubility of each moiety of the molecule in the solvent rather than the charge of the hydrophilic head groups what distinguishes one surfactant from another. Still, surfactants can be seen as molecules built from a lyophilic skeleton to which lyophobic structures are attached. The balance between the lyophilic and lyophobic moiety of the surfactant is relevant for the geometry of the aggregates and will determine its scope of application. The factors which determine the effectiveness of a surfactant as a detergent are the characteristic surface concentration in the admicelle and the characteristic timescales for the dynamics at the surface. These differ for individual surfactants in every solvent.

Detergency in New Media

According to the DDM the mass transfer is considerably enhanced by the presence of well chosen surfactants. Diffusion through a boundary layer of many micrometers is eliminated as the rate limiting step in the mass transfer. The model bridges the gap between the experimental observations and the theory by adding the notion that the Sinner factors chemistry and mechanical action do not act separately, but synergy between them at a given temperature determines the time and effectiveness of the laundering process [4].

The essential aspects of the model, slip along the surface in the pores, a steady state of re- and de-micellization, surfactant flow in the admicelle and, mass transfer at supersaturated spots should be general features in all detergents. Although most of the research in this area has been done in aqueous systems, the fundamentals of the DDM are independent of the solvent. The physical chemistry of detergents should, in principle, be applicable in any solvent. But the detergency in a given medium with a wide choice of surfactants will always be determined by the structure of the different surfactant molecules and their interaction with the solvent.

Designing a detergent for dense CO_2-solutions implies defining such a chemical structure. The success of such a design could, indeed, have important consequences, and not for dry-cleaning alone. Many other processes than laundering with new solvents involve mass transfer rates and could be analyzed according to the DDM. This could, for instance, be used to improve the detergency of the additives in lubricant oils for combustion engines along the same lines as in our project. The novel approach of designing a specific detergent for dry-cleaning with dense CO_2 could create a first in a class of improved mass transfer processes, involving the dynamics of surfactant micelles and admicelles in liquids that flow over solid surfaces.

Chapter 3

Design of a Detergent for Dry-Cleaning in Liquid CO_2

Design Methodology

Engineering science has developed a specific methodological pathway for the design of a chemical product [32, 33]. We have used this procedure (see Fig. 3.1) quite successfully for designing a detergent that can be used for dry-cleaning in liquid CO_2.

The starting point for design activities will always be that there is a problem. This problem may be felt by industrial marketing managers or e.g by a government agency. It is a latent need, for which a technical solution is desired. In our own case there was a need to introduce liquid CO_2, somehow, as an alternative for Perc in the dry-cleaning industry. The first action of a designer (e.g. a chemical engineer) or of a design team is then, to translate these vaguely described wishes into quantitative technical terms. This generates a list of explicit technical criteria, which must be implicit in any solution for the problem.

In our case it was perfectly clear that dry-cleaning in CO_2 was impossible without a detergent. Some product had to be invented for such applications. The criteria for acceptable detergency with our solvent define target specifications (the "deliverables") for the new additive that must be designed, which is not yet defined itself as a chemical compound or formulation at this stage.

A process called "synthesis" is the next phase of the design activity (see Fig. 3.1). It is the most creative phase in the procedure. The project team investigates the

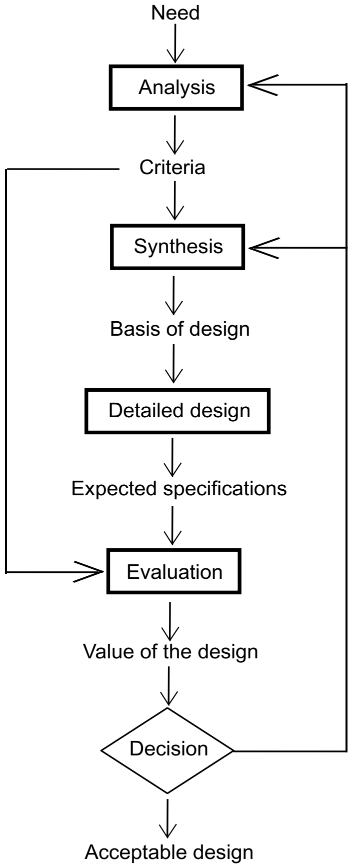


Figure 3.1: The Basic Cycle of Design.

literature around the problem, or, more to the point, the ideas of producers and of users in the pertinent industry (which we did describe in the first two chapters of this thesis). These intelligence results and knowledge are used by the team in creative methods like "brainstorming" to generate a number of proposals for the new product. Each proposal describes one possible solution that could meet the criteria for such a detergent.

The list of creative ideas must then be critically evaluated. The team has to select only one of them - and hopefully the most promising idea - for a Basis of Design (BOD). The real BOD for the project is, in fact, a document. It contains all the original proposals and gives all the objective and subjective arguments why the team (i.e. this particular team) has chosen a particular idea as the result of the selection process. The BOD is communicated to all the parties in the project. After it has been modified and accepted by the project managers and the design team, it becomes the basis for all the design activities which follow. After that the BOD can not be altered in the course of the process, neither by the designers, nor by the managers. It serves as a frame of reference during the project. Of course, it can be necessary or attractive to deviate from the original ideas, but such decisions have to be reported against the background of the original BOD, and validated before they can be made effective as part of the design.

A BOD for a chemical product like a detergent will, generally, describe classes of chemicals which shall be put together in a "formulation" of the product. For a detergent such a formulation might consist of one species out of a selected class of surfactants (e.g. the anionic amphiphiles), one solvent (like Perc or water) and possibly also cosolvents (alcohol), and enzyme (protease), and a complexant like TAED to bind Ca - ions.

Molecular compositions of these ingredients and their optimum percentages in the formulation must be established in the phases of the design process after the BOD. The result will be a "Detailed Design" or "Conceptual Product Design" (CPD), which is, again, a document that describes the product and its properties in a prescribed format. This is a period of fact finding. In laboratory experiments, in market analysis and other economic evaluations and in theoretical considerations about chemical and toxicological properties (if the BOD specifies new, yet unknown, chemicals). In this phase of the project unexpected cross-effects between components of the formulation and new theories about the properties of the product will come to the fore. New insights about such, yet uncharted, effects can have considerable impact on the directions which a design process may take.

What we shall report about designing detergents for liquid CO_2 in the next three chapters is an adapted description of this kind of work. Eventually, the design team will come up with its CPD. This report addresses the scientific, the technical and the economic [16] aspects which are considered relevant for the evaluation of the result. For evaluation, the performance of the product must also be tested in experiments and compared with the original target specifications. This experimental evaluation of the product as a detergent is described in Chapter 6 of this thesis. An outcome of the evaluations, which fails to meet the original target specifications of the BOD would call for a complete reiteration of the Design Cycle (see Fig. 3.1). If, on the other hand the conceptual design has produced the target deliverables, the CPD document can become the basis for further industrial developments, logistics and so on which must follow to bring the new product to the market.

Target Criteria for a Detergent in Liquid CO_2

Our design for a detergent that is effective in liquid CO_2 will be based on the DDM-model. This model has been described in Chapter 2. The detergent must be soluble in the extremely apolar solvent. It must be a surfactant which does adsorb at interfaces between the solvent and the textile fibers. We note that these fibers are, generally, more polar than the solvent itself.

Therefore, the detergent molecules must be amphiphilic. The carbophilic moiety (or head group) would, as a molecule, be miscible with the solvent in all proportions. Chemically attached to the head group of the molecules is a carbophobic, more polar, moiety. It reduces the solubility of the surfactant but makes it surface-active for adsorption at the more polar surface of the textile fibers. A surfactant with a more polar part as the carbophobic tail of the molecule, like specified here, will not adsorb at the solvent/vapour interface, because the gas phase is even less polar than the solvent itself.

According to the DDM the amphiphilic detergent molecules must form micelles in the solvent and densely packed, continuous admicelles at the interface in the pores of the textile. The surfactant molecules in these associated structures are mobile and flow away when mechanical forces are applied. The inner parts of these self assembled micelles and admicelles must be carbophobic and much more polar than the solvent. These polar parts of the admicelles and of the micelles must also be somewhat hydrophilic to take up some water from the textile and dissolve it in the micelles as a cosolvent.

Under laundering conditions the detergent must be present in solution concentrations (either as monomers or as micelles) which allow surfactant diffusion rates to keep up with the flow of concentrated surfactant in the admicelle. Preferably, this places the c.m.c in this solvent in the same range as those for effective detergents in other media, like water. A ballpark estimate of the target c.m.c would then be of the order of 1 mM/l. With size and molecular mass of the detergent molecules like in usual detergents this gives optimum detergent concentration in the washing fluid at about 0.1 wt%.

At the operating temperature of the dry-cleaning process (i.e. "room temprature") the overall solubility of the detergent in liquid CO_2 must exceed the c.m.c. This is to ensure that enough surfactant can be added in the washing liquid for the formation of complete dense admicelles in the textile pores and for the replenishing of these admicelles when their adsorption equilibrium is disturbed by the mechanical action of the washing process.

Another requirement of the model is the mobility of the detergent molecules in concentrated systems like an admicellar layer. It is not favorable for the mobility when the carbophobic moieties would tend to form hydrogen bonds and crystallize from concentrated solutions in liquid CO_2, as would undoubtedly occur with carbohydrates and amino compounds. Neither should the carbophobic moieties be too hydrophilic, like poly-alcohols are. Textiles are polar materials and contain a percentage of water. If the cores of micelles and admicelles are too hydrophilic, water absorption will stabilize the micelles. This creates difficulties for the relaxation rates which may then become rate limiting.

The target properties delineate several classes of chemicals which could be good detergents in liquid CO_2. The best detergent is expected to give a comparable dry-cleaning result as with Perc. This technological evaluation of the detergent is deferred to Chapter 6. First we shall follow the Delft design methodology, investigate classes of promising compounds and research the physical chemistry of their solubility and phase behavior (Chapter 3), aggregation (Chapter 4) and surfactant properties (Chapter 5). For the BOD we shall select a surfactant, which does, at least theoretically, meet the DDM criteria for detergency in liquid CO_2. The bandwidth of properties within homologous series of chemicals will allow fine tuning of the proposed detergent during the evaluation of laundering properties which follows. Side effects, technological as well as economical factors must be considered at that stage, to eventually generate the detailed design of a detergent for dry-cleaning in liquid CO_2.

Solubility in Liquid CO_2

High density CO_2 as a Solvent

Dense CO_2, either liquid or supercritical, is a very non-polar solvent. As a near critical liquid under our operating conditions, this solvent has properties like its density and viscosity, which are tunable with pressure. Near the critical state, kinetic properties like diffusion coefficients can vary between those in a dense gas and in a liquid. For applications of such a solvent it is important to compare these properties with those of other substances (see Table 3.1). The solvent properties of dense CO_2 are not intrinsically different above and below the critical conditions. Most technological investigations on the application of such a solvent have been conducted in the supercritical region. Interesting and technically useful temperatures, pressures and solubility levels in CO_2 are found around the critical conditions ($P_c = 73.1$ bar;

Table 3.1: Properties of gases, liquids and Supercritical fluids

	Density (kg/m^3)	Viscosity (mPa.s)	Diffusion coef. (m^2/s)
Typical gas	1	0.02	0.1
Supercritical Fluid	**300-800**	**0.03-0.1**	$\mathbf{10^{-8}}$
Liquid	1000	1	10^{-9}

$T_c = 31\,°C$) [34].

A qualitative estimate of solubilities in liquid CO_2 can be obtained with at least four different criteria. These same criteria should also allow predictions about the carbophobic or carbophilic character of moieties inside a molecule. Estimates can be based on calculating *solubility parameters*, on *hard and soft acid/base properties*, on the relation between mixing entropies and *glass transitions temperatures* for substances with flexible molecules and on macroscopic considerations like the *dielectric properties* or the *polarizability* of the molecules.

a. Dielectric constant and polarizability

Dense CO_2 has a very low dielectric constant ϵ and polarizability per volume α/ν. It is, therefore, a poor solvent. Not only for electrolytes, but also for most other nonvolatile lipophilic and hydrophilic solutes. Linear alkanes like pentane and hexane are miscible with the solvent in all proportions. These molecules can be considered carbophilic, but the miscibility decreases for the higher alkanes. Compounds with smaller polarizability α/ν than the lower alkanes, e.g. fluorocarbons, are more soluble in dense CO_2 than hydrocarbons [35, 36]. In fact, the work of Hyatt [34] suggests that the polarizabilities per volume of liquid CO_2 and supercritical CO_2 are even lower than those of fluorocarbons. Therefore dense (but still compressible) near critical CO_2 can be considered as a solvent which bridges the gap in polarizability between the liquid fluorocarbons and a rarefied gas phase.

There is a link between these phenomenological observations and solubility parameters of molecular substances. Da Rocha *et al.* [35] has also pointed out that, due to the low value of ϵ and α/ν for CO_2, really carbophilic functional groups like fluorocarbons, fluoroethers, and siloxanes will automatically obtain low c's and thus low δ's in the terminology of the solubility parameters.

b. Glass transition temperatures

Fink et al. [37] and Sarbu *et al.* [38] have observed that for a compound to be soluble in CO_2, the free energy of mixing must be negative. Flexible chains in a molecule favor the mixing, due to their larger entropy of mixing. Solvation of these chains by solvent molecules stiffens a long chain molecule, but because of the small interactions of solute molecules with CO_2 this effect will be all but absent in dense CO_2. Polymers and oligomeric moieties with highly flexible chains will often exhibit relatively low glass transition temperatures T_g. Hence, a low T_g is indicative for chain flexibility in polypeptides, polyethers and the like. This offers a criterion by which their solubility in dense CO_2 can be estimated. Especially, carbophilic fluorinated compounds can be ranked in order of their relatively low T_g's. Again, a low T_g is also associated with low c and thus with low δ in terms of solubility parameters.

c. Solubility parameters

Hildebrand's original theory of solubility parameters is an application of regular solution theories. It states that two substances will be miscible when their solubility parameters δ match. This solubility parameter δ is defined as

$$\delta = \sqrt{c}, \tag{3.1}$$

where δ is in $(\mathrm{MPa})^{1/2}$ and c, the cohesive energy density, in (KPa).

The cohesive energy density in a substance is a measure of intermolecular interaction. In this version of the theory it is assumed that interaction of two molecules with equal δ is equal to the interaction between two molecules of the solvent or of the solute. Therefore they form ideal solutions, or at least regular solutions when the interaction energies do not differ very much. Differences in solubility parameters cause a reduced solubility of a solute in a solvent.

This very crude model has been made more subtle by introducing additional (empirical) parameters. These should take account of different types of molecular interaction contributing to the cohesion energy. But for our problem of very nonpolar solvents and substances, like dense CO_2 and the molecules which can dissolve in it, one could think of van der Waals forces as the only interaction between the molecules. In that case the original Hildebrand approach could rank the carbophilic or carbophobic character of different solutes.

The solubility parameter δ for CO_2 at normal pressure is 12.3 $\mathrm{MPa}^{1/2}$ and increases with the density of the liquid (i.e. with the pressure). For short n-alkanes, typically between C_5 - C_{12}, δ varies from 14.4 to 16.2 $MPa^{1/2}$ [39]. Therefore C_5 to C_{12} moieties and molecules should be carbophilic and dissolve in CO_2 as a regular solution. This is also found experimentally: according to Francis [40] n-alkanes from C_2 to C_{13} do dissolve in liquid CO_2.

Based on δ, we would expect that many substances which dissolve in short n-alkanes would also dissolve in dense CO_2. However, experiments have shown the contrary. According to Harrison *et al.*[41], the explanation is that 20% of the solubility parameter of CO_2 should be attributed to the quadrupole interactions with the solute. The non-polar (dispersion) component of δ, δ_d, for CO_2 is then considerable less than for n-alkanes. Similarly, δ is smaller for perfluorohexane and perfluorononane than for n-alkanes: 11.5 and 11.7 $MPa^{1/2}$ respectively. Therefore, fluoroalkanes in dense CO_2 form more ideal solutions than alkanes, which is indeed found experimentally.

d. Hard and Soft Acids and Bases (HSAB)

The HSAB approach, due to Orchin *et al.* [42], is a qualitative ranking of the acidities and basicities for Lewis acids and bases. In this method molecules are classified hard, soft or borderline Lewis acids c.q. - bases, depending on a combination of electron donating/accepting properties and polarizability. The principle is shown in Table 3.2.

Table 3.2: HSAB classification

Polarizability	**Electron donating**	**Electron accepting**
Low	Hard base	Hard acid
High	Soft base	Soft acid

In general, hard acids prefer to combine (i.e. dissolve) with hard bases, whereas soft acids prefer to interact with soft bases. This principle allows the HSAB classification to be used as a tool for predicting affinities and favorable interactions between solvent and solute molecules. In Table 3.3 some Lewis acids and bases have been ranked in the HSAB. In this ranking table the strength of hard acids and bases decreases from the top down. CO_2, at the bottom position for hard acids, is only moderately hard. The best solute/solvent interaction are expected with moderately hard bases. Softer bases will be less favorable solutes and soft acids even less. A ranking of relevant molecules and groups can be made (see Table 3.3) for increasingly favorable interactions with CO_2:

Table 3.3: HSAB ranking of acids and bases

Acids		**Bases**	
Hard	**Soft**	**Hard**	**Soft**
H^+, Li^+, Na^+	Cu^+, Ag^+, Au^+	H_2O	R_2S
Mg^{2+}, Mn^{2+}	Pd^{2+}, Pt^{2+}	HO^-	RS^-
Al^{3+}, Sc^{3+}	Ti^{3+}, $Ti(CH_3)_3$	F^-	CN^-
Cr^{3+}, Co^{3+}	RS^+	AcO^-	C_2H_4
Si^{4+}, Ti^{4+}	I^+, Br^+	ROH	C_6H_6
BF_3, $B(OR)_3$	BH_3	R_2O	H^-
RSO_2, SO_3	I_2, Br_2	RO^-	R^-
RCO^+, CO_2		RNH_2	C=O

- Aliphatic hydrocarbons (soft bases)
- Aromatic hydrocarbons (soft bases)
- Carbonyl (soft base)
- Water (hard base)
- Alcohols, ROH (hard base)
- Ethers, R_2O (hard bases)
- Fluoride (moderately hard base)
- Amines, RNH_2 (moderately hard base)

Ions like Na+, K+, Cl- or I- will not dissolve in dense CO_2, and the presence of a sulfonic acid group in a molecule, like in many industrial surfactants, would have a moderately detrimental effect on the solubility in dense CO_2. Fluorinated hydrocarbons and dense CO_2 appear as rather compatible substances. An interesting peculiarity in this classification is the relatively strong interaction of dense CO_2 with water, as opposed to hydrocarbons.

The parameters δ, T_g, ϵ and α/ν are somehow related. A molecule with low values for each of those parameters should exhibit appreciable solubility in dense CO_2. In combination with the HSAB criteria rather accurate information is available to estimate solubilities of substances and the carbophobic/carbophilic character of groups and moieties in molecules. This is a starting point for the selection of potentially suitable surfactants in liquid CO_2.

Surfactant Selection

Surfactans are amphiphilic molecules. In dense CO_2 these molecules must consist of a carbophilic and a carbophobic part. The list of conventional surfactants that are insoluble in dense CO_2 is impressive [43]. This came as a shock and great desillusion for engineers who sought to simply replace Perc with dense CO_2 and rely on existing surfactant formulations for optimum detergency. But from the standpoint of physical chemistry the lack of solubility was not at all surprising, as was discussed in the previous paragraph.

A surface active substance must always be sparingly soluble to begin with, because of its amphiphilic molecular structure. And most existing detergents for dry-cleaning rely on surfactants which were originally developed for applications in water. These molecules have indeed a lyophobic and a lyophilic moiety as a mirror image of the affinity to water as a solvent. And in solvents like Perc they will form "inverse" micelles. In liquid CO_2 a surfactant molecule must have a carbophilic head group to start with. That group must fit into the dense outside region of the self-assembled micelles in the solvent and of adsorbed admicelles at more polar interfaces. In the amphiphilic molecules carbophobic structures must be chemically attached to the carbophilic head group. These make the molecule so incompatible with the solvent that it becomes sparingly soluble, surface active and prone to micellization. The carbophobic parts of the molecules must fit into the core of a micelle, inside a closed shell of head groups. The core properties of such a micelle are an essential aspect of detergency, for the micellar core is the carrier of the insoluble soils in a washing fluid.

