The Antisolvent Crystallisation of Sodium Chloride

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The Antisolvent Crystallisation of Sodium Chloride

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Dr. R.M. Geertman, Akzo Nobel

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CHAPTER 1

1.1 History of Salt and Salt Production
1.2 Today's Salt Production Technologies
1.3 World Salt Production
1.4 Aim of this Study
1.5 Outline
1.6 Literature Cited
1.1 History of Salt and Salt Production

Salt or sodium chloride, has probably been on earth from the beginnings of geologic time, and has been necessary either directly or indirectly in all stages of the evolution of life. The earliest records of salt and its uses fade backward until lost in the mists of prehistory. Salt seems to have been used almost universally, in all times and places. Salt was used in cooking wheat and barley five thousand years ago, according to the evidence of grain varieties and pottery fragments found in Belgian cave-man dwellings (Kaufmann, 1960). In ancient Troy, salt preserved fish was eaten some thirteen centuries before Christ. The Egyptians salted ducks, quail, and sardine of the Nile. Roman soldiers were partly paid in salt. The word soldier is claimed to be derived from - sal dare, meaning to give salt. From the same source we get the word salary, salarium. To sit above or below the salt identified the ranking in the seating arrangements at a feast. Not to be worth one's salt was a great insult and the Bible compliments some men as being the salt of the earth (Forbes, 1968).

Man’s first substantial salt supply was the natural deposit of salt as a result of solar evaporation of shallow sea water pools. This was followed by deliberate impounding of sea water in shallow lagoons, to be evaporated by the sun’s heat - the beginnings of modern solar evaporation. Rock salt is the mineral found in nature, also known as mineral salt or halite. The rock salt mines of the eastern Alps were operated from the later Bronze Age, about 1400 BC, and possibly even earlier. The earliest artificially evaporated salt was made by dropping brine on burning wood or heated stones and scraping of the efflorescence. This method was used in Europe until Caesar’s salinators taught the natives of Cheshire to boil the brine in small shallow evaporating pans over open fires. The modern vacuum pan method of producing salt as fine cubic crystals was first used in 1886, so all earlier artificial production methods were of the open-vessel type, which produced flakes, cubes, or a mixture of the two (Kaufmann, 1960).
1.2 Today’s Salt Production Technologies

Solar Salt
Salt has been manufactured by solar evaporation from sea water and from inland underground or lake brines since time immemorial. In most developing countries, this method still predominates. Sea water contains about 3.5 wt% dissolved minerals. Sodium chloride is 77 wt% of that amount, or about 2.7 wt% of sea water. The other 0.8 wt% consists mainly of calcium, magnesium and sulfate ions. The extraction of salt from sea water consists of progressive evaporation of brine in large open ponds using solar heat. As the brine evaporates its concentration rises and the constituent salts crystallise in a set order. During this process, the sodium chloride fraction is separated from the brine. The principal salts that crystallise from sea water along with sodium chloride are the chlorides and sulphates of magnesium, calcium and potassium. Crude salt produced in a properly designed salt works has a purity of 90-95 wt% NaCl, 1 wt% calcium salts and 1-2 wt% magnesium salts and 5-8 wt% water. If the salt is washed and dried its purity can be improved up to 99.7 wt% (dry basis).

MINED SALT
Solid rock deposits of salt occur widely in North America, Europe and Central Asia, at depths ranging from a few hundred meters to more than a thousand meters. Where the deposits are fairly shallow, the dry mining method is preferred. Where the deposit is very deep, solution mining is used. By this method, fresh water is injected at high pressure through a pipe into the salt layer where it dissolves the salt and forms a cavity. The saturated brine then travels through a concentric pipe upwards to the surface where it is purified. The $SO_4^{2-}$ is precipitated by adding an excess of $Ca^{2+}$ and the excess of $Ca^{2+}$ is precipitated by adding $CO_3(g)$ to the solution. Subsequently the brine is evaporated in vacuum pans to yield a high purity product.

Sodium chloride is produced by evaporative crystallisation in very large amounts. In the Netherlands alone approximately 5 Mton salt is produced per year by evaporative crystallisation (1997). A typical vacuum plant for salt making consists of a series of closed vessels, or 'effects', containing circulation heaters. In Figure 1 an example of a quadruple effect evaporation plant is displayed (Jongema, 1983). In such a configuration approximately 0.85 ton steam (140 °C, 3.6 bar) is needed for the production of 1 ton salt, corresponding to
1.82 MJ/kg salt. In the first effect the brine is heated by condensing low pressure steam which is often obtained from an on-site steam power plant, and the brine boils at a temperature dictated by the inlet steam pressure. As the brine boils in the first effect it produces steam. As a result of this a supersaturation is created and salt crystals are formed. The steam produced in the first effect, is used in the circulation heater of the second effect. The resultant suspension is fed to the second effect and is circulated over the heater. Pressures (and boiling temperatures) become successively lower through the evaporators with the last three operating within a vacuum enabling the brine to boil at much lower temperatures. This succession of