In a design of a detergent we will attempt an *imaginary surfactant building procedure.* The solubility of each moiety in the solvent and its effects on the solubility of the surfactant, the adsorption at interfaces and the formation of micelles will be the basis. Successively binding larger and larger lyophobic groups to the lyophilic head group must then enhance or reduce these effects. The result of the tinkering can be checked empirically, in experiments with homologous series of amphiphilic molecules in dense CO_2.

The Carbophilic Moiety as a Starting Point for the Design of a Detergent Molecule

Hydrocarbons up to C_{12} are soluble in liquid CO_2. Therefore, they can serve as the carbophilic moiety, head group, around which a surfactant molecule can be built up. Fluorides and siloxanes are also carbophilic, and thus fluorocarbons and silicones could be good alternatives as the head group. Surfactants based on fluorocarbons and silicone head groups have been proposed for application in liquid CO_2 by De Simone and Johnston in the USA. Unfortunately, these carbophilic groups have some serious disadvantages, technologically, economically and toxicologically. Fluorocarbons are environmentally toxic. This makes them incompatible with the development of a green dry-cleaning process. The need was to replace the technologically attractive Perc-technology for environmental reasons. Silicones, on the other hand, will adsorb very strongly onto textiles surfaces. They are sometimes used as fabric softeners for that reason. But this creates a problem for the dynamics of soils removal and flushing after dry-cleaning. Finally, both chemicals are very expensive. This makes them unattractive from an economical viewpoint. Therefore, we selected hydrocarbons as the most promising carbophilic head groups in the design of our detergent molecule.

Linear alkanes show good solubility in liquid CO_2 and branched hydrocarbons are comparable, or even better. Branched chains are more compact than linear chains in the same (good) solvent. Therefore the volume of the head group is, in principle, adaptable. It can be made to fit optimally into a micellar geometry for the surfactant which holds all the carbophobic material in the core volume.

Attaching two carbophilic groups instead of one long chain, e.g two linear but smaller hydrocarbons, to a carbophobic moiety is an alternative. Such structures could be favorable for packing more individual surfactant molecules into a micelle. But this bidentate or tandem type of surfactant gives more stable micelles, i.e. with a higher τ_2. This slows down the rate of (de-) micellization. Moreover, the bidentate structure is more difficult to fit into a dense admicelle. According to the DDM a dense admicelle is a necessary condition for detergency. The performance of a detergent will depend on the characteristic micellization time τ_2 and mobility in the surfactant film along the S/L interface. For those reasons, molecules with two carbophilic head groups are not preferred in our DDM-based design. The starting point in the BOD will be the linear hydrocarbon chain as the carbophilic head group for the detergent.

Adding the Carbophobic Moiety

The number of insoluble compounds in liquid CO_2 is vast and diverse. Therefore, no problems are anticipated in the selection of a fitting carbophobic tail for the detergent molecule. Unfortunately, that is an oversimplification. The carbophobic tail of the amphipilic molecule determines the solubility and the surface activity. The solubilization capability depends on the number of carbophobic tails in the core of the micelle, which have segregated as a drop of polar solvent of colloidal size. And in this highly concentrated region there must be no tendency for crystallization of the micellar core into a solid particle. The selection of an appropriate carbophobic moiety is relevant for the detergency in the liquid CO_2 solvent.

Ionizing groups in the micellar cores would be certainly desirable for the solubilization of water and, indeed, many water soluble compounds like calcium ions. However, ions are extremely insoluble in liquid CO_2. Attaching a tail with ionisable groups would make every surfactant monomer insoluble. Moreover, insufficient screening of the polar groups would oppose and even prevent spontaneous formation of micelles in pure dense CO_2. It has been demonstrated that the formation of "inverse micelles" (i.e. of micelles which are hydrophilic inside, inverse from the situation in water) is promoted by adding extra water, as a cosolvent, in an ionisable system. But those micelles are too stable again and there is no adequate detergency.

The use of two (branched) linear carbophilic moieties per molecule can compensate repulsive interaction between ionised groups in the core of the micelles. "Inverted" micelles are formed spontaneously [44] with that type of surfactant. However, as we have just mentioned, bidentate surfactants are not suitable for detergency purposes. Consequently, most existing ionic and cationic surfactants, even those that may give micelles in liquid CO_2 with the help of a cosurfactant, must be eliminated from the list of potentially good detergents for liquid CO_2.

The choice of useful carbophobic tails is then reduced to polar nonionic groups. Attaching a methanol group (-CH-OH) to the carbophilic head group reduces its solubility. Successive attaching of more hydroxyls (glycol, glycerol, erythritol, etc.) until the molecule reaches the right size and solubility for a detergent would end in a carbophobic moiety of a similar structure as a hexose sugar. In fact, attaching hexane to glucose would be a realistic option for a surfactant in dense CO_2. But we had to decide against this alternative. The hydroxyls would form hydrogen bonds in the micellar core and increase the enthalpy of micelle formation. With glucose and similar molecules as the micellar core, the surfactant would tend to crystallize like syrup. Crystallization kills the kinetics of the DDM. Rigid and/or highly viscous structures are formed in the admicelle layers so that there is no mobility of individual surfactant molecules. And without mobility there will be no lubricated slip and no detergency. Since mobility in the admicelle is the decisive aspect in detergency, sugar based surfactants have to be stricken from the list of suitable detergents in liquid CO_2.

Other carbophobic tail groups, like oligomers of poly-vinyl alcohol (PVA), amines and ketones have also been considered. But, like the ionisable electrolyte groups, these moieties were too hydrophilic for the tails. They extract water from the textiles and the solvent. This does stabilize the surfactant micelles but is detrimental for the dynamics behind optimum detergency.

Eventually, we selected another classical non-ionic class of surfactants, n-alkanes with attached oligomeric ethylene/propylene-glycol ethers for our detergent design. Neither monomer in the carbophobic tail is completely miscible in liquid CO_2 [40]. The solubility of ethylene-glycol is less than half that of propylene-glycol and poly ethylene-glycol is also more hydrophilic. In this class of compounds relevant properties of the surfactant molecule, like its HLB - value, can be adjusted to some extent by using copolymers in the carbophobic tail. In a tailored detergent, successively building up the molecule, its solubility and surface-active properties can be optimized by the number of ether bonds in the tail (E_j) relative to the number of methylene groups (C_i) in the head group. A shorthand description of this class of surfactants is the formula C_iE_j.

The (bulky) size of the carbophilic alkane chains, relative to the length of the flexible carbophobic polyether tails is another factor which can be adjusted. In this way the molecules obtain the best geometrical shape for filling the core space and the outer shell in a spherical micelle. The synthesis procedure of specific C_iE_j molecules allows optimization of detergent properties for application like dry-cleaning. It is, therefore, possible to select the best surfactants from the class of C_iE_j compounds and adjusting their relevant molecular parameters to the demands of the DDM model.

Basis of Design

After assembling an imaginary surfactant molecule from carbophilic and carbophobic moieties we had to reject existing, commercially available surfactants (and among them all "ionic" surfactants) for the application of dry-cleaning in liquid CO_2. As a Basis of Design for the detergent we did select the group of polyoxyethylene / polypropy leneether - alkane surfactants with general formula $[C_iH_{2i+1} - (O - CH_2 - CH_2)_j - OH]$. This class of surfactants, generally known as C_iE_j, contains promising candidates, because the molecular properties can be adjusted to optimum values for the theoretical detergency requirements in a given solvent.

The amphiphilic character (i.e. the HLB - value) of those C_iE_j molecules is the consequence of selected sizes and shapes of the carbophilic (linear hydrocarbon) and carbophobic (ethylene oxide) moieties. The polar nature of ethylene oxide, paired with the non-polar carbophilic alkane chain, favors adsorption from liquid CO_2 on (more polar) textile materials. C_iE_j molecules would be good detergents in liquid CO_2 provided that their solubility, their micellization rates in the solvent and their mobility in adsorbed layers meet the functional requirements in the DDM - model. It can be determined experimentally, in the laboratory and in the technological dry-cleaning tests, which particular C_iE_j compound fits into the target specifications for a detergent in dense CO_2.

Chapter 4

C_iE_j solutions in liquid CO_2

Solubility and Phase Behavior

A surfactant is always a sparingly soluble compound. It is only because of micellization that enough surfactant can be stored in a solvent for application like laundering and dry-cleaning. And it is essential for these applications that the surfactant will remain in the liquid state - instead of precipitating as crystalline material - under the conditions of a laundering process. The requirement of non-crystalline mobility of the detergent molecules also applies inside the very concentrated cores and shells of micelles and admicelles, which participate in adsorption and phase equilibria throughout the system.

Dense CO_2 is a peculiar solvent. Near the critical point densities of solvents vary strongly with temperature and with pressure. And the surface tensions vanish as the system approaches the critical state. This affects the interaction energies and entropies of the solvent with a solute - a characteristic which is successfully exploited in extraction and crystallization near the critical point. It will then depend on the temperature and the pressure wether a solute molecule, or even a part of such a molecule like the head or the tail moiety in a surfactant, should be considered carbophobic or carbophilic. That liquid CO_2 seems attractive for the innovation of the dry-cleaning industry is, at least partly, because its critical temperature and pressure at the moderate values of $T_c = 304\,\mathrm{K}$ and $P_c = 73.1\,\mathrm{bar}$ respectively. Solubility, surface activity, micellization and other relevant properties for detergency will be a function of the industrial conditions. To set and optimize process specifications for dry-cleaning detergents we need data about solubility and phase behavior in specific C_iE_j - detergent solutions with liquid CO_2 at technologically relevant pressures and temperatures.

Cailletet Experiments

We measured solubility characteristics of C_iE_j - compounds in liquid CO_2 at different temperatures, pressures and concentrations in a Cailletet experiment. The apparatus allowed pressures up to 120 bar, which is far above the critical pressure for the solvent. By visual observation of phase transitions in mixtures of a known, constant overall composition it was possible to determine the regions in a phase diagram where the surfactant is soluble in liquid CO_2.

In order to prepare the sample, the Cailletet tube is weighed and then the C_iE_j - sample is introduced, which was a liquid at room temperature. The required concentration X (in wt%) of the solution is obtained by adjusting the pressure at which a constant volume of CO_2 gas, 99.9% purity, from Aga Gas, was injected into the tube. The moles of CO_2 are calculated with the equation of state of a perfect gas (with R as a constant and P, V and T known for the experiment).

The filled Cailletet tube is placed in an alcohol bath, which allows to control the temperature. At this temperature the pressure is increased (via the mercury column which seals the tube) until the CO_2 is liquified. The pressure is controlled with the help of a pressure balance. An scheme of the equipment is presented in Fig. 4.1.

For the determination of the phase transitions a constant temperature is ensured

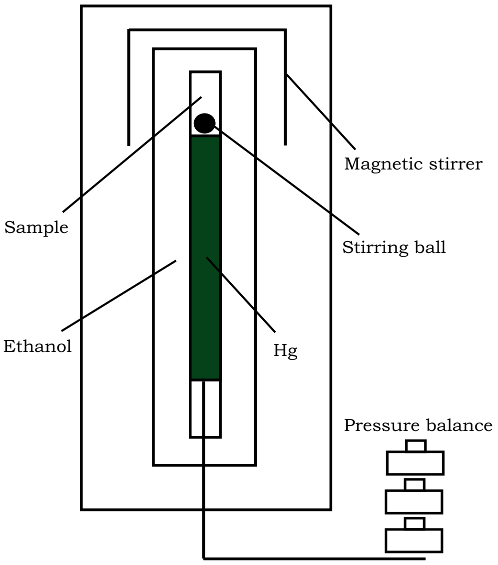


Figure 4.1: Cailletet apparatus.

first. The mixture is then gradually compressed and this change in conditions induces the phase transition. The observation of the transition is visual. It is important to notice that the phase transitions were determined in such a way, that one of the phases is vanishing (and not forming). Increasing the pressure changes the solvent properties and nucleation problems of a new phase are avoided by registration of the pressure at which a phase disappears. After inducing a phase transition the system is decompressed and separates again into two different phases. The same mixture is then compressed again in smaller pressure intervals. This procedure is repeated until the conditions for phase transition have been determined within the smallest accessible interval for the Cailletet apparatus. Thereafter, another temperature is set and the whole procedure is repeated. The measurements were done for different solution concentrations in the temperature range between 276 K and 293 K.

Results

The P-T phase diagrams for all the measured surfactants have one, characteristic form (see Fig. 4.2). At low pressures, the CO_2 is a gas at these temperatures. The system consists of a liquid (the surfactant) and the surrounding CO_2 - rich vapor phase. At

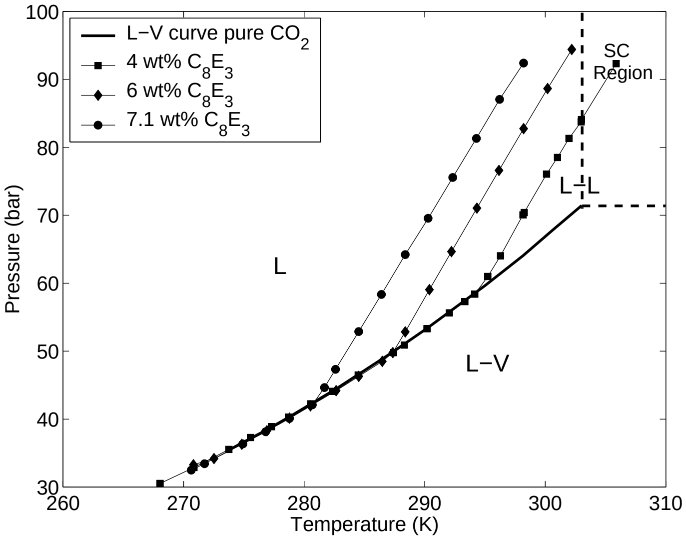


Figure 4.2: P-T phase diagram of C_8E_3 in liquid CO_2 for three different concentrations. The different phases: L-V, L and L-L are also shown. Increasing the concentration, the L-L curve shift to lower temperatures.

lower temperatures the CO_2 becomes a liquid solvent upon compression and the surfactant dissolves completely in a single liquid phase. Under those conditions and with low concentrations the surfactant is fully miscible in the solvent. However, at higher temperatures the solubility of the carbophobic and the carbophilic parts in the surfactant molecules changes and a second phase exists at these same pessures. In this part of the phase diagram the system separates into two liquid phases, one rich in surfactant and the other much less concentrated. The density of the surfactant rich phase is not very different from that of the solution, but optically the two phases are very different. This suggests that the surfactant - rich phase is a lyotropic, birefringent liquid crystal and contains elongated surfactant micelles.

C_iE_j compounds with different (i) and (j) were obtained from Sigma and from Kreussler (Chemische Fabrik Kreussler & Co. GmbH, Wiesbaden, Germany) respectively. We used two different (laboratory and industrial) qualities of these surfactants. The main difference between the laboratory and the industrial sample is in the industrial ethoxylation process. This produces the C_iE_j compounds with a considerable spread in the number (j) of ethylene oxide groups. Without further separation, the industrial product is a mixture of molecules with larger and smaller ethyleneglycolethers oligomers. The number (j) is some average value. This variation in the length of the carbophobic tails can have considerable consequences for the solubility, the surface activity and the micellization of the different surfactant fractions in the solution. The compounds used in this study are listed in Table 4.1.

Table 4.1: C_iE_j surfactants studied

Product	**Source**
C_6E_3	Kreussler
C_8E_3	Sigma, Kreussler
$C_{11}E_3$	Kreussler
C_8E_4	Kreussler
$C_{12}E_4$ (Brij 30)	Sigma
C_6E_5	Sigma, Kreussler
C_8E_5	Sigma, Kreussler
$C_{12}E_5$	Sigma
C_8E_6	Kreussler
$C_{12}E_9$	Sigma

With all the surfactants, upon increasing concentration, the L-L curve shifts to lower temperatures (see Fig. 4.2). The one-phase solution is thus reduced in pressure and in temperature at higher concentrations. This is analogous with nonionic surfactants solutions in water (see Fig. 1.3). An analogous shift of the L-L curve, which is the boundary for the two phase region, is observed when either the length of the hydrocarbon tail (C_i) or the number of ethylene oxide groups (E_j) is increased.

It is important to notice that the phase behavior in the supercritical region (P≥ 73.1 bar, T≥ 304 K) does not change at all. The L-L curve does not experience any change in slope or discontinuity when the solvent enters the supercritical region. This observation validates our first guess: the phase transition in this system is dictated by the surfactant. It is the interaction between the surfactant molecules (and not with the solvent) or surfactant self assembly what drives the phase transitions. Consequently, each point on the L-L curve corresponds to the CP of the solution for a given set of conditions (P, T).

Very many experimental results are summarized in Table 4.2. The maximum miscibility of all the measured compounds, Kreussler (K) and Sigma (S), is given for the operating conditions in liquid CO_2.

Table 4.2: C_iE_j maximum miscibility ($P = 50 - 65$ bar and $T = 283 - 288$ K)

Product	**Max. mis.(wt%)**
C_6E_3	> 10(K)
C_8E_3	7(S), 4.5(K)
$C_{11}E_3$	-
C_8E_4	3(K)
$C_{12}E_4$ (Brij 30)	-
C_6E_5	5(S), 4(K)
C_8E_5	4(S), 2.3(K)
$C_{12}E_5$	-
C_8E_6	2(K)
$C_{12}E_9$	-

Phase diagrams for $C_{12}E_j$, with $j = 4, 5, 9$ and for $C_{11}E_3$ could not be obtained with the Cailletet apparatus. At the lowest concentration it was not possible with these surfactant samples to obtain a single phase solution in the range of temperatures and pressures considered for dry-cleaning. This does not imply that the compounds are in fact insoluble. Under the circumstances their solubility is *Small*, which means: lower than 1 wt%. This was the minimum surfactant concentration that could be studied in our apparatus.

Industrial Preparations

It was found in our Cailletet experiments that for $\mathrm{E}_j \geq 4$ the solubility became less sensitive for the chain length in the industrial samples. Also, we discovered in all the industrial products that the maximum miscibility was lower than in the more uniform laboratory samples with comparable "average" (i) and (j). It appears that the longer carbophobic tails are dominating the phase behavior in the industrial samples. This observation is important for the technological application of the detergent. A considerably polydispersity of the ethyleneoxide moieties in combination with a monodisperse alkane head group leads to phase separation at lower weight percentages of surfactant.

The presence of less ethoxylated molecules (e.g. $\mathrm{E}_j = 0, 1, 2$ in an industrial sample with average $\mathrm{E}_j = 5$) is not able to compensate the negative effect that the high ethoxylated molecules have on the miscibility. These smaller molecules are less carbophobic than the average but they will be extracted from the homogeneous solution by micelles of larger surfactant molecules. The smaller fractions in the industrial samples had better be thought to act as cosolvents rather than surfactants. They introduce, however, a polydispersity of the carbophobic tails in the core of the detergent micelles. Polydispersity in the tail length of surfactants is known to reduce the characteristic time τ_2 in micelle formation and in demicellization.

The differences in average E_j for industrial products are mainly because of the

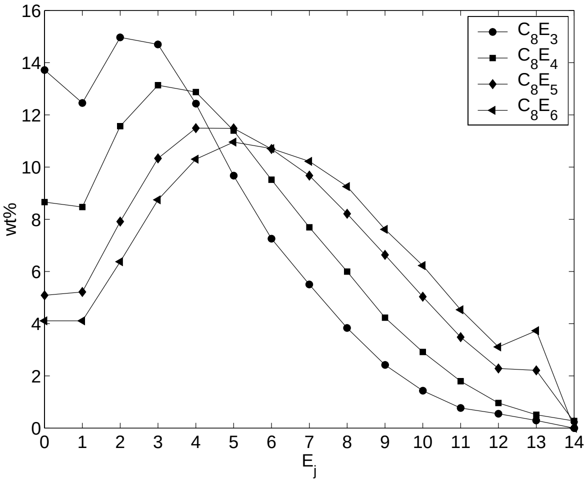


Figure 4.3: Ethylene oxide distribution of $\mathrm{C}_8\mathrm{E}_j$ industrial surfactants.

percentage of short tails molecules, i.e. of a cosolvent, in the samples. Looking at Fig. 4.3 we see that the distribution of the longer ethylene-oxide chain lengths ($E_j \geq 4$) is always very similar. This explain why the measured phase behavior for the industrial compounds with $j > 4$ is not affected very much by differences in the average E_j.

The more insoluble character of $C_{12}E_j$ (with $j = 4, 5, 9$) and of $C_{11}E_3$ did at first surprise us. We had reckoned that these, commercially accessible, surfactants should readily dissolve in liquid CO_2, because of their "oversize" alkane moieties. But the reduced carbophilicity of the longer alkanes indicates that the solubility criteria, which are based on the idea of group contributions, begin to fail when the chains of groups become too long. The length of the hydrocarbon chain (C_{11}, C_{12}) comes close to the critical value (C_{13}) for the experimental miscibility of alkanes in liquid CO_2 which has been reported in older studies [40]. For the amphiphilic $C_{12}E_9$, moreover, the ethylene oxide chain becomes not only too carbophobic, but it is probably also too bulky to fit into a spherical micelle. Its size causes screening problems and the molecules would fit better into planar or cylindrical structures. This shows our Cailletet experiment: the concentration for phase separation is relatively low. It also explains the low solubility of the surfactant in Table 4.2. However, as difficult as the micellization may become, individual molecules of such substances can still be slightly soluble in the lowest concentration range (< 1 wt%).

Light Scattering Experiments

Experimental

The visual observation of a macroscopic phase transition in a Cailletet tube is a determination of the Cloud Point (CP) of the solution. Measuring changes in light scattering is a more sensitive detection method for the incipient formation of small objects like micelles in solution. We used this method to investigate the low range of concentrations in the surfactant solutions. What we were looking for, as a relevant parameter in the detergency theory, was not the CP of the surfactant solutions, but the critical micellar concentration (c.m.c.). The c.m.c. heralds the first association into micellar structures of individually dissolved surfactant molecules. It also determines the limit value of the surface excess for the detergent molecules in an admicelle through the equilibrium with the solution at the c.m.c.

Experimentally, the c.m.c. is the concentration where the isotropic surfactant solution begins to scatter light because the micelles begin to appear. The micelles are very small association colloids, which scatter some light because they have a different refractive index from the solvent. We did the light scattering experiments in collaboration with Kreussler GmbH, at Wiesbaden, in their high pressure flow cell apparatus. This setup allows measurements at very low solution concentrations

A scheme of the equipment is shown in Fig. 4.4. The flow cell has a volume of 150 ml between optically flat windows. It is equipped with a stabilized halogen light source, a photovoltaic cell and a thermocouple, which monitors the temperature of the flowing solution during the experiment. A high pressure pump, a flowmeter, water bath, gas cylinder and, an injection system (with a dosage of 0.2 ml) complete the experimental setup. In order to do a measurement, the cell is filled with liquid CO_2 and conditioned at a fixed pressure and temperature. The light transmittance is calibrated at 100% with CO_2. The surfactant sample is directly injected into the solvent. When the flowing liquid is completely mixed and the system has reached equilibrium, the transmittance can be recorded. The flow of the liquid is temporarily stopped during the determination of experimental transmission values.

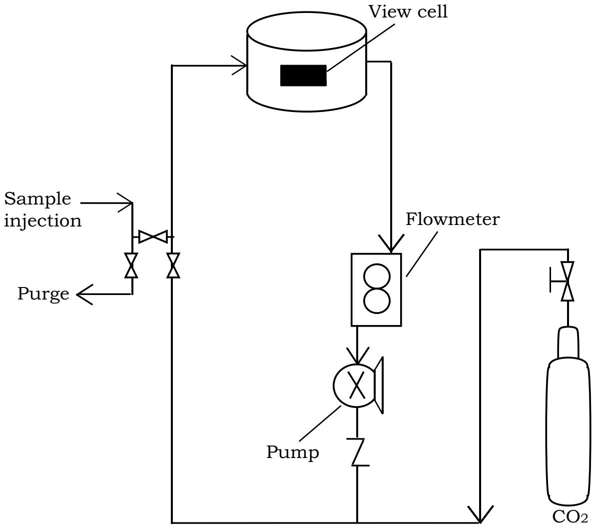


Figure 4.4: High-pressure flow cell equipment.

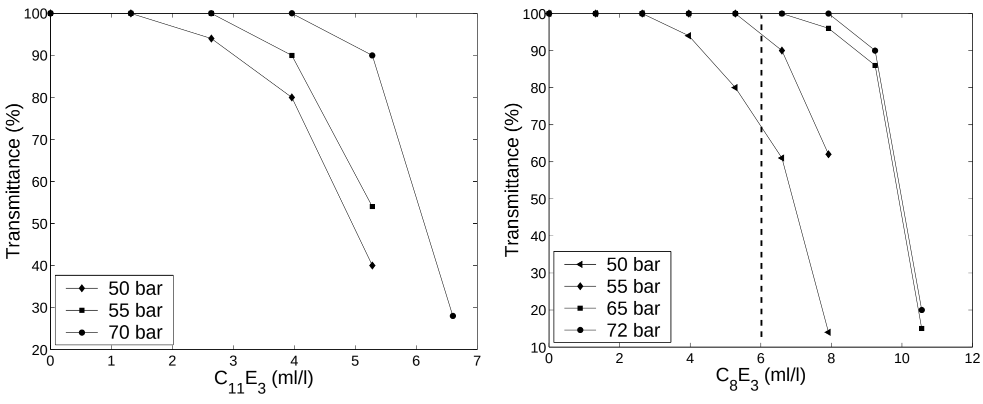
The addition of surfactant to the solution is repeated in small steps, from zero concentration till the CP. At that concentration the transmission decreases sharply. The presence of the second-phase at the cloud point was also confirmed by visual inspection. The whole procedure for a single surfactant was repeated twice to ensure reproducibility.

The samples for the light scattering experiment (C_8E_3 and $C_{11}E_3$) were both synthesized by Kreussler. The previous investigations had indicated C_8E_3 as the most promising detergent on the basis of the DDM. $C_{11}E_3$ was the economically more attractive alternative. This rather well defined compound is already in production (for other applications) on a pilot industrial scale.

Results

The light scattering results with the high pressure flow cell show the transmittance as a function of concentration. In Fig. 4.5 we can clearly see that $C_{11}E_3$ is miscible in liquid CO_2. Its CP is found at a lower concentration than the CP of C_8E_3. The maximum CP concentrations under dry-cleaning conditions were 10 ml/l and 5 ml/l, or 1.0 wt% and 0.5 wt% for C_8E_3 and $C_{11}E_3$ respectively. The CP value for C_8E_3 is smaller than in the Cailletet experiment (Table 4.2). This is because these samples were less polydisperse and contained a smaller porcentage of "cosolvent" with $E_j < E_3$.

The interesting aspect of Fig. 4.5 is the effect for which we looked in this light scattering experiment. For both samples, from a well defined concentration on, the light transmittance begins to decrease while the solution remains homogeneous and transparent. There is no macroscopic phase separation yet at these concentrations below the CP. Upon further increasing the concentration the cloud point is reached. There, the transmittance drops dramatically and the system becomes turbid, as would be indicative for the formation of a second phase. A plausible explanation for this light scattering result is, that from the concentration on where the transmittance



(a) $C_{11}E_3$ *(b)* C_8E_3

Figure 4.5: Transmittance of $C_{11}E_3$ and C_8E_3 solutions in liquid CO_2.

decreases (linearly with the amount of added surfactant) the solute molecules begin to form small micellar aggregates. That concentration is the c.m.c. and detergents can only form mobile admicelles and show detergency above this concentration. The much steeper rise in the turbidity, which is characteristic for CP measurements, is caused by the phase transition from clear, isotropic micellar solution to the birefringent liquid crystalline phase.

The DDM says that the operating window for a detergent in a dry-cleaning solvent is between the c.m.c. and the CP concentrations. The light scattering method is highly recommended for the determination of these values. It allows quick measurements in a short time and delivers the information about solution parameters, which is needed as a predictive tool for the development and optimization of detergent formulations.

Conclusions

The phase diagrams, the CP as well as the c.m.c. determinations for C_iE_j molecules show that these surfactants are - as predicted - sparingly soluble in liquid CO_2. The miscibility is limited because of the carbophobic/carbophilic balance in the molecule, which is the equivalent of a HLB value in dense CO_2. For $C_i \geq 11$ the effective carbophilicity of the alkane moiety is reduced and the miscibility in liquid CO_2 is thus lower than expected. We have also obtained indications that in polydisperse mixtures the molecules with $E_j < 3$ behave as cosolvents rather than as surfactants and dissolve in micelles of the molecules with the longer carbophobic tails. Within those constraints, and for an operation window which is determined by temperature, pressure and the carbophobic / carbophilic balance in the detergent, we consider that C_iE_j molecules with $6 \leq i \leq 11$ and $j \geq 3$ are the most suitable for the proposed dry-cleaning technology. The important factors are solubility, miscibility and micellization characteristics. On the basis of the DDM, the operation window for the surfactant is also limited, either by a too high solubility to be an effective surfactant (like C_6E_3) or by a too low solubility (like with $C_{11}E_3$). Too small a concentration of the detergent monomers in the micellar liquid gives problems with the replenishing rate of the detergent in small pores of textiles.

Chapter 5

C_iE_j as surfactants in dense CO_2

Introduction

For the use of C_iE_j as detergents in liquid CO_2, it is essential that the amphiphilic molecules are surface-active in that solvent. That they adsorb at the liquid CO_2/textile interface and form the *admicelle* is the key element in the physical chemistry of the DDM (see Fig. 5.1).

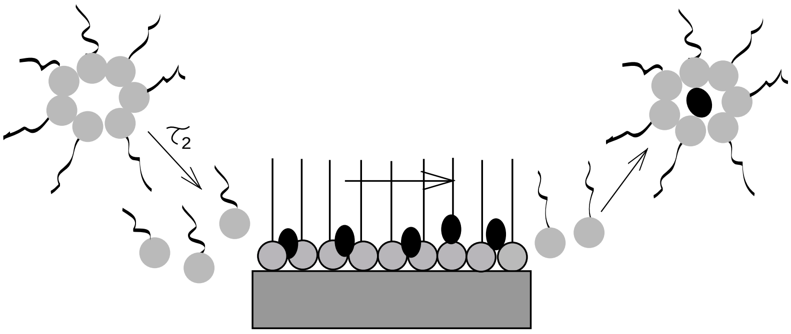


Figure 5.1: Flowing admicelle in dynamic equilibrium with micelles.

The flow of the surfactant in the admicelle is primarily responsible for the extraction and the removal of of soil substances. It creates Marangoni forces, which can disperse the liquid soils and pull the solid soot particles away from the textile pores. Local undersaturation and supersaturation are the non-equilibrium situations which are effected by this flow. Undersaturated spots at the interface need replenishing from the micellar solution to keep the flow in the admicelle going. Where the interface becomes supersaturated, the equilibrium is restored by the formation of new micelles. These disjoin from the surface and carry the extracted soils away into the solution. Moreover, a real detergent must also have micelles for solubilizing polar soil substances. With liquid CO_2 the solvent itself is much too apolar to dissolve such materials. And furthermore, the detergent should, preferably, also act as an emulsifier and help to disperse liquids and stabilize colloids in the washing fluid. For these functions it is helpful to add selected cosurfactants and cosolvents. But the surfactant which forms the admicelles will always be the basis for an effective detergent formulation. And in our design that basic surfactant is one if the C_iE_j compounds.

A direct way to investigate surface-activity and adsorption is measuring interfacial tension (IFT). As is indicated by the Gibb's equation (2.1), the reduction of the IFT with increasing surfactant concentration is a marker of surface-activity. But, of course, the surface activity of a surfactant depends on the properties of the surface too. Surfactant solutions in water can be studied in great detail with surface tension measurements, because almost every surface, including that with air, is less polar than the solvent itself. Amphiphilic molecules are adsorbed on any of them. But with liquid CO_2, effective surfactants should adsorb on surfaces which are more polar than the solvent. In that case the surfactant has no affinity for the L/G interface of the solution, which is even more apolar than the solvent itself.

The traditional method to identify the c.m.c. of a surfactant solution is to find the abrupt change in slope of the IFT for the L/G surface, plotted logarithmically as a function of the surfactant concentration. But that does not work with liquid CO_2 under those conditions. As an alternative, some authors have measured IFT - plots for water/CO_2 L/L interfaces trying to determine c.m.c. values for C_iE_j compounds. But this is a complicated situation, with c.m.c.'s of the surfactant in both immiscible phases.

An indirect way to determine micellization is through the study of dye dissolution in micellar fluids. A dye is injected into the surfactant solution. In pure CO_2 the dye is like an insoluble particulate soil. But the dye molecules can dissolve in an admicelle (adsolubilization) or in the core of a micelle (solubilization) [45]. These association colloids are present in the solution when the concentration exceeds the c.m.c. Therefore, dye dissolution signals that micelles and admicelles have been formed in the solution and at the more polar interfaces of the solvent.

Interfacial Tension (IFT)

Hebach *et al.* [46] have determined IFT's of (C_iE_j in liquid CO_2)/water interfaces. They measured the interfacial tensions using a quasi-static modification of the pendant drop method. In this method a water drop is immersed in the liquid CO_2, which contains the surfactant, and kept at a controlled temperature (283 K) and a pressure of 50 bar. The shape of the water drop is determined by the (pressure dependent) density difference between the surfactant solution and water and by the IFT. The evolution of the drop shape is monitored by a CCD-camera. From extrapolations of this shape the IFT can be calculated, using an image evaluating software.

The concentration in the surfactant solutions was the same in all these experiments. At 0.0041 wt% for all the surfactants, it was much lower than in any washing fluid. But comparing the measured effect of the surfactants on the IFT is indicative of their surface activities. At those low concentrations every surfactant was fully miscible in liquid CO_2. Three successive measurements were done for each sample to ensure reproducibility. The C_iE_j surfactants were provided by Kreussler, like those in our experiments.

At this constant concentration all the surfactants gave a decrease in the IFT relative to the value of 24 mN/m for the binary water/CO_2 system (see Fig. 5.2).

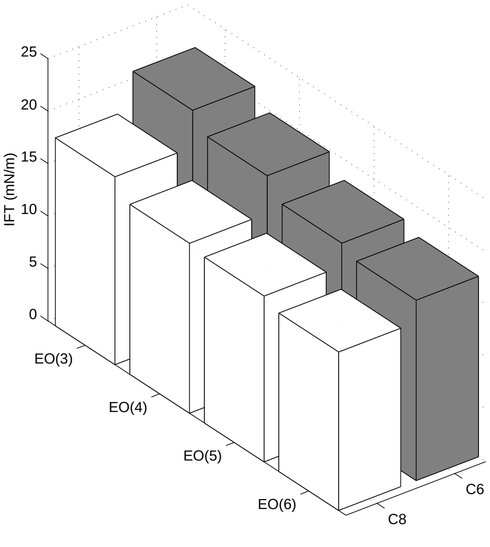


Figure 5.2: Reduction of the IFT between water and liquid CO_2-surfactant solutions (0.0041 wt%) of C_iE_j's as a function of i and j.

The magnitude of this IFT reduction, which is due to adsorption at the interface, differs for the individual surfactants. It is a measure for the surface activity of the $C_iE_j$compounds at the polar (water/CO_2) interface. With the rather small C_6E_3 molecule the reduction of the IFT is small. It increases for $j = 4$ but beyond the length $j = 4$ of the carbophobic (but rather hydrophilic!) tail, the reduction of the IFT levels off. This is also observed in the homologous series for C_8E_j with $j = 3, 4, 5, 6$.

It becomes clear from this experiment how the surface activity of C_iE_j molecules depends on the size of the carbophobic and carbophilic chain elements. The lowest IFT, i.e. the strongest surfactant adsorptions, were for molecules with high i and j. The smallest effect was obtained with low i and low j.

To explain their results, the authors proposed a structure-effect relation for surface activity of C_iE_j compounds. Long hydrocarbon chains (and low ethylene oxide number j) make the surfactant carbophilic enough to dissolve in liquid CO_2. High ethylene oxide numbers will, on the other hand, increase the affinity towards a polar interface. Therefore, the higher the value of i and j, the lower the IFT for a given low concentration and the higher the surface-activity of the surfactant. However, i and j have a maximum value when the molecules are in the solid state at the conditions of the measurements.

This analysis would explain why the lowest IFT is obtained with $C_{12}E_9$ and the highest with C_6E_3 at equal concentration. Moreover, the structure-effect relation suggest a synergistic effect in the polydisperse, industrial type surfactants. The highly ethoxylated compounds have the most surface active molecules. They begin to associate in concentrated micelles and admicelles at low concentrations. However, their solubility is very low in the liquid CO_2 phase. It is the availability of the more soluble molecules with a low ethylene oxide number and a lower surface activity what allows the completion of the micelles. These molecules help as a cosolvent for the highly ethoxylated molecules, and this make the micellar cores more liquid and faster in micellization and demicellization processes. This is a good property for a surfactant detergent according to the DDM.

Dye Dissolution

The formation of micelles and their structures have been studied by means of the spectroscopy of solubilized molecules. Dyestuffs, which are insoluble in a solvent can, nevertheless, been solubilized in a micellar solution. The presence of the micelles is, of course, a prerequisite. The inside of the micelles offers small pockets with different solvent properties, since lyophilic moieties of amphiphilic surfactant molecules are concentrated in the shell and lyophobic tails of these molecules form the concentrated core of a micelle. The insoluble dye powder will only dissolve and begin to color the solution at surfactant concentrations higher than the c.m.c. In this way the c.m.c. of a surfactant solution can be determined and an impression can be obtained of the micellar size. With small micelles the transition in the solubility of the dye at the c.m.c. - from a solution with separate surfactant molecules to a micellar system of association colloids - is less abrupt than for micelles with a fairly large association number.

Therefore we carried out some dye dissolution experiments in the same high pressure flow cell equipment that was used for the light scattering experiments described in Chapter 4. The handling of the apparatus and the compounds were the same as for determining the light scattering. But this time 0.2 ml of a dye solution in decanol was injected into the system before the stepwise addition of the surfactant. The dye was Sudan Red 7B (SR) from Fluka. It comes in the form of a powder and is insoluble in liquid CO_2. Since solids could not be injected in the flow cell, the dye had to be dissolved prior to the measurement as a 0.62 wt% solution in decanol (not fully miscible in liquid CO_2 [40]). Upon introduction of this solution in liquid CO_2, without added surfactant, the dyestuff would precipitate out as a fine colloid and reduce the level of the transmission to 80% relative to pure CO_2. The colloidal solution was slightly orange colored under these conditions. The surfactant in this colorimetric experiment was C_8E_3 from Kreussler. Each determination of the transmission at a given surfactant concentration was repeated twice, so that reproducibility was ensured. The measurements were done at 60 bar pressure. The temperature, as usual, was 283 K.

In Fig. 5.3 the results of these measurements are presented. The transmittance is plotted as a function of the surfactant concentration.

Upon surfactant addition there is, initially, no change in the transmittance of the solution. This changes dramatically, however, when the surfactant concentration in the flow cell reaches 8 ml/l (0.8 wt%). At this point the transmittance drops steeply and the solution turns deeply red. It is important to notice that the solution remained essentially clear during this change and that no macroscopic phase transition is observed. Upon a further increase of the concentration, the CP for the surfactant is eventually reached, and the second phase gives the solution a turbid appearance.

The dye SR itself is barely soluble in liquid CO_2 [47] and the presence of the dye as a dilute dispersion gave a constant level of the light transmission at lower surfactant concentrations. The sudden color change at the surfactant concentration of 0.8 wt% is

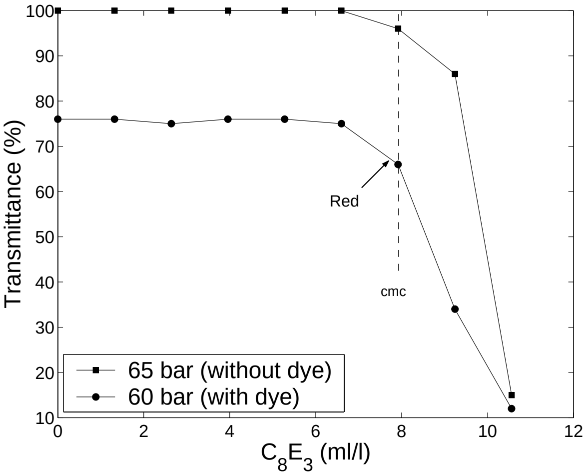


Figure 5.3: Transmittance of the C_8E_3-liquid CO_2 system with and without the addition of the dye Sudan Red. The dashed line indicates the c.m.c.

due to the formation of small micelles, which we had anticipated at that concentration because of the light scattering results. Upwards from that concentration all the dye that is available will be in the core of the micelles. The c.m.c. for C_8E_3, of 8 ml/l (i.e. 0.8 wt%), according to the dye dissolution experiment coincides exactly with the value from the light scattering observations at 60 bar (see Fig.4.5). We conclude that the dye dissolution experiment identifies the weak light scattering above 0.8 wt% surfactant as the incipient formation of C_8E_3 micelles in liquid CO_2 under these experimental conditions. The c.m.c. of this surfactant is thus 0.8 wt%.

Micellar Structure

Sudan red is a lipophilic dye, readily soluble in hydrocarbons. The ethylene-oxide core interior of the micelles, on the other hand, is rather polar. The dye solubilization, therefore, could be thought of as taking place in the micelles' ethylene-oxide cores, but also in the densely packed hydrocarbon shell between that core and the liquid CO_2 outside. The SR and the decanol, in which it was originally dissolved, both have their most favorable microenvironment to dissolve inside the the lipophilic shell around the micelles.

Following up the promising results with dye dissolution in surfactant micelles, which were obtained in the high pressure flow cell, we constructed a more elaborate experiment. In addition to the measurement with SR, this experiment involved

Methylene Blue (MB) as another, polar, dye which is insoluble in liquid CO_2 but soluble in the core of C_iE_j micelles. This dye is a rather polar, solvatochromic substance. Its UV-Vis absorption spectrum changes with the polarity of the medium which surrounds the dye molecule. Measuring at the wavelength of the absorption peak it is then possible to probe the polarity in the core of the surfactant micelle. The idea of this type of experiment was to compare the changes in the absorption spectra of the two different dyes, which were present in a pressurized autoclave at a constant concentration, relative to a series of C_iE_j samples in liquid CO_2 with increasing concentrations of surfactant. Both dyes, SR and MB are insoluble in pure liquid CO_2 at any pressure or temperature in the experimental window. But both dyes will be solubilized inside surfactant micelles, which gives a deep coloration of the solutions above the concentration of the c.m.c. The SR will be solubilized in the alkane layer on the outside of the micelles, whereas the more polar MB will dissolve in the micellar core of ethylene-oxide tails. That the MB is dissolving in the polar medium at the inside of the micelles can be seen from the solvatochromic change in the UV-Vis absorption spectrum.

For these experiments we set up a measuring equipment at Avantium (Delf, The Netherlands). A scheme of this equipment is drawn in Fig. 5.4.

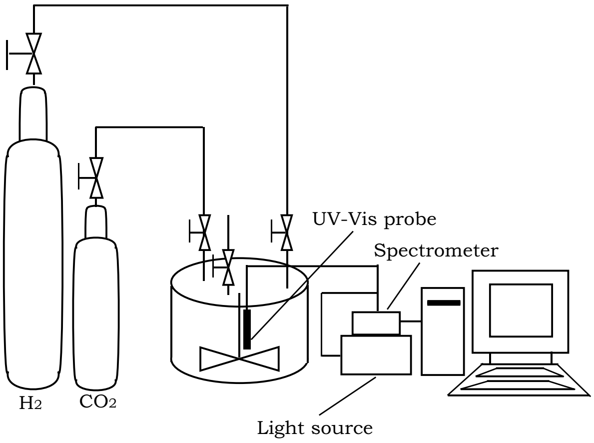


Figure 5.4: Scheme of the autoclave at Avantium.

The heart of the equipment is a high pressure autoclave, Premex Reactor AG, with a volume of 500 ml and workable until pressures of 200 bar and temperatures of 548 K. The autoclave is placed in the thermostatting jacket and through the lid it has a thermocouple, a stirring system, an optical probe and three valves. The autoclave can be pneumatically lifted up and down from the lid. For our measurements we inserted a UV-Vis reflection probe from Avantes (Eerbeek, The Netherlands) through the lid. One of the valves is used for venting. The other two are for the injection of gases and liquids into the system. In our experiments the autoclave was filled with liquid CO_2. Extra Hydrogen was used to increase the pressure in the system, when needed. The UV-Vis probe is connected to a Deuterium-Halogen light source (DH-2000) and to a miniature fiber optic spectrometer (AVS-USB200). The spectrometer is directly plugged into the USB bus of a computer. Finally, the AvaSoft-full software (version 5.1), that allows the processing of the data, completes the setup. All the components were purchased through Avantes.

In the measurement the autoclave is cooled down and the surfactant and dye sample are placed into it. Two types of dyes were used in this study; SR and Methylene Blue (MB), both from Fluka, and two different surfactants: C_8E_3 and C_8E_5, both from Kreussler. The autoclave which then contains the intended amounts of surfactant and of dye, is sealed and flushed three times with hydrogen, in order to remove traces or air from the system. Immediately afterwards, the liquid CO_2 is injected. The supply bottle of liquid CO_2 is weighed, so that the amount of CO_2 solvent in the autoclave is known. Finally the pressure in the autoclave is set at the desired value.

In contrast with the Cailletet method the hydrostatic pressure in the autoclave was generated by hydrogen gas above the liquid CO_2. The compressibility of the CO_2 under the experimental conditions is such that its solvent properties depend on the hydrostatic pressure in the autoclave. Hydrogen was selected as the pressurizing gas since its solubility in liquid CO_2 at the conditions of the measurements ($T = 281 - 283\,\mathrm{K}$ and $P \geq 50\,\mathrm{bar}$) is negligible. That is due to the sharp slope of the bubble point curve of the H_2-CO_2 system (see Fig. 5.5).

After the CO_2 injection is completed, the experiment can start. The temperature is kept between $281 - 283\,\mathrm{K}$ and there is a constant stirring during the measurements. Before the collection of spectroscopic data starts, one calibration experiment was done to measure the absorption spectrum of the pure solvent (liquid CO_2). This spectrum (at the pertinent temperature and pressure) was used as a reference (base line) for all the following spectroscopic observations.

For calibration of this experimental method we repeated the colorimetric experiment with C_8E_3 + SR in liquid CO_2. The measured spectra of red solutions had identical shape for all the different concentrations. The maximum absorption peak of SR was at the wavelength $\lambda_m = 516\,\mathrm{nm}$. The absorbance at 516 nm was used as an indication of dye solubilization. The results are given in Fig. 5.6

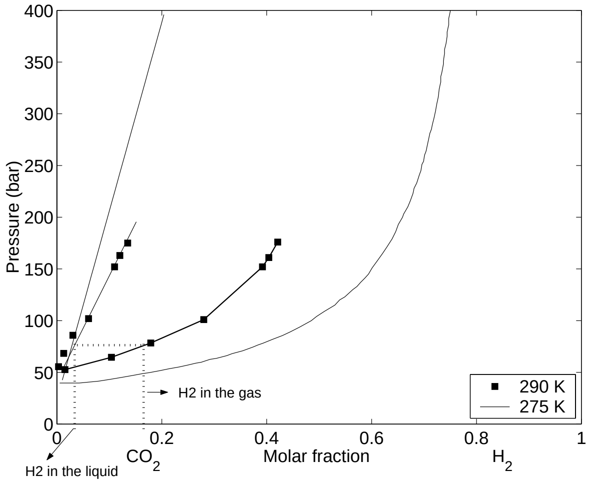


Figure 5.5: Mutual solubility of the Hydrogen - CO_2 system.

The absorbance of the dye is seen to increase linearly in range of increasing surfactant concentration. It levels off for concentrations higher than 0.8 wt%. From there on, the absorbance is stable with small fluctuations around the plateau value. The width of the concentration range with increasing absorbance might be indicative for micelles with a rather small association number. But, because of the construction of

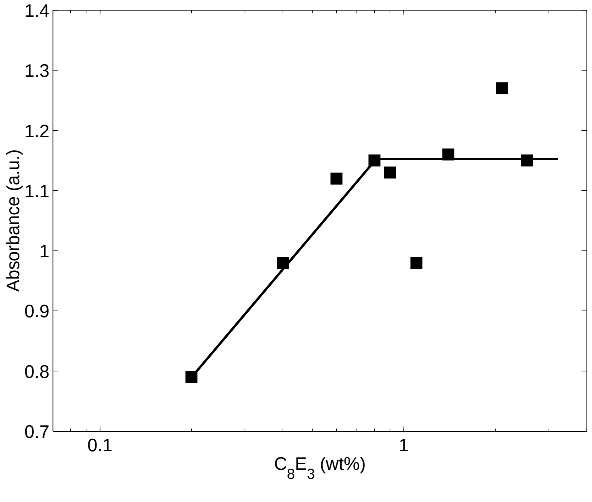


Figure 5.6: SR absorbance in liquid CO_2-surfactant solutions at P= 64 bar as a function of C_8E_3 concentration.

the Avantes reflection probe, it could be also due to the surfactant adsorption with the ethylene oxide groups directed towards the (polar) optical glass interfaces with the solution. The adsorbed layer of surfactant molecules consists of hemimicelles, which increase in number and surface coverage as the surfactant concentration increases and transform gradually into a continuous admicelle in the concentration range below the c.m.c. [48]. Dye molecules will solubilize in these structures (i.e. in the optical path of the probe) as well as in the normal micelles above the c.m.c. (see Fig. 5.7). The c.m.c. in the solution is found when all the available dye is solubilized in the micelles of the surfactant solution at 0.8 wt%, as in the experiment with the flow cell.

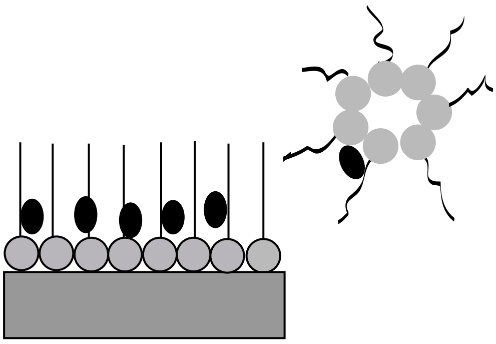


Figure 5.7: Illustration of SR dissolution.

That the dye is indeed dissolved in the densely packed hydrocarbon part of the admicelle and in the micelle shell, is corroborated by the analysis of the λ_m of the dye as a function of the polarity of the solvent. Looking at Table 5.1 we see that the value of $\lambda_m = 516$ can just be reached if the dye molecule is *surrounded* by hydrocarbon molecules.

Table 5.1: Polarity Index, $E_T(30)$ and λ_m of SR for various solvents.

Solvent	Polarity Index	$E_T(30)$ (kcal/mol)	λ_m (nm)
Ethanol	5.2	51.9	540
Dichloromethane	3.1	40.7	538
Toluene	2.4	33.9	535
Pentane	0	31.0	518

The carbophobic Core of the C_iE_j - Micelles

UV-Vis measurements of dye solubilization were then done with MB in an analogous way and in a MB+C_8E_5+liquid CO_2 system. C_8E_5 was chosen as the surfactant. It has a relatively high solubility in liquid CO_2 at the experiment's conditions. The higher ethylene oxide number could facilitate the dissolution of polar, highly hydrophilic, dyes like MB. With this experiment we wanted to demonstrate that the polar dye molecules (which may be considered as a model substance for polar soils in actual dry-cleaning), can indeed be dissolved in the carbophobic core of C_iE_j micelles, without the need for addition of extra water or any other polar cosolvent.

This experiment gives the absorbance of MB, at $\lambda_2 = 653\,\mathrm{nm}$, as a function of the surfactant concentration (see Fig. 5.8). This wavelength is the absorption maximum for MB in a polar environment. The value of the absorbance is proportional with the amount of MB in the cores of the micelles. As with SR we saw a linear increase of the absorbance, which levels off at concentrations higher than 0.6 wt%. But at above twice that concentration, above 1.1 wt% the absorbance increases with the concentration. Linearly, and with similar slope.

The explanation for the shape of the absorption curve in Fig. 5.8 is analogous to the SR solubilization. That is, solubilization of the dye in hemimicelles which, upon increasing surfactant concentration, will transform gradually into a continuous admicelle. At 0.6 wt%, full surface coverage is reached and from then on MB will

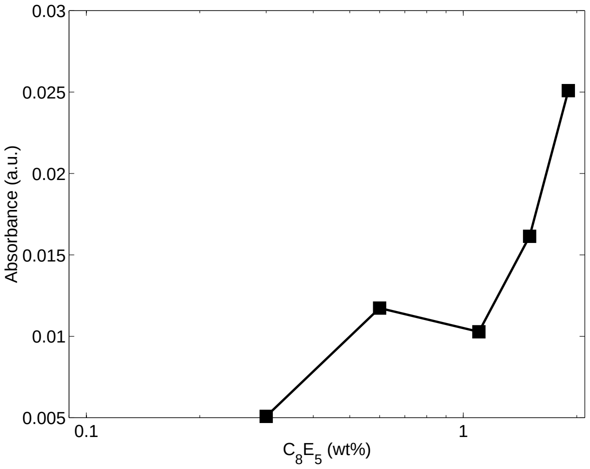


Figure 5.8: MB absorbance as a function of surfactant concentration at $\lambda_2 = 653\,\mathrm{nm}$.

dissolve in the admicelle as well as in the polar ethylene-oxide core of the micelles (see Fig. 5.9). However, at concentrations higher than 1.1 wt% a new increase in the absorbance is observed. The explanation for this second inflexion point comes from the analysis of the absorption of MB at $\lambda_1 = 514\,\text{nm}$.

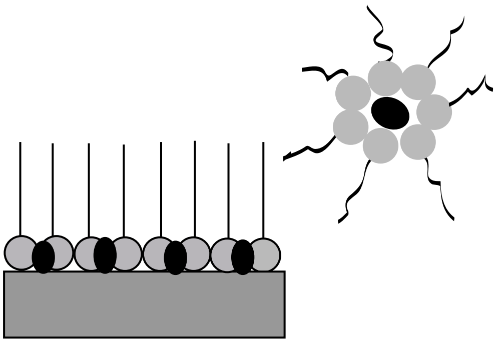


Figure 5.9: Illustration of MB dissolution.

The peak at λ_1 is associated to the formation of a 1:1 complex between MB and ethylene-oxide groups and appears upon micellization [49, 50]. Looking at Fig. 5.10 we see that, as deduced from the MB absorbance at λ_2 (free MB), the c.m.c. is indeed located at around 0.6 wt%. Below this concentration no absorbance takes place at λ_1

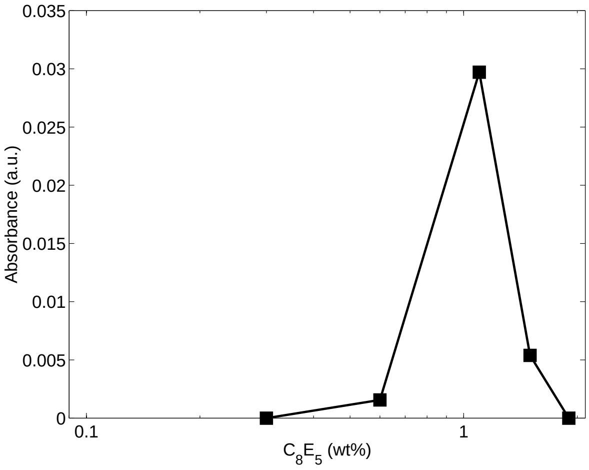


Figure 5.10: MB absorbance as a function of surfactant concentration at $\lambda_1 = 514\,\text{nm}$.

and, therefore, also no micellization. Above this value of 0.6 wt%, micelles are formed and MB is dissolved in the admicelle but also in the micelles, both in the free form but preferentially forming a complex. Upon further increase of surfactant concentration (above 1.1 wt%) the core of the micelles begin to growth. These micelles, with larger aggregation numbers, offer a more polar microenvironment. As a consequence, MB dissolves now preferentially in the free form, inducing the sharp drop in the absorbance at λ_1 and the further increase in the absorbance at λ_2.

The analysis of λ_2 as a function of solvent polarity provided information about the polarity, sensed by MB, in the core of C_8E_5 - micelles in liquid CO_2.

In Table 5.2 we see that λ_2 for MB in the core of the C_8E_5 - micelles is in the same range as in ethanol and 2 - propanol. Like for SR, this value of $\lambda_2 = 653$ nm can only be reached if MB is *surrounded* by the polar ethylene-oxide groups. Even compared to the value for MB dissolved in pure C_8E_5, λ_2 for our system indicates a higher polarity. That is, once more, an indication that the dye molecules is found in the polar core of a surfactant micelle [51].

Table 5.2: $E_T(30)$, λ_1 and λ_2 of MB for various solvents.

Solvent	$E_T(30)$ (kcal/mol)[a]	λ_2 (nm)[c]
Water	63.1	668
Ethanol	51.9	658
2-propanol	48.4	657
Liquid CO_2	33.8[b]	-
Cyclohexane	30.9	-
Cyclohexane + $C_{12}E_4$	Not known	-
Cyclohexane + $C_{12}E_4$ + Water	Not known	663[d]
C_8E_5	Not known	635
Liquid CO_2 + C_8E_5	Not known	653

[a] [52]
[b] [34]
[c] This work.
[d] [50]

In both experiments we have found that admicelles are present at surfactant concentrations below the c.m.c. Colored molecules of polar soils, like the MB dye, solubilize in the ethylene-oxide core of C_iE_j - micelles. This is possible without the extra addition of a cosolvent (like water or alcohol) or of a cosurfactant (with shorter ethylene-oxide chains) to the detergent formulation.

Conclusions about Valid Detergents

The IFT measurements, as well as our experiment with the dye dissolution reveal that C_iE_j molecules ($E_j \geq 3$) are surface active in liquid CO_2. They adsorb at polar surfaces and form micelles in the solution at concentrations of the order of 1 wt%. They can, as a matter of fact, be considered as promising surfactants for the use as a detergent in dry-cleaning with CO_2.

The dye dissolution experiments show also that molecules, which are insoluble in the liquid CO_2 solvent, can effectively be extracted and dissolved in the admicelle and micelles of those C_iE_j surfactants. Our design of a detergent satisfies the requirements for an effective detergent according to the DDM. The specifications for the Sinner factor C (chemistry) of an effective detergent (i.e. solubility in the medium; surface-activity and the formation of solubilizing admicelles and micelles) can be demonstrated in independent laboratory experiments.

Evaluation of the Detailed Design for the Detergent

We are now in a position to set specifications for a detergent in liquid CO_2. We use the DDM - approach as a model for detergency and our own experimental results and theoretical speculations to select the best chemical for this purpose. We can even describe the more elaborate Detailed Design, which set details for a most promising version of the product.

In this fashion we do predict that C_8E_3 and $C_{12}E_4$ will be our best choices, among the preferred C_iE_j surfactants which we have investigated, to deliver the specified high detergency in liquid CO_2.

The C_8E_3, at a concentration upwards from the c.m.c. at 0.8 wt% and below the cloud point for the "industrial" product, seems the best proposition in terms of chemical functions like solubility, surface activity and micellar properties.

If its solubility is enough, $C_{12}E_4$, in about the same concentrations range, would seem the favorite proposition for the process economy of dry-cleaning. However, its solubility is not enough. It would be attractive for the first introduction in the industry, because it is already an existing industrial surfactant for aqueous applications. With both detergents, and with liquid CO_2 as the solvent, the operating window of temperatures and pressures for dry-cleaning is between $T = 283 - 288\,\mathrm{K}$ and $P = 50 - 65\,\mathrm{bar}$, respectively.

The proof of technological relevance for a designed product is not that it seems to meet theoretical specifications. The design must stand the test in a technical evaluation and then deliver the specified targets in the practice of the envisaged application.

During such technological tests of washing performance, as will be described in the next Chapter, it must be explored wether the designed detergent works. Its chemical formulation should bring a cost effective compromise with the other two Sinner factors M (mechanical power input) and T (processing temperature) and deliver acceptable detergency under the specified operation's conditions. The final evaluation of the designed detergent has to be in dry-cleaning tests, rather than in the research laboratory, with liquid CO_2 as the solvent and the selected C_iE_j - surfactants as the detergents.

Chapter 6

Technical Evaluation of C_iE_j Detergents in Dry-Cleaning Tests

Designing a Washing Test

Assuming that the DDM does hold then the C_iE_j detergents, designed on the basis of this model and for which we proved that they satisfy all the physical-chemical requirements of it, should do the job of dry-cleaning in liquid CO_2. The DDM implies that cleaning rates are increased by mechanical action for the extraction of molecular soils which dissolve in the medium if a detergent solution is added to the medium. However, it should be altogether impossible to remove particulate soils within an hour or so in the absence of detergent molecules which form a mobile admicelle at concentrations above the c.m.c. Observations like this could be made in actual dry-cleaning experiments under well-controlled conditions. The model says that for effective laundering the concentration of the detergent in the laundering liquid must be chosen high enough for sustaining the rate of replenishing detergent from the solution to the adsorbed layer. It must keep pace with he flow of surfactant in the admicelle. This flow is created by the friction forces as the liquid is forced through the narrow pores of the textile fabric by stretching. The stretching of the yarns, produced by the tumbling of the textiles inside the drum, depends on the viscosity of the fluid but also on the difference in density between the two media contained in the washing machine; water-air in a conventional washing machine and vapour-liquid CO_2 in our case. In general, the lower the density difference, the less efficient the tumbling effect.

Therefore, the results of actual dry-cleaning experiments are expected to depend on the detergent concentration in the washing fluid and the mechanical action exerted on the fabric (stretching).

Monitors for Detergency

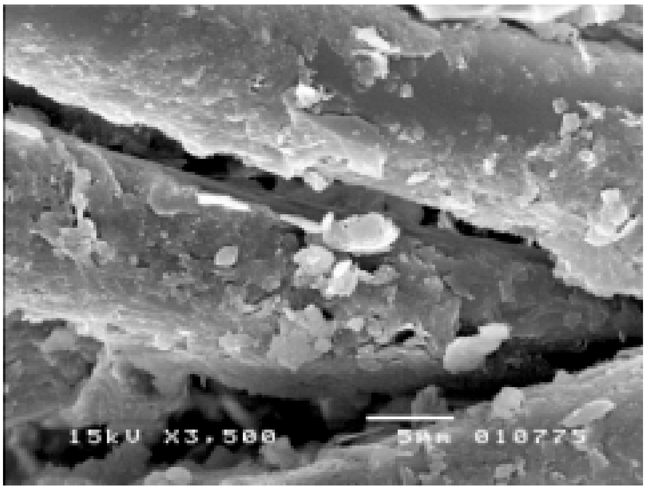
Monitoring the result of a detergency test is only possible under well controlled testing conditions. We have already discussed that there exists a nearly infinite number of permutations in the combination of textiles and soils. For our purpose of testing the applicability of the DDM in dry-cleaning with liquid CO_2, a careful choice must be made of soiled textile monitors which will be cleaned in the tests.

In general, textile soiled with particulate dirt will be more difficult to clean. In such systems particles like soot, clay or iron oxide cannot dissolve in a non-aggressive laundering medium like water, Perc or liquid CO_2. The solvent in the medium must, of course, be non-aggressive lest the textile to be cleaned be damaged. In fact, dry cleaning is the preferred technology for delicate textiles like woolen fabrics, which can be damaged by laundering them in (warm) water.

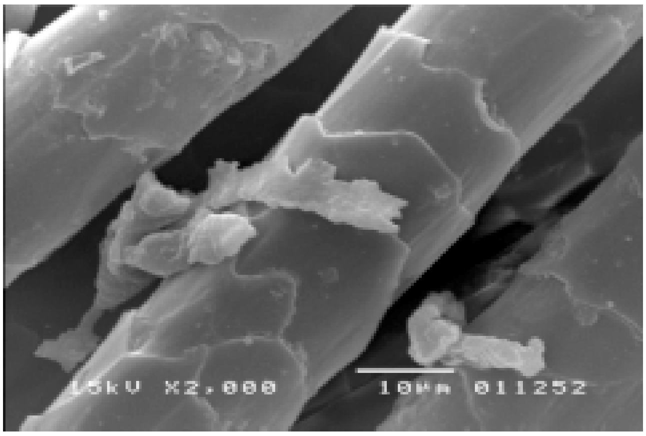
We have selected wool as the standard test material for our detergency monitors because it is considered to be the target fabric for the dry-cleaning industry. To serve as a detergency monitor, the wool fabric must be reproducibly soiled with a well defined dirt substance. As particulate soil for our monitors we have selected clay and carbon black. Clay is a plate-like mineral material which presents great affinity for water. For washing monitors *bandy-black research clay* is normally used. Carbon black, on the other hand, is an organic material produced as a result of partial combustion of natural gas and oil, and which is able to adsorb some amount of water. When large particles are required, water is used to form big carbon black chunks. In our monitors, clay particles adhere individually to the wool fibers while carbon black particles (*flame soot* 101, particle size 95 nm) are first suspended in a fatty substance called *sebum*, a transparent skin-fat that readily dissolves in liquid CO_2, and then pasted on the wool textile. Other particles also form part of this pigment which is adhered to the wool with sebum: iron oxide yellow, iron oxide black and kaolin.

The particle size is an important factor for the fixing of the soil on the textile substrate and also in the removal mechanism. For large particles, of the order of 100 μm and higher, the prevailing soiling mechanism is entrapment [53]. That means that particles would be trapped preferentially between the yarns in the weave. For their removal mechanical action is considered the most important factor. In the case of small particles, the soiling and thus the adherence is mainly due to Van der Waals forces. Those small particles deposit not only on the fibre surface but they can also be found in the microscopic holes and crevices of the fibres. It is for the removal of those particles that the detergency action of surfactants described by the DDM is required.

All the monitors used in the washing test were purchased from the Center for Testmaterials B.V. (Vlaardingen, The Netherlands). The analysis of the monitors with scanning electron microscopy (SEM) provided insight into the particle size distribution (see Fig. 6.1). The clay particle size was estimated between $0 - 10\,\mu$m and it was



(a) CW



(b) SW

Figure 6.1: SEM pictures of the CW and SW monitors (taken by P.F.M. Durville).

observed that they tend to agglomerate and collect in cracks and holes. For the carbon black particles, the size was estimated between $0 - 20\,\mu$m and they are found to be primarily deposited at the surface of the fibres [53].

Cleaning Performance Index (CPI)

In the cleaning industry, detergency action is tested by measuring the Cleaning Performance Index (CPI)[%]. This parameter expresses the performance of a washing process by comparing the intensity of the color of the cleaned monitor with that of the unsoiled monitor, $CPI = 100\%$ by definition. The CPI is calculated from colorimetric data. We use two definitions

$$\begin{aligned} CPI(\Delta Y) &= 100\left(\frac{\Delta Y_{\text{washed-soiled}}}{\Delta Y_{\text{unsoiled-soiled}}}\right) \\ \text{and} \qquad & \\ CPI(\Delta E) &= 100\left(1 - \frac{\Delta E_{\text{washed-unsoiled}}}{\Delta E_{\text{soiled-unsoiled}}}\right), \end{aligned} \tag{6.1}$$

where the parameters ΔY and ΔE, defined below, measure color differences on the monitors. Formulae in (6.1) require all monitors to be measured before an after the washing process.

Color measurements are based on the standard spectral value functions which were officially established by the CIE (Commission International de l'Eclairage) in 1931. Those functions represent the eyes' average capacity to perceive color.

In the retina of our eyes there are three types of color-sensitive cells which react to three different areas of wavelength: red, green and blue. All the others colors we perceive are a blend of those three. In this way, each of those spectral value functions describes one of these colors (see Fig. 6.2) where $\overline{x}$ correspond to red, $\overline{y}$ to green and $\overline{z}$ to blue [54, 55].

Since our sight perceives small angles somewhat differently than large angles, the CIE has for this purpose defined the $2\,^\circ$ and $10\,^\circ$ standard observer geometry.

If the surface reflectance and the light source distribution are known, their product defines color as $C(\lambda)$, which can be now expressed in terms of the standard chromatic

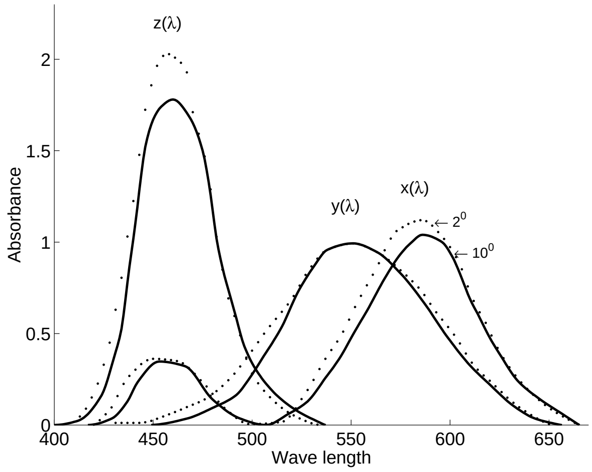


Figure 6.2: Spectral value functions.

values XYZ using the following set of definitions:

$$\begin{aligned} X &\equiv k\int_{\lambda} C(\lambda)\overline{x}(\lambda)\,d\lambda, \\ Y &\equiv k\int_{\lambda} C(\lambda)\overline{y}(\lambda)\,d\lambda, \quad \text{and} \\ Z &\equiv k\int_{\lambda} C(\lambda)\overline{z}(\lambda)\,d\lambda. \end{aligned} \tag{6.2}$$

Here the value of k is chosen so that Y carries the luminescence information (brightness), having a value of 100 for bright white and 0 for black.

The values of XYZ lead to a definite arithmetic description of a color and refer to standard light spectrum (white). That is due to the fact that our perception of colors strongly depends on wether they are viewed in daylight or under artificial light. The most important standardized types of light are:

- Type A for the light emitted by an incandescent light bulb
- C, D 50 and D 65 for different types of daylight.

Unfortunately the XYZ chromatic values are not accurate enough to discriminate the hue and brightness of a color. This problem was partially solved by the CIE with the development of the *standard color table*. In this table a color is described by the coordinates Yxy where Y as mentioned before, describes the brightness of a color and

$$x = \frac{X}{X+Y+Z} \quad \text{and} \quad y = \frac{Y}{X+Y+Z} \tag{6.3}$$

the relative weight of red and green respectively. Since $x+y+z=1$, the z component bears no additional information and it is thus often omitted. Both values of x and y range from 0 to 1.

An analogous concept was used in 1976 for the development of the *Lab* and *Luv color spaces.* In a color space (see Fig. 6.3) all colors can be described by three coordinates (*Lab* or *Luv*). These color spaces are currently the most important methods for a quantified description of a reflected color. Formulae for the conversion of XYZ into *Lab* or *Luv*, according to the new standard, were defined in 1990. *Lab* is obtained via the expressions

$$\begin{aligned} L &= 116\sqrt[3]{(Y/Y_n)} - 16, \\ a &= 500\left[\sqrt[3]{(X/X_n)} - \sqrt[3]{(Y/Y_n)}\right], \\ b &= 200\left[\sqrt[3]{(Y/Y_n)} - \sqrt[3]{(Z/Z_n)}\right], \end{aligned} \tag{6.4}$$

where X_n, Y_n, and Z_n are the standard chromatic values of an off-white body in a specified type of light. In this color space, L describes the brightness, a red-green

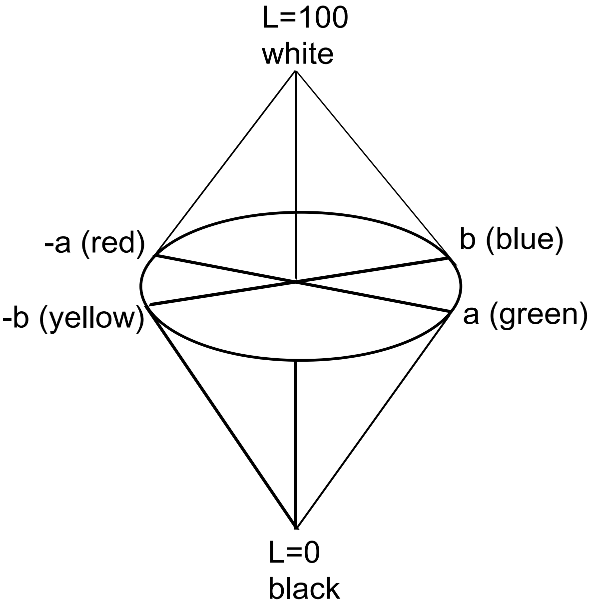


Figure 6.3: CIE*Lab* color space.

values and b the yellow-blue values. The value of L, like Y, ranges from 0 for black to 100 for white; a and b range from -a (red) to a (green) and -b (yellow) to b (blue) respectively. For the estimation of *Luv* values, similar expressions are available for u, v. L remains the same.

In those systems, color differences are quantified by Δ-values and thus in *Lab* we have: ΔL for differences in brightness and $\Delta a, \Delta b$ for differences in color. The color difference between two points is measured by

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}. \tag{6.5}$$

Color differences less than $\Delta E = 1$ are practically invisible while differences of $\Delta E = 3$ and over are clearly visible. The expressions are equivalent for the *Luv* color space.

Although colorimetry is the standard procedure used for textile monitor quantification, there is no general agreement concerning the parameters to be evaluated. Some people use ΔY or equivalently ΔL, while others prefer ΔE, which they consider a more general parameter and therefore more appropriate. Therefore, in order to make a choice it is necessary to consider not only the samples to be measured but also the relevant information that we need to obtain from them.

Nowadays, a number of equipments to perform colorimetric measurements are available in the market. Most of these equipments, provide the XYZ values and also calculate automatically all the other related parameters.

In our test, the colorimetric measurements on both the clay on wool (CW) and sebum on wool (SW) monitors were done using a type C light source and 10° standard observer geometry. Light intensities were obtained with the Spectrocam 75 RE spectrometer. The results were expressed as ΔY or ΔE in series of experiments, depending on whether such series contain only one (SW) or two (SW and CW) types of monitors. If we compare experimental values obtained with only one type of soil, then the brightness (Y) provides the most sensitive detergency criteria whereas, for different soil material of visible differences in color, the detergency action of a surfactant can only be judged and compared in terms of the color difference ΔE.

Testing Equipment

The DDM describes the effects of the Sinner factors M (mechanical action) and C (chemistry) and states that it is the interplay between those two what determines the detergency action on particulate soils.

The mechanical action of the liquid medium on the textile depends on the viscosity of that medium and the stirring action inside the test equipment. In dry-cleaning with liquid CO_2, the volatility of the solvents imposes rigorous restrictions on the values of the Sinner factor T (temperature) and on the pressure inside the washing compartment of the apparatus. Special testing equipments had to be built: a laboratory scale 350 ml test equipment at TNO-RT and a 25 l dry-cleaning machine at TUD-API.

The TNO lab-scale machine is based on the principle of the Atlas Linitest apparatus used for laundering tests with non pressurized solvents like water and Perc. It consists of a thermostatic water bath in which two high pressure autoclaves of 350 ml provided with a thermocouple rotate (see Fig. 6.4). In this equipment, the rotation speed as well as the temperature and washing time can be fixed. The standard washing program used in all the measurements was set to: 35 rpm, 288 K and 15 min.

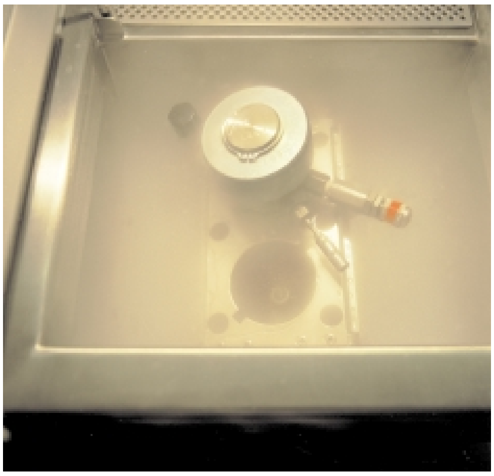


Figure 6.4: TNO-RT linitest equipment.

In all the tests, *a soiled and an unsoiled* monitor were washed together. The purpose of the unsoiled monitors is to check whether or not redeposition occurs. In other words, whether or not the soil was effectively dispersed in the washing liquor. A decrease of the Y for the unsoiled textile value after the washing, which is visually seen as greying, indicates that the soil, although removed from the original stain, has partly redeposited. This redeposition phenomenon has a detrimental effect on the final washing performance.

In the autoclaves, the two monitors and the surfactant (from Kreussler) are placed, taking care that they do not come into contact before the washing cycle starts. For higher levels of mechanical action, two stirring balls with a diameter of 17 mm are also added. The filling of the autoclaves was conducted so that a fixed amount of liquid CO_2 (99.9 % purity) was injected. That was facilitated by cooling down of the autoclaves prior to the liquid CO_2 injection. The autoclaves were weighed before and after the injection so that the total amount of CO_2 was known. The average value was 287 g ± 3 %. The proportion washing-liquor to textile is thus large compare to a conventional washing process.

At the end of the washing cycle the autoclaves were taken out of the Linitest and the washing liquor temperature was measured. After that, they were placed upside down so that once the venting valve is open, liquid CO_2 is first released. The releasing is carried out as slowly as possible in order to avoid ice formation on the textile surface.

The operation of the TUD-API equipment is described fully in van Roosmalen *et. al.* [53]. Essentially it operates a normal type of washing drum inside a 25 l autoclave with facilities for introducing CO_2 at elevated pressures and also for letting the CO_2 out, back to atmospheric pressure.

The experiments are done so that first the monitors, attached to filling white cotton material, are placed into the autoclave. After that, the desired amount of surfactant or formulation is added directly to the textiles pieces and the autoclave is closed. The desired amount of liquid CO_2, 9 Kg in our tests, is injected into the system after which the washing program can start. The standard washing program consists of a 30 min cycle at 75 rpm. The tests were done at 287 K and 50 bar.

Rinsing with pure liquid CO_2

The liquid CO_2 would evaporate when the pressure in the autoclaves is released. The surfactant and all the other less volatile substances, which are present in the medium, would stay behind and precipitate either on the fabric or on the autoclave's walls. Under these conditions, particulate soil material would be redeposited onto the monitors. This effect will affect considerably the CPI.

In order to quantify this redeposition effect on the CPI, we have introduced a rinsing step on the monitors. After the washing procedure, when the washing liquid has already been removed, pure liquid CO_2 is introduced into the autoclaves and the monitors are rinsed for 10 min with low levels of mechanical action. Differences in the CPI prior and after this rinsing step were large. In this way it was established that redeposition of particles but also of surfactant (in concentrated solutions) has an important effect on the CPI.

Preliminary Washing Tests

Results with clay on wool monitors in lab-scale tests

The washing tests with CW monitors seem to be the most simple model system from the point of view of the DDM. The results of a series of such lab-scale experiments, expressed as $CPI(\Delta E)$, are shown in Fig. 6.5. In fact, what it is depicted is the result of testing different formulations of detergent and cosolvent in one experiment.

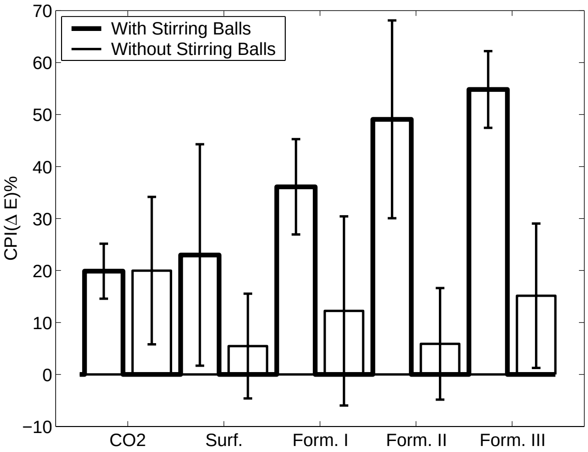


Figure 6.5: CPI(ΔE) for CW washed with pure liquid CO_2, with liquid CO_2-$C_{11}E_3$ and formulations containing this surfactant and a cosolvent (TBP). The formulations labelled I, II and III contained 0.5 wt% $C_{11}E_3$ and 0.5 wt%, 1.5 wt% and, 2.5 wt% of TBP respectively.

The detergency in this system follows the expectations from the DDM for particulate soil, at least at a first glance of the results. There is hardly any detergency in pure liquid CO_2 and the results improve when surfactant is added at concentrations somewhat above the c.m.c, around 0.4 wt%. Mechanical action is identified as a very important parameter. The detergency increases with the mechanical action up to some level, which is a function of the surfactant/co-solvent concentration. At low levels of mechanical action, the detergent action is obscured behind redeposition effects. The importance of redeposition for the test results becomes clear in the interpretation of the experiments with other monitors in terms of the optimum washing formulation, a subject that needs to be discussed first.

Complications with sebum on wool monitors

Clearly, a more complicated situation than with CW monitors arises in washing tests with SW monitors. In these monitors, the insoluble carbon black particles are now glued to the the wool with sebum, a substance which readily dissolves in liquid CO_2.

Our first experiments with this system, shown in Fig. 6.6, gave rather puzzling results.

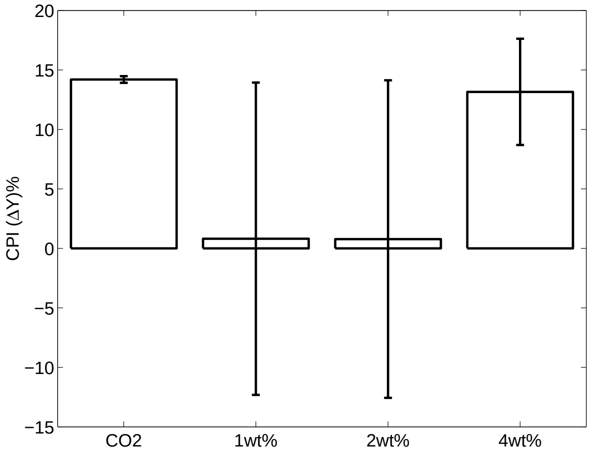


Figure 6.6: CPI(ΔY) for SW washed with pure liquid CO_2 and with liquid CO_2-C_8E_3 solutions.

This is an example of the difficulties that do arise in studying such complex systems. In these experiments, C_8E_3 was used as a surfactant, which seemed to be the most suitable from the homologous C_iE_j series according to Chapter 5. No cosolvent was added to the washing fluid.

The measured CPI's show some detergency action for C_8E_3, but only at the highest concentration. At low concentrations no improvement is measured in this test. Visually however, the surfactant action can be clearly seen. The swatches washed with 1 wt% and 2 wt% of surfactant are, in fact, cleaner than the ones washed with liquid CO_2. But, it is at the highest surfactant concentration that a real clearing up of the monitors is observed in terms of the CPI. Visual assessment of the monitors under a standard light source confirms this observations, which is, moreover, reproducible.

At this point one question arises. Why does the CPI not reflect the visual observations?. To answer this question is necessary to look at the results with the unsoiled monitors that were washed together with the soiled ones.

The decrease of reflection ($Y_{\text{after washing}} - Y_{\text{before washing}}$) displayed in Fig. 6.7 points out the occurrence of redeposition, which is low for liquid CO_2 but sharply increases with the addition of surfactant.

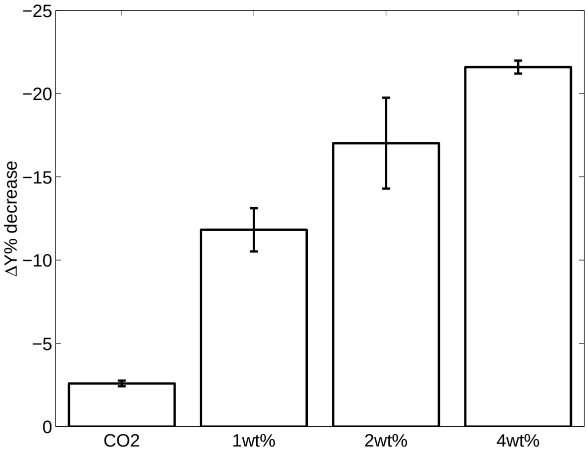


Figure 6.7: ΔY % for the brightness decrease of unsoiled wool monitors washed with pure liquid CO_2 and with liquid CO_2-C_8E_3 solutions.

Consequently, particle redeposition could be the cause of the low CPI values which are measured in Fig. 6.6. However, at high detergent concentration the samples look visually clean and no particle seems to be redeposited. The effect can then only be due to surfactant accumulation. No rinsing is carried out after the washing. Surfactant would certainly precipitate on the textile at the end of the washing process, and this is more likely to occur at high surfactant concentrations. At those concentrations, the binary surfactant- liquid CO_2 system finds itself in the vicinity of the liquid-liquid equilibrium line where small changes in pressure can drive it into a two phase system (see Fig. 4.2), with one of the phases being a surfactant rich phase. Such pressure changes are experienced by the system during the release step. Experimentally, at high surfactant concentrations, after the washing it was observed that the monitors were wet with surfactant, which could also be retrieved at the bottom of the autoclave. Therefore the excess of surfactant or surfactant accumulation on the monitors, which reduces the scattering of light of the fibres, is the other factor contributing to the discrepancy between the CPI's and the visual assessment.

Reinterpreting these experiments we concluded that C_8E_3 does indeed have detergency action in liquid CO_2 but it does not stabilize the colloidal particles. The measured effect is, unfortunately, counteracted by the occurrence of redeposition. Particle redeposition can be overcome by the use of highly concentrated liquid CO_2-surfactant solutions. These, however, cause another problem, surfactant immiscibility.

In order to solve the problem of particle redeposition, more carbophilic surface-active molecules and other cosolvents, could be added to the system. Those cosolvents would increase the soil carrying capability of the washing fluid. Moreover, as discussed in Chapter 2, they would also have an effect on the dynamics of micelle formation. In this way particle redeposition can be tackled without the adverse consequences of surfactant immiscibility.

Comparing the SW and CW detergency results

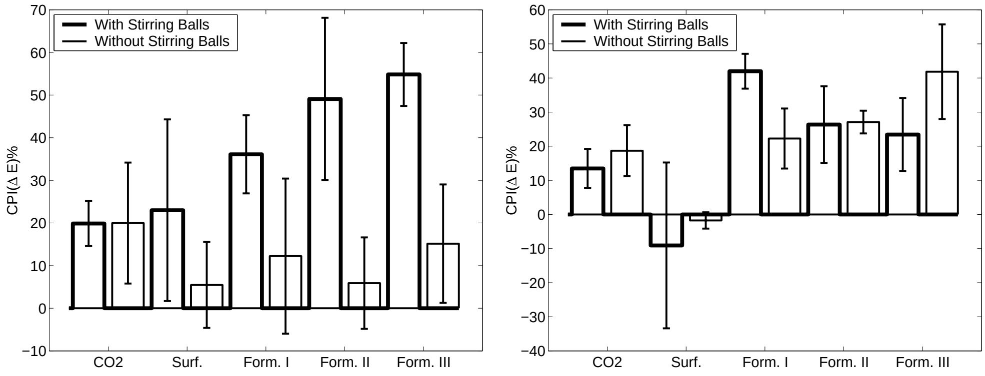
Having identified the problems that are faced during a washing test and some possible solutions to them, we did a series of experiments in order to establish the effect of co-solvent addition combined with mechanical action on the washing performance. With this purpose, 1-tert.Butoxy-2-propanol (TBP, 99% purity, Fluka) was chosen as a co-solvent. This product is one of the main components of Rynex, a commercially available product used in the dry-cleaning industry, that shows high solubility in liquid CO_2 ($>> 4\,\mathrm{wt}\%$) at the experiment's conditions. As a surfactant, $C_{11}E_3$ from Kreussler was selected. Its lower c.m.c ($\simeq\ 0.4\,\mathrm{wt}\%$) compared to C_8E_3 makes it a preferred candidate of surfactant producers.

In the tests 0.5 wt% of $C_{11}E_3$ was added alone and in formulations. The formulations labelled I, II and, III contained, apart from the surfactant, 0.5 wt%, 1.5 wt% and, 2.5 wt% of TBP respectively.

The results of this series of washing test, carried out for SW monitors and CW monitors are shown in Fig. 6.8.

For both monitors, once again, we can see that pure liquid CO_2 has little effect on particle removal. Upon surfactant addition, the results diverge. While for CW the expected increase in the CPI is observed, for SW negative values are observed, which must be caused by redeposition, an effect, which is much more pronounced in the case of a complex soil like sebum.

Looking at the results we see that added cosolvent did certainly help to counteract



(a) CW *(b)* SW

Figure 6.8: CPI(ΔE) for CW and SW washed with pure liquid CO_2 and with liquid CO_2-$C_{11}E_3$ formulations solutions.

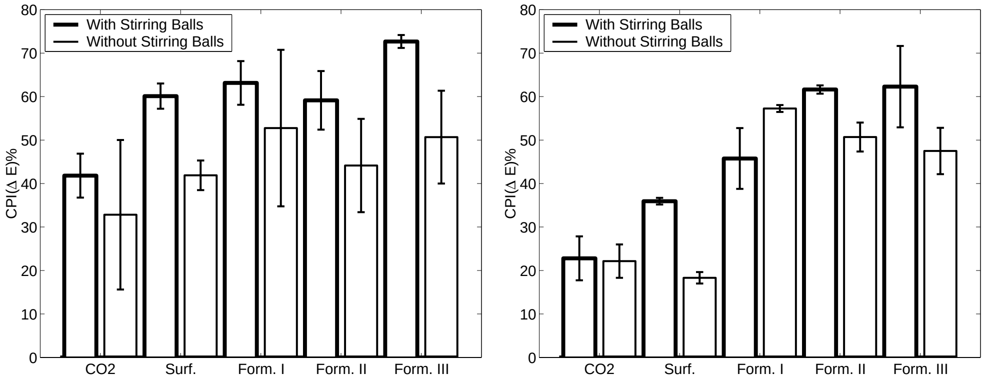
the effects of redeposition.

For both monitors significant increases of the CPI are observed at high levels of mechanical action. However some differences between the monitors immediately arise. In the CW monitors, where the soil removal can only be due to surfactant action and will not be favored by the dissolution of other soil components, the combined effect of surfactants and mechanical action is clearly visible. At low levels of mechanical action detergency is very little or does not take place at all. Then, adding surfactant and cosolvents can only promote redeposition. That explains the lower CPI's than with pure liquid CO_2. But at high levels of mechanical action, where the surfactant working conditions are optimum, detergency begins to be effective and the cosolvent antiredeposition effect becomes important. However, this effect is limited once redeposition has been overcome. No further CPI increase is observed upon addition of extra cosolvent.

In the case of the SW monitors, particle removal does always occur in the system, even at low levels of mechanical action. The dissolution of the sebum in liquid CO_2 causes particle detachment from the textile. At low levels of mechanical action, the increasing amount of TBP in the formulations counteracts the effect of redeposition and high CPI values are obtained. At high levels of mechanical action, where the surfactant works at its optimum level, high detergency and thus high degree of redeposition can occur. Under those circumstances, the cosolvent is less effective because of the faster heterocoagulation of the small carbon black particles on the clean fabric fibers. Increasing cosolvent concentration, this effect becomes more predominant and thus lower CPI's are observed.

To further eliminate the effect of redeposition, the same samples were compared after a rinsing step with pure CO_2. During the rinsing, the so called prespotting effect, discussed in Chapter 1, comes into being in the precipitated detergent that covers the textile after the release of the CO_2 from the autoclaves. Additional particle removal is promoted by this effect.

Fig. 6.9 shows the significant increase in the CPI's, which is the effect of rinsing. For the CW monitors, the increase is particularly important at high levels of mechanical action during the first washing operation. The positive effect of cosolvent addition appear to become less significant and only at high concentrations an extra increase of the CPI is found. In the case of the SW monitors, positive CPI's values are now obtained and these are greatly improved by the addition of cosolvent, preferentially under high levels of mechanical action. Like described before for the CW, this improvement has a limit. The levelling off of the CPI values with increasing cosolvent concentration is seen again.



(a) CW *(b)* SW

Figure 6.9: CPI(ΔE) for CW and SW washed with pure liquid CO_2 and with liquid CO_2-$C_{11}E_3$ formulations solutions **after rinsing**.

These results for the SW and CW monitors after rinsing verify that particle redeposition played a mayor role in the washing performance. Considering that the rinsing is carried out under the same conditions for all the samples, the only explanation for the differences between the samples washed with and without stirring balls and between the the different surfactant formulations is redeposition. During the rinsing, prespotting could only have a significant effect on particles, which have been redeposited on the monitor surface. Those particles, which are loosely attached to the textile surface, are more easily removed that the deposited soil.

SW and CW Detergency Results on the Semi-Pilot Scale

Considering the experience with the lab-scale washing tests, we designed a test method for the semi-pilot equipment so that emphasis was put on the surfactant's detergency action. These experiments compared pure liquid CO_2 and formulation III for SW and CW monitors. Using formulation III, we expected to minimize the effect of redeposition. The results of such tests are presented in Fig. 6.10. As a comparison, the results on the same monitors and under the same conditions with a cosolvent/additive formulation obtained by Van Roosmalen (API) are included.

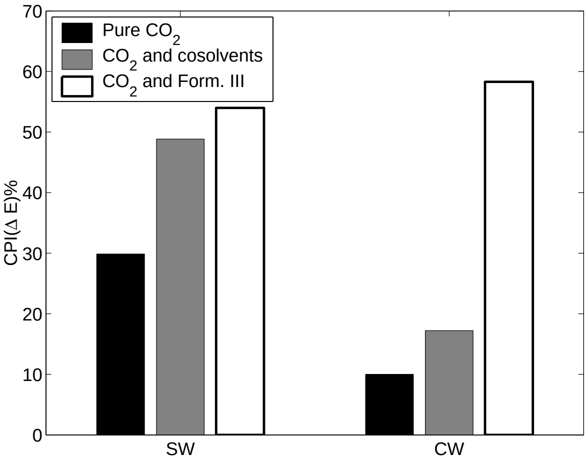


Figure 6.10: CPI values for SW and CW washed with pure liquid CO_2 and with formulations III in comparison with those of van Roosmalen (API).

The results show that, similarly to the lab-scale tests, pure CO_2 has little effect on particle removal. However, with the addition of cosolvents and water some improvement is observed, because of the dissolution of the sebum in the washing fluid. When a formulation was used, significantly higher washing performances were reached for the CW swatches, clearly showing the detergency action of surfactants. The lower CPI for the SW monitors, although important, points out, once more, the effect of carbon black redeposition.

Van Roosmalen *et al.*[53] proved that for the removal of other soils than particles, it is only necessary to add cosolvents and small amounts of water. Besides, they also observed that big particles like sand (size 20-100 μm) can be removed by mechanical action alone. However, they have also come to the conclusion that small particulate soil can *only* be removed with the help of surfactants. This is exactly what is predicted by the DDM-model.

Mechanical action

Although we have seen that the results of the semi-pilot washing test exhibit the same tendencies as on the lab-scale, the detergency is considerably lower. Looking at Fig. 6.11 we observe that this difference can be as high as 14%.

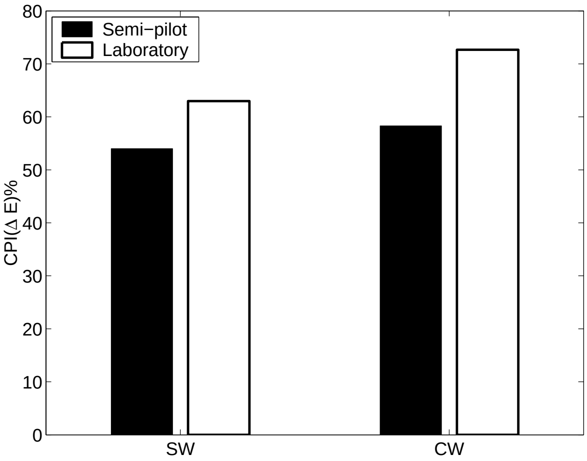


Figure 6.11: Comparison of CPI values of the laboratory and semi-pilot tests for SW and CW washed with liquid CO_2-formulation III.

These experiments were carried out under comparable conditions of pressure and temperature and identical surfactant formulations were used. The only explanation for the significant difference in washing performance can be found in the mechanical action exerted on the fibres. As discussed previously, the stretching effect of the tumbling inside the rotating drum is drastically reduced when the two media, liquid-gas, have similar densities. Looking at the impact velocity (V_{imp}) [53], a measure of the mechanical action exerted on a given piece of textile, in Table 6.1 we can clearly see this effect for CO_2. Comparing the value of $\Delta\rho$ for CO_2 with that of water ($\Delta\rho$ = 999 Kg/m^3) or Perc ($\Delta\rho$ = 1618 Kg/m^3) we see that mechanical action of the machinery is much less in liquid CO_2. Those differences have to be taken into account when comparing washing results. It is interesting to notice that for CO_2, high rotation speeds have a negative effect on the impact velocity.

Table 6.1: Impact velocity of a fabric (V_{imp}) inside a rotating drum.

CO_2	65 rpm V_{imp}[m/s]	75 rpm V_{imp}[m/s]	85 rpm V_{imp}[m/s]
$P = 45\,\text{bar}$, $T = 283\,\text{K}$ $\Delta\rho = 726\,Kg/m^3$	0.99	1.16	1.11
$P = 71\,\text{bar}$, $T = 302\,\text{K}$ $\Delta\rho = 317\,Kg/m^3$	0.67	0.71	0.62
$P = 75\,\text{bar}$, $T = 311\,\text{K}$ One phase $\rho = 245\,Kg/m^3$	0.61	0.62	0.51

We can then conclude that it is the contact between the steel balls and the textile which produced the required stretching of the fibres in the lab-scale tests. The comparison of these two tests clearly signals the fundamental role of mechanical action on the optimum detergent performance.

The Qualification Test for the Detergent Design

Specified target and delivered results

In the described washing tests we have learned to cope with redeposition (by rinsing and by the use of cosolvents) and eliminate its effect from the measured results. Surfactants must be added to a detergent formula for the removal of particulate soils and they are helpful for extracting molecular soils and solubilizing theses in their micelles. Surfactants will not be effective without mechanical action during the washing process and the level of mechanical action is essential, both for the redeposition of particulate dirt on the textiles and for the working of the detergent.

All these observations must be taken into account in a final "qualification" test of the designed detergent for dry-cleaning in liquid CO_2 solutions.

A test like that would consist of a washing and a rinsing step. Times and pressures in these steps were as before. Monitors SW and CW were used to measure the most difficult detergency effect: that on particulate soils. In addition to the rinsing, addition of cosolvent was necessary to eliminate the unacceptable level of redeposition at the end of the washing step.

The surfactant was added as in detergent formulation III, together with TBP as a cosolvent and in the same concentrations as before (i.e. 0.5 wt% $C_{11}E_3$ and 2.5 wt% TBP in liquid CO_2). The TBP also served to dissolve water and molecular soils (including sebum) in the medium and prevent their redistribution in the textile. The mechanical action was at the optimum level for the laboratory apparatus (35 rpm in the Linitest machine, with steel balls in the autoclaves) and 75 rpm in the pilot equipment. Pressures and temperatures were as in the previous tests. Results of such test under optimal process conditions are shown in Fig. 6.12.

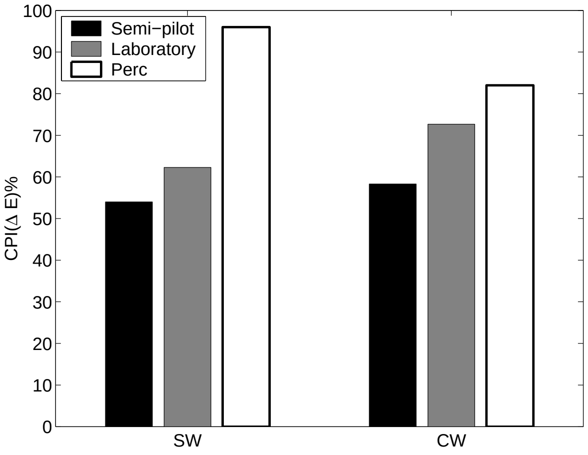


Figure 6.12: Comparison of CPI values of the laboratory and semi-pilot tests for SW and CW, washed with liquid CO_2-formulation III and with Perc.

It is seen that dry-cleaning in liquid CO_2 is possible under those conditions: using a detergent which has been designed on the basis of the dynamic detergency model and its requirements for the static and dynamics aspects of adsorption, micellization and solubility of the surfactant. The higher CPI values which are obtained in the laboratory-scale experiment compared with the pilot-scale washing process indicate the importance of mechanical action in this detergent formulation. The Sinner factors C and M must be optimized together to obtain the best washing results.

Relevant in terms of target specifications is the observation that the results with this detergent in CO_2-based washing fluids are comparable with those for a completely optimized Perc-based formula - even for the most difficult types of stains. This is the standard which is demanded by industrial dry-cleaners for the application of the new technology.

An economical analysis of the two competing process (Perc and CO_2) is found in a PhD-thesis (Delft 2003) by van Roosmalen [16]. She argues that the higher cost of the elevated pressure in the CO_2 technology can be compensated by the less intense need for drying and pressing garments after the laundering process in liquid CO_2.

Summarizing our test results with the designed detergent for dry-cleaning in liquid CO_2 we conclude that the detergency of the formula which we have developed here meets the target specifications for the design. *Following the methodological pathway for a product design (see Fig. 3.1) and taking the Dynamic Detergency Model as our scientific basis we have successfully obtained a detergent formula for dry-cleaning in liquid* CO_2. The formula contains the surfactant $C_{11}E_3$ at the concentration of 0.5 wt% (which exceeds the c.m.c) and the cosolvent TBP to make up the required percentage of additive which is needed for enough carrying power of soils in the washing fluid. In liquid CO_2 this formula shows the target performance, both in lab-scale and in semi-pilot washing tests. Very significant, from an economic viewpoint, is the fact that detergency is comparable with that of the standard Perc technology. This is indeed a remarkable result, considering that no further optimization of our detergent formula has been carried out yet. Given the relative drawbacks of liquid CO_2 like a low density and low viscosity, one could suspect that the present procedures for dry-cleaning in Perc can, in fact, still be improved on the basis of the DDM. But in the EET-project we have reached a plausible alternative at this stage, which seems toxicologically and environmentally more attractive than the Perc technology could ever become.

Chapter 7

Theses about Detergency in Liquid CO_2

Outlook

Ours has been the *ab initio* development of a new technology for dry-cleaning. Technical improvements on the present results may be expected from many different directions. A chemical approach involves fine tuning of the geometry of the detergent molecules. These must be fitting together in micelles and admicelles with their carbophobic tails and their carbophilic head groups. But they must not fit together all too snugly. For then the micelles become too stable, the molecules too immobilized and the surfactant behaves as an emulsifier rather than a detergent.

Branched instead of linear alkane moieties could create an optimum head size group and head group solubility in liquid CO_2. Another concept for further improvement is optimalization of the distribution in the length E_j of the polyethyleneoxide chains of the surfactant. We found that the polydispersity of the carbophobic tail lengths affects the micellization times and concentration, and according to the DDM these properties should be matched with the mobility and the flow of the surfactant admicelle. A third concept which can be explored to improve the detergent is regulation of the hydrophilicity in the cores of the micelles by using co-oligomers of ethylene-oxides and propylene-oxides for the carbophobic tail moieties in the surfactant. Water is always present in the dry-cleaning process because of the moisture in the textiles. A detergent must be able to handle the water content by solubilizing it in the micelles, rather than emulsifying it in liquid water drops. These properties can be controlled via the composition - consisting of carbophobic tail moieties in combination with cosolvents and water - in the micellar cores. No other members of the homologous series of C_iE_j - surfactants and no other cosolvents than TBP were systematically tested for optimization of these effects.

The high washing performance in the tests was not surprising from a theoretical point of view. It underlines that a surfactant, which is designed so that it satisfies all the requirements for detergency in liquid CO_2 established by the DDM, is an effective detergent. This observation demonstrates the validity of the model and the importance of dynamic aspects in the detergency theory. Both moieties of the surfactant molecule were selected so that their effect on the solubility, surface-activity and dynamics of micellization of the whole molecule were taken into account. As a result of this step by step analysis, the C_iE_j molecules arose as the most plausible choice. This became our Basis of Design for the detergent.

The detailed considerations for defining an effective detergent were based on solubility measurements (phase diagram and light scattering), structure-effect relations in interfacial tensions and dye dissolution experiments in liquid CO_2 solutions. This was needed for a Detailed Design and produced quantitative data on the surface activity and the micellization in liquid CO_2 solutions of the individual C_iE_j - compounds, which belong to the proposed class of detergents. Within the range of suitable candidates according to the DDM ($6 \leq i \leq 12$ and $j \geq 3$), the choice of $C_{11}E_3$ was guided by economical reasons. Its low c.m.c and the availability in kilograms quantities, which are required for systematic dry-cleaning tests, made it the preferable candidate in the eyes of the surfactants' producers. The selection of the cosolvent was based on simple criteria. TBP is a compound which is more soluble in liquid CO_2 than the required 4 wt%, it is commercially available and the product is already used by the dry-cleaning industry (which takes care of potential safety problems in its application as a cosolvent for our detergent formula).

The strong temperature and pressure dependency of the solvent power is characteristic for a near critical phase like liquid CO_2. This imposed a number of restrictions in the design and, consequently, in the performance of the detergent. Therefore, as important as the detergent itself, is the set op parameters (temperature and pressure) which must be specified. Only under these specific, constant conditions, the surfactant properties (solubility and surface-activity) can be assured to give the required detergency.

However, tuning the solvent power characteristic of dense CO_2, by varying the pressure in the system (at constant temperature), could open new alternatives for process design when the principles of the DDM are applied. In extraction operations, for example, selective separations are already performed by just adjusting the pressure. But the same idea can be applied to the carbophilic and carbophobic moieties in a surfactant molecule. In dry-cleaning applications, one could think of a process design in which pressure waves of the order of 1 Hz frequency, far away from ultrasound, modulate the solvent power of liquid CO_2 (i.e. Fig. 7.1). At the maximum pressure points in the sinusoidal waves the solvent power is high. The near critical liquid acquires a higher density and becomes a better solvent for the lyophobic (carbophobic) moiety in the amphiphilic molecules of the added detergent. This molecule then turns into a normal solute and is no longer a surfactant. And at the minimum pressure points, where the near critical liquid is almost like the gas phase and exhibits poor solvent characteristics, the molecule does effectively act as surfactant again. As a surfactant, and at a concentration above the c.m.c., the detergent compounds adsorb strongly at more "polar" interfaces, in the form of an admicelle and forms micelles in the solution. The local concentration of the surfactants in the admicelle, at the surface of the solid material, exceeds the average solution concentration more than thousand-fold. Which implies, at a modulation frequency of 1 Hz, that 1 second later, at the maximum of pressure, we will have several orders of magnitude difference between the local concentration at the interface and in the solution, of the surfactant, which has now become an ordinary solute. There is supersaturation of the solution at the interface and a rapid diffusion transport into the solution.

The oscillatory pressure waves ensure that such a system does never reach equi-

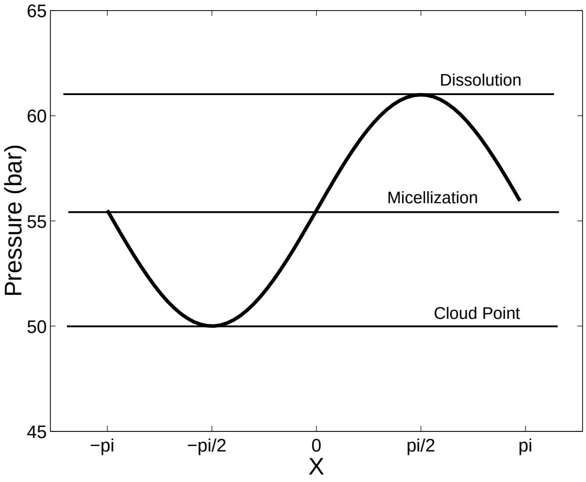


Figure 7.1: Effect of Pressure waves on C_8E_3 behavior in liquid CO_2. Based on data taken from Fig. 4.5 (b) at a concentration of 6 ml/l.

librium. A permanent situation of periodic adsorption-desorption non-equilibrium is created at the interface. And this, in line with the DDM, would concentrate local supersaturation and Marangoni flows at the interface. These are the requirements for effective detergency, i.e. for accelerated mass transfer from the solid surface into the solvent. We speculate, on the basis of our experience with the DDM, that surfactants will be effective promoters for the rate of mass transfer processes in near critical extraction solvents when pressure waves are used to modulate their surface active properties.

One of the advantages of such an innovative strategy for the dry-cleaning process could be that wear of textiles would be avoided. Wear is an essential consequence of the mechanical action which creates the dynamics in the detergency model. This is a very important issue, specially for delicate garments, in the dry-cleaning industry. The key element in such a process would be a surfactant that is not only designed to satisfy all the requirements of the DDM. As extra target specification for the application in an oscillatory pressure process with near critical CO_2 it must also exhibit the right solubility - pressure relations for the carbophobic and carbophilic moieties of the detergent molecule in the pressure window $45 < \mathrm{P} < 65\,\mathrm{bar}$ at temperatures near the critical value of $\mathrm{T} = 304\,\mathrm{K}$.

In the technical evaluation of the surfactant design for conventional dry-cleaning in liquid CO_2 (i.e. with washing tests involving tumbling and flow of the washing fluid), the synergistic effect of the Sinner factors "Mechanical action" and "Chemistry" was identified as the key parameter for the washing performance. This observation, again, highlights the importance of the DDM for the understanding of laundering process. The lowest values for the cleaning performance index (CPI) were obtained for the tests with low levels of mechanical action. In fact, there is no detergency without surfactants, but also no cleaning whenever the mechanical action in the washing liquid is too small.

The standard intensities of the mechanical action in machinery designed for laundering with water or with perc were insufficient for optimum dry-cleaning in liquid CO_2. This was discovered in the work with the pilot dry-cleaning apparatus, as described by van Roosmalen *et al.*[53] and corroborated by our own laboratory studies. What counts is the effect of the mechanical action in terms of the elongational forces which are exerted on the textile cloth. They will depend on the size of the cloth (the monitors!) and the flows in the washing liquid. In the case of liquid CO_2 the deformation of the textile is much lower than in water or perc. That is because of the lower viscosity and similar densities of the liquid and the gas phase in the tumbling drum of the washing machine. As a consequence the stretching of the fibres, essential for detergency action, is drastically reduced. But after the treatment of cleaning and drying there is less wrinkling of the textile cloth.

Unfortunately, the effect of mechanical action can not be increased easily. It is impossible to use metal impellers to move the fluid without damaging the textiles. Without rethinking and redesigning the apparatus for dry-cleaning in liquid CO_2 on the basis of the dynamic model (involving flow inside the micropores of the textile itself), the route towards increasing efficiency for the washing process must be expected from systematic work on the improvement of detergent formulations. Above, we have indicated some opportunities for extended research in this area. Such efforts would, without great doubt, lead to the development of even more efficient detergents.

From the point of view of physical-chemistry our research contributed deeper insight in factors like the solubility of surfactants and their relation to detergency, and in particular in surfactant micellization in a non-polar solvent like liquid CO_2. Our results show that C_iE_j micelles are formed in liquid CO_2 without the addition of water. We proved that the interior of these aggregates exhibit polarities in the same range as e.g. ethanol and, therefore, polar substances can be effectively dissolved.

Detergency, and surfactant behavior in non-polar solvents in general, are underdeveloped research subjects, where not very much of what people believe is really known. In the development of an application like dry-cleaning, theories and concepts are - more often than not - extrapolated erroneously from the situation in water and, without correcting the terminology or adjusting the properties of would be detergent molecules for their desired interaction with a particular solvent. It could indeed be of some significance that the basic notions about laundering textiles and, in particular, the theoretical insights of the DDM could be applied successfully in this thesis, for the first time, to the methodical design of a detergent in a solvent different than water. This result has extended the scope of the DDM and could have innovative impact for a broader range of technological applications, as a demonstration of speeding up mass transfer process by using surfactant systems.

Theses

As is customary in dissertations from the Delft Laboratory of Physical Chemistry, we have summarized our ideas in the following theses:

The Dynamic Detergency Model was developed for the understanding of detergents in aqueous systems, but it can be generalized for mass transfer technologies involving other solvents.

Timmerman developed the DDM-mechanism to understand why detergents speed up laundering processes above the threshold of diffusion limitation. But these ideas about the dynamics of flow in adsorbed surfactant layers along the surfaces of narrow pores can be applied in many other technologies which involve mass transfer from a solid surface into a liquid. The model specifies properties for the surfactants that are effective in such processes, and when other solvents are used these surfactant characteristics must still be present.

The presence of water and other polar cosolvents can make a surfactant in a non-polar medium ineffective as a detergent and change it into an emulsifier for W/O emulsions.

The inside of an ”inverted” micelle in an apolar solvent is a more polar and hydrophilic medium than the rest of the system. Water molecules can be solubilized in the cores of such micelles, but these cores can also be so hydrophilic that they swell and form O/W emulsions under those conditions. The latter behavior is certainly expected with surfactant molecules that will be ionized in polar solvents, and that is why such compounds can not be effective detergents in apolar media. The stability of the emulsion drops causes sluggish demicellization dynamics and according to the dynamic model that is a drawback for good detergency.

Extraction (of molecular substances) and detergency (i.e. removal of colloidal particles) from a solid surface into a flowing fluid are both speeded up by mechanical action. The Dynamic Detergency Model explains why the mass transfer rate in surfactant solutions can be increased beyond the limit of diffusion through boundary layers.

Effective laundering or dry-cleaning processes must rapidly remove dirt and soils from the microscopic pores in textiles materials. If the mass transfer from the textile to the washing fluid was limited by diffusion boundary layers such a process would take hours. The combination of mechanical action which leads to slip flow in narrow pores and the presence of surfactants in a mobile admicelle which covers the interface between the solid and the solution provides a transport mechanism that shunts out the diffusion limitation inside the porous materials.

An effective detergent in a specified medium (like liquid CO_2) can be designed on the basis of the Dynamic Detergency Model and the group contributions to the molecular properties of a surfactant, which are determined by the HLB-value and can be converted into, e.g., a carbophobic/carbophilic balance.

A surfactant molecule consists of a lyophobic and a lyophilic moiety and is, therefore, sparingly soluble in any solvent. As an effective detergent such a surfactant must be capable of micellization and adsorption in mobile admicelle layers. Its special properties in adsorption free energy and micellization are determined by the size or shape of the two moieties and by the balance between the opposing properties of the two. These properties can be obtained experimentally from solubility data of the separate substances which constitute the halves of the detergent molecule or from group contributions to the interactions with the solvent as described in regular solution and analogous theories.

Bibliography

[1] N. Marks and D. Luhring. Dry-cleaning. Electronic Citation, 2003.

[2] K. Johnson. *Dry-Cleaning and Degreasing Chemicals and Processes.* Park Ridge, 1973.

[3] G. Frens and A. ven der Put. Adhesion of polymers coils to a solid surface: influence of the depletion effect. *J. Adhesion Sci. Technol.*, 12(12):1355–1360, 1998.

[4] A. Timmerman. *Understanding Detergency The Role of Surfactant Dynamics in Efficient Textile Cleaning.* Thesis/dissertation, Delft University of Technology, 2002.

[5] N. M. van Os. *Unpublished results.*

[6] G. Frens and J.Th.G.Overbeek. Repeptization and the theory of electrocratic colloids. *J. Colloid Interface Sci.*, 38(2):376–387, 1972.

[7] H. R. Kruyt. *Colloid Science*, volume 1, page 358. Elsevier, Amsterdam, 1952.

[8] M. F. Cox. Surfactants. In K. R. Lange, editor, *Detergents and Cleaners a Handbook for Formulators*, book chapter 3, pages 43–90. Hanser Publishers, 1994.

[9] E. W. Kaler. Basic surfactant concepts. In K. R. Lange, editor, *Detergents and Cleaners a Handbook for Formulators*, book chapter 1, pages 1–28. Hanser Publishers, 1994.

[10] D. F. Evans and H. Wennerström. Phase equilibria, phase diagrams, and their application. In *The Colloidal Domain Where Physics, Chemistry, Biology and Technology Meet*, Advances in Interfacial Engineering, book chapter 10, pages 407–450. VCN publishers, 1994.

[11] R. J. Stokes and D. F. Evans. *Fundamentals of Interfacial Engineering.* Advances in Interfacial Engineering. Willey-VCH, New York, 1997.

[12] Statutory instruments 2003 sor/2003-264 to 287 and si/2003-142 to 143. *Canada Gazette*, 137(17):2038–2251, 2003.

[13] W. Leither. Designed to dissolve. *Nature*, 405(6783):129–130, 2000.

[14] R. J. Hunter. *Introduction to Modern Colloid Science.* Oxford University Press, Oxford, 1993.

[15] H. Sinner. *Vom Umgang mit Hauhaltwasmachinen.* Haus und Heim Verlag, Hamburg, 1960.

[16] M. J. E. van Roosmalen. *Dry-cleaning with high-pressure carbon dioxide.* Thesis/dissertation, Delft Univeristy of Technology, 2003.

[17] P. Brasser. *Recycling of surfactants from wastewater of laundry washing plants.* Thesis/dissertation, Delft University of Technology, 1998.

[18] H. M. Willemen, A. T. M. Marcelis, and E. J. R. Sudhölter. Thermodynamics of micellization of cholic acid based facial amphiphiles carrying three permanent ionic head groups. *Langmuir*, 19(7):2588–2591, 2003.

[19] A. M. Al Sabagh, N. Gh. Kandil, A. M. Badawi, and H. El-Sharkawy. Surface activity and thermodynamics of micellization and adsorption for isooctylphenol ethoxylates, posphates esters and their mixtures with n-diethoxylated perfluorooctanamide. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 170(2-3):127–136, 2000.

[20] J. Lyklema. *Fundamentals of Interface and Colloid Science*, volume 3 (page 4.72) of *Liquid-Fluid interfaces.* Academic Press, London, 1991.

[21] D. H. Everett. *Basic Principles of Colloid Science.* Royal Society of Chemistry Paperbacks. Royal Society of Chemistry, 1988.

[22] L. D. M. van den Brekel. *Hydrodynamics and mass transfer in domestic drum type washing machines.* Thesis/dissertation, Delft University of Technology, 1987.

[23] C. Cheikh and G. Koper. Stick-slip transition at nanometer scale. *Phys. Rev. Lett.*, 91(15):156102, 2003.

[24] N. V. Churaev, V. D. Sobolev, and A. N. Somov. Slippage of liquids over lyophobic surfaces. *J. Colloid Interface Sci.*, 97(2):574–581, 1984.

[25] Y. Zhu and S. Granick. No-slip boundary condition switches to partial slip when fluid contains surfactants. *Langmuir*, 18(26):10058–10063, 2002.

[26] J. C. J. van der Donck, A. So, and G. Frens. The influence of stretching on salt release from porous yarns. *Tenside Surfactants Detergents*, 35(2):119–122, 1998.

[27] V. A. Nierstrasz. *Marginal Regeneration.* Thesis/dissertation, Delft University of Technology, 1996.

[28] D. J. M. Bergink-Martens and G. Frens. Dynamic surface tension of a detergent solution in its relation to washing performance. *Tenside Surfactants Detergents*, 34(4):263–266, 1997.

[29] Y. Moroi. *Micelles Theoretical and Applied Aspects.* Plenum Press, New York, 1992.

[30] A. Patist, S. G. Oh, and D. O. Shah. Kinetics of micellization: its significance to technological processes. *Colloids and Surfaces A: Physicochem Eng. Aspects*, 176(1):3–16, 2001.

[31] S. Pandey, B. Palla, A. Patist, B. M. Singh, and D. O. Shah. Engineering the surfactant film at the interface using molecular interactions among polar groups and hydrocarbon chains for the improved disperson stability of oil/water and solid/water dispersions. Surfactants in Solution Symposium (SIS). UB - oficina de congresos, 2002.

[32] J. Grievink and C. P. Luteijn. *Conceptual process design: instruction manual.* Delft, 2000.

[33] N. F. M. Roozenburg and J. Eekels. De structuur van het ontwerpproces. In *Produktontwerpen, structuur en methoden*, book chapter 5, pages 75–112. Lemma, 1996.

[34] J. A. Hyatt. Liquid and supercritical carbon dioxide as organic solvents. *J. Org. Chem.*, 49(26):5097–5101, 1984.

[35] S. R. P. da Rocha, K. L. Harrison, and K. P. Johnston. Effect of surfactants on the interfacial tension and emulsion formation between water and carbon dioxide. *Langmuir*, 15(2):419–428, 1999.

[36] K. L. Harrison, S. R. P. da Rocha, M. Z. Yates, K. P. Johnston, D. A. Canelas, and J. M. de Simone. Interfacial activity of polymeric surfactants at the polystyrene-carbon dioxide interface. *Langmuir*, 14(24):6855–6863, 1998.

[37] R. Fink, D. Hancu, R. Valentine, and E. J. Beckman. Toward the development of "CO_2-philic" hydrocarbons. 1. Use of side-chain functionalization to lower the miscibility pressure of polydimethylsiloxanes in CO_2. *J. Phys. Chem. B*, 103(31):6441–6444, 1999.

[38] T. Sarbu, T. J. Styranec, and E. J. Beckman. Design and synthesis of low cost, sustainable CO_2-philes. *Proceedings of the Fifth International Symposium on Supercritical Fluids*, 2000.

[39] A. F. M. Barton. *Handbook of solubility parameters and other cohesion parameters.* Boca raton, Florida, 1983.

[40] A. W. Francis. Ternary systems of liquid carbon dioxide. *J. Am. Chem. Soc.*, 58(12):1099, 1954.

[41] K. Harrison, J. Goveas, and K. P. Johnston. Water - in - carbon dioxide microemulsions with a fluorocarbon - hydrocarbon hybrid surfactant. *Langmuir*, 10(10):3536–3541, 1994.

[42] M. Orchin, F. Kaplan, R. S. Macomber, R. M. Wilson, and H. Zimmer. *The Vocabulary of Organic Chemistry, page 429.* John Wiley and Sons, Toronto, 1980.

[43] K. A. Consani and R. D. Smith. Observations on the solubility of surfactants and related molecules in carbon dioxide at 50 °C. *J. Supercrit. Fluids*, 3(2):51–65, 1990.

[44] J. Eastoe, A. Paul, S. Nave, D. C. Steytler, B. H. Robinson, E. Rumsey, M. Thorpe, and R. K. Heenan. Micellization of hydrocarbons surfactants in supercritical carbon dioxide. *J. Am. Chem. Soc.*, 123(5):988–989, 2001.

[45] B. Kitiyanan, J. H. O'Haver, J. H. Harwell, and S. Osuwan. Adsolubilization of styrene and isopropene in cetyltrimethylammonium bromide admicelle on precipitated silica. *Langmuir*, 12(9):2162–2168, 1996.

[46] A. Hebach, A. Oberhof, N. Dahmen, and E. Dinjus. Correlation between structure and interfacial tension of aeos in compressed carbon dioxide. International Detergency Conference, pages 267–270. wfk-Forschungsinstitut fur Reinigungstechnologie, 2003.

[47] M. Z. Yates, E. R. Birnbaum, and T. M. McCleskey. Colored polymers microparticles through carbon dioxide-assisted dyeing. *Langmuir*, 16(11):4757–4760, 2000.

[48] P. Somasundaran and S. Krishnakumar. Adsorption of surfactants and polymers at the solid-liquid interface. *Colloids and Surfaces A: Physicochem Eng. Aspects*, 123-124:479–489, 1997.

[49] D. Pramanick and D. Mukherjee. Molecular interaction of methylene blue with triton x-100 in reverse micellar media. *J. Colloid Interface Sci.*, 157(1):131–134, 1993.

[50] L. Qi and J. Ma. Investigation of the microenvironment of nonionic reverse micelles using methyl orange and methylene blue as absorption probes. *J. Colloid Interface Sci.*, 197(1):36–42, 1998.

[51] N. M. Correa, M. A. Biasutti, and J. J. Silber. Micropolarity of reversed micelles: comparison between anionic, cationic, and nonionic reversed micelles. *J. Colloid Interface Sci.*, 184(2):570–578, 1996.

[52] C. Reichardt. Solvatochromic dyes as solvent polarity indicators. *Chemical Reviews*, 94(8):2319–2358, 1994.

[53] M. J. E. van Roosmalen, M. van Diggelen, G. F. Woerlee, and G. J. Witkamp. Dry-cleaning with high pressure carbon dioxide - the influence of mechanical action on washing results. *J. Supercrit. Fluids*, 27(1):97–108, 2003.

[54] G. Wyszecki and W. S. Stiles. *Color science, concepts and methods, quantitive data and formulae.* John Wiley and sons, 2nd edition, 1982.

[55] R. W. G. Hunt. *Measuring color.* Ellis Horwood, 2nd edition, 1992.

Samenvatting

Het onderwerp van dit proefschrift is "Waskracht in vloeibaar Koolzuur". Waskracht ("Detergency") is de versterkte reinigingswerking door het toevoegen van hulpstoffen, in het bijzonder surfactants, aan een wasvloeistof. Vloeibaar koolzuur wordt vanwege toxicologische en milieu-overwegingen beschouwd als een alternatief voor het gebruikelijke oplosmiddel perchloorethyleen (Perc) bij het chemisch reinigen ("dry-cleaning") van textiel. De vraag naar zo'n alternatief werd aangepakt volgens de ontwerpmethodologie van de chemisch technoloog. Met een "Basic Cycle of Design" (BCD) -benadering werd de gevraagde detergent ontworpen. Het BCD-stramien bepaalde ook de structuur van dit proefschrift - dat dus gelezen kan worden als een rapportage over het ontwerpen van een (succesvol) chemisch produkt: een werkende detergent voor dry cleaning in vloeibaar koolzuur.

Hoofdstuk 1 beschrijft de bestaande technologie voor wassen en chemische reiniging: de verschillende soorten textiel en de typen vlekken die verwijderd moeten worden, de veronderstelde reinigingsmechanismen en het effect van oppervlakte-actieve stoffen op het wasproces. Ook wordt de keuze van koolzuur in plaats van Perc als oplosmiddel bij het chemisch reiniging besproken.

In Hoofdstuk 2 wordt aan de hand van modellen voor de waskracht een inconsistentie in de theorie blootgelegd. Een analyse van onderzoekresultaten die hebben geleid tot het "Dynamische Detergentie Model"(DDM) wijst uit, dat de werking van de surfactants met dit model goed te beschrijven is. Het genoemde model levert dus een rationeel beginpunt voor het ontwerpen van detergents in vloeibaar koolzuur.

Hoofdstuk 3 begint met een korte beschrijving van de BCD-ontwerpmethodologie voor een chemisch produkt. Als eerste stap worden wensspecificaties opgesteld voor een stof die als detergent moet werken in vloeibaar koolzuur. Zo'n stof moet een surfactant zijn, d.w.z. tamelijk slecht oplosbaar in het oplosmiddel, maar daarin wel micelvormend en oppervlakte-actief. Aangezien nauwelijks gegevens beschikbaar zijn over oplosbaarheid van stoffen in (sub-kritisch) vloeibaar koolzuur moest een methode gezocht worden om die oplosbaarheden te schatten. Met behulp van verschillende parameters werd inzicht verkregen in de afzonderlijke bijdragen van individuele carbofobe en carbofiele groepen in het oplosgedrag van amphifiele moleculen in vloeibaar koolzuur. Op basis daarvan werd stap voor stap een denkbeeldig surfactantmolecuul opgebouwd, dat volgens het DDM de gewenste eigenschappen zou moeten hebben. Als onze meest plausibele keuze voor de Basis of Design (BOD) van het gevraagde detergent leverde dat stoffen op uit de homologe reeks C_iE_j van alkaan/poly-oxyethyleen verbindingen.

De experimenten uit Hoofdstuk 4 dienden er voor om vast te stellen welke stoffen uit onze Basis of Design werkelijk het voorspelde gedrag vertonen. Met Cailletet-experimenten en lichtverstrooiing werd het oplossen van C_iE_j-verbindingen in vloeibaar koolzuur bestudeerd. Bij de gespecificeerde temperatuur en druk voor het chemisch reinigen werden optimale ketenlengtes gevonden, zowel voor de carbofiele C_i- als voor de carbofobe E_j-groepen van het detergentmolecuul. Er was een groot verschil in oplosgedrag tussen monodisperse (laboratorium) preparaten en industrieel bereide stoffen met polydisperse ketenlengtes in de carbofobe E_j-"staarten" van de surfactantmoleculen.

In Hoofdstuk 5 wordt experimenteel onderzocht of de gekozen stoffen zich in koolzuur werkelijk gedragen als surfactants (dus sterk adsorberen aan de grensvlakken van de oplossing en met elkaar tot micellen associeren). Het bleek dat C_iE_j-moleculen de grensvlakspanning tussen water en vloeibaar koolzuur effectief kunnen verlagen. Ze zullen dus óók oppervlakte-actief zijn aan het oppervlak van textielvezels. Met de combinatie van lichtverstrooiings- en UV-Vis absorptiemetingen werd de oplosbaarheid van kleurstoffen in vloeibaar koolzuur bepaald als functie van de toegevoegde hoeveelheid detergent. Dit gaf de kritische micelvormingsconcentraties voor C_iE_j-verbindingen in het beoogde oplosmiddel. Polaire stoffen, die in vloeibaar koolzuur zeer onoplosbaar zijn, worden wél gesolubiliseerd in de binnenkern van deze micellen. Met oplosbaarheid en commerciële beschikbaarheid als belangrijke criteria werden vervolgens de twee meest geschikte verbindingen uit de BOD, C_8E_3 en $C_{12}E_4$, geselecteerd voor de technische evaluatie van de ontworpen detergents.

Deze technische evaluatie wordt beschreven in Hoofdstuk 6. Het is de meest essentiële stap in ieder produktontwerp. In deze fase van de ontwerpcyclus wordt de waarde van het resultaat vastgesteld, door de werkelijke prestaties van het chemische produkt te vergelijken met de vastgelegde wensspecificaties uit de BOD. Voor het evalueren van de nieuwe technologie met vloeibaar koolzuur als oplosmiddel waren ook nieuwe testmethoden nodig. Zo moesten representatieve "monitors" worden gevonden (wollen weefsels, reproduceerbaar vervuild met kleideeltjes en met een suspensie van roet in huidvet). De colorimetrische methode voor het kwantitatief vergelijken van de reinigingsresultaten moest daar op worden aangepast. Er moest apparatuur bedacht en gemaakt voor wasproeven in autoclaven bij hoge (koolzuur) gasdruk. In die apparaten moest de stromingsintensiteit van de wasvloeistof op verschillende niveaus instelbaar wezen. En er moest een reproduceerbare methode worden ontwikkeld om het natte textiel na het wassen uit te spoelen met schoon oplosmiddel (anders slaan de detergenten er op neer bij het aflaten van het koolzuur uit de wastrommel!). Eerst geven we een korte beschrijving van de colorimetrische meetmethode voor de wasresultaten. Dat geeft inzicht bij de interpretatie van standaard indexen voor onderlinge vergelijking van de waskracht. De tests leren ons hoe aan de hand van het DDM goede wasresultaten bereikt (kunnen) worden met de voorgestelde detergenten. Dat geldt zowel voor moeilijk verwijderbare nanodeeltjes (klei) als voor de meer gecompliceerde vlekken van sebum(vet) met roetdeeltjes daar in. Geheel in overeenstemming met het Dynamische Detergentie Model is ook de sleutelrol van de mechanische actie (stroming) in de prestaties van een detergent. Redepositie van vuildeeltjes uit de wasvloeistof bleek één van de grootste problemen voor een vloeibaar-koolzuurtechnologie. Maar dit kon in principe opgelost worden met een polair co-solvent als extra hulpstof in de detergentformulering. Ook op vergrote (pilot) schaal werden goede wasresultaten bereikt. In deze tests gaf de detergent de gespecificeerde wasresultaten, zelfs zonder verdere optimalisering van de chemische formulering. Als het ontworpen detergent ingezet wordt voor dry cleaning met vloeibaar koolzuur als oplosmiddel is het reinigingsresultaat inderdaad vergelijkbaar met dat van de bestaande Perc-technologie.

Hoofdstuk 7 ontwikkelt vanuit de verkregen inzichten enkele nieuwe voorstellen om de dry cleaning van textiel verder te verbeteren. Dat kan door nauwkeuriger formuleren van de detergenten en door een aangepaste procesvoering, die inspeelt op de specifieke aard van vloeibaar koolzuur als oplosmiddel. En aan het eind hebben we, zoals in Delft gebruikelijk bij de dissertaties uit het Laboratorium voor Fysische Chemie, onze conclusies over detergentie samengevat in een viertal slotstellingen.

Resumen

En esta tesis se estudia el fenómeno de detergencia en CO_2 líquido. Detergencia se define como el efecto positivo que sobre el lavado tienen los aditivos, en particular surfactantes, incorporados al líquido de lavado. CO_2 líquido es considerado tanto por razones medio-ambientales como toxicológicas, una alternativa al percloroethyleno (Perc), el solvente más usado mundialmente para el lavado en seco. Los problemas inherentes a tal transición tecnológica fueron confrontados haciendo uso de la metodología de diseño de la ingeniería química. El enfoque del Ciclo Básico de Diseño, Basic Cycle of Design (BCD), fue utilizado como guía para el diseño de un detergent para CO_2 líquido. El BCD también establece el marco de referencia sobre el cual se estructura la tesis y que puede, por tanto, ser leída como un informe sobre el diseño exitoso de un producto químico: un detergente para el lavado en seco con CO_2 líquido.

En el Capítulo 1, se revisan los conceptos básicos sobre lavado y lavado en seco incluyendo: los tipos de suciedad encontrados en las prendas, los mecanismos para remover tales suciedades y la acción de los surfactantes en tal proceso. Finalmente, se presentan los criterios considereados para la selección de CO_2 líquido como solvente.

En el Capítulo 2, se analizan los diversos modelos existentes que explican el fenómeno de detergencia y se exponen algunas inconsistencias encontradas en tales enfoques. En detalle, se analizan los resultados de investigaciones anteriores que llevaron a la formulacion del Dynamic Detergency Model (DDM), que exitosamente logra explicar el rol de los surfactantes en el proceso de lavado. Este modelo es tomado como punto de partida para el diseño racional de un detergente para CO_2 líquido.

El Capítulo 3, comienza con una breve revisión de la metodología BCD para el diseño de un producto químico. A continuación, se definen los requerimientos básicos que debe satisfacer un surfactante para ser considerado un detergente en CO_2 líquido. El surfactante debe: ser levemente soluble en el solvente, ser tensioactivo y capaz de formar micelas. Dada la carencia de datos de solubilidades en este solvente. Un número de parámetros fueron analizados que permitieron estimar la contribución individual de grupos tanto carbofílicos como carbofóbicos al parámetro de solubilidad de una molécula de surfactante en CO_2 líquido. Con este enfoque, un proceso imaginario de construcción de tal molécula de detergente fue llevada a cabo. El resultado fue la elección de la familia de surfactantes no-iónicos polyetoxilados, más conocidos como C_iE_j, como la opción más plausible en las bases de diseño, Basis of Design (BOD), para el producto deseado.

Los experimentos en el Capítulo 4 establecen cuales de las moléculas incluídas en el BOD fueron, tal como se predecía, solubles en CO_2 a las condiciones de presión y temperatura estipuladas para el lavado en seco. Experimentos independientes realizados en el equipo Cailletet y utilizando light scattering muestran la solubilidad de las moléculas C_iE_j en el solvente. En este análisis marcadas diferencias en miscibilidad fueron encontradas entre las muestras monodispersas, o de laboratorio, y las polydispersas, o industriales, con respecto al numero de óxidos de ethyleno-E_j. Para las condiciones requeridas, un largo optimo tanto para la parte carbofílica de la molécula (C_i) como para la carbofóbica (E_j) fue determinado.

En el Capítulo 5, se diseñaron experimentos para verificar que las moléculas seleccionadas efectivamente se comportan como surfactantes (tensioactivas y capaces de formar micelas en solución). Mediciones en la interfase CO_2 líquido-agua mostraron que la adsorbción de las, levemente solubles, moléculas C_iE_j reducían la tensión en la interfase. Estas moléculas seran consecuentemente, tambien tensioactivas en la interfase tela (o tejido)/CO_2 líquido. Experimentos utilizando colorantes, insolubles en CO_2, y monitoreados a través de Light-scattering y UV-Vis mostraron las concentrationes a partir de las cuales estas moléculas comienzan a formar micelas en solución. Los experimentos demostraron también que compuestos polares, altamente insolubles en CO_2, pueden ser disueltos en el interior de tales micelas. Considerando la solubilidad del surfactante y su disponibilidad, C_8E_3 y $C_{12}E_4$ fueron propuestos como los candidatos más idóneos para una evaluación técnica.

En el Capítulo 6, se realiza una evaluación técnica del detergente. Etapa vital en todo proceso de diseño, pues es aquí donde se testea el valor del diseño comparando el desempeño del producto con las metas planteadas en el BOD. Con este propósito se diseñaron tests cuantitativos de lavado que incluyen: la selección de los monitores o muestras a ser lavadas (tejidos de lana estandarizadamente ensuciados con arcilla y con sebo/hollín), el método colorimétrico utilizado para la evaluación de los resultados de las pruebas de lavado, los equipos utilizados y la posibilidad de incluir agitación mecánica controlada y una etapa de enjuague. Se incluye una pequeña introducción a la colorimetría que permite entender el origen y significancia del índice de lavado utilizado para evaluar las muestras. Los resultados muestran que, tal como predice el DDM, altos índices de lavado pueden ser obtenidos con los surfactantes C_iE_j tanto para la remoción de material puramente particulado (arcilla), como para sistemas más complejos (sebo/hollín). Tal como enfatiza el modelo, el grado de agitación o acción mecánica en el líquido de lavado es un factor clave en el desempeño del detergente. La redeposición de la suciedad fue identificada como uno de los principales problemas del lavado en seco con CO_2 líquido. Este problema puede ser, sin embargo, neutralizado utilizando una formulación que incluya un cosolvente polar. Experimentos fueron también realizados a escala semi-piloto, obteniéndose una vez mas altos índices de lavado. Los resultados de los tests demostraron que nuestros detergentes, cuya formulación no ha sido optimizada, alcanzan las metas estipuladas. De hecho, los índices de lavado obtenidos son tan satisfactorios como los mostrados por Perc.

En el capítulo 7, se revisan y analizan en un contexto más amplio los resultados presentados en esta tesis incluyéndose propuestas de carácter técnico y netamente de formulación que podrían mejorar la eficiencia del proceso. Finalmente, y como se ha vuelto tradición para las tesis desarrolladas en el Laboratorio de Físico-Química de la universidad de Delft, las principales ideas expuestas en la tesis son resumidas en cuatro proposiciones.

Curriculum Vitae

María Pilar Gárate was born on March 23, 1974 in Santiago, Chile. After completing the secondary school, from March 1992 until December 1998 she studied Chemical Engineering at the Catholic University in Santiago. She graduated with a thesis in Saint John's wort Extraction under the supervision of prof. J. M. del Valle.

From August 1999 until February 2004 she carried out a doctoral research at the Laboratory of Physical Chemistry of Delft University of Technology. The research project was financed by the EET project K98044 and was entitled "Detergency in Liquid CO_2". In this function she carried out this research under the supervision of prof. dr. G. Frens.

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I particularly enjoyed to work in such a lively and international group. The different cultures and mentalities created a very stimulating work atmosphere where social life was far from absent. The Kolonisten-dinners were always welcome as well as the table-tennis competitions at Lianjie's house that ended up with a delicious Chinese meal. I do not want to forget Veronica's great food and valuable advices. Special mention deserves the endless but always exciting cooking competition with Christophe, a very good friend whose ”génie culinaire” and readiness to help I highly appreciate.

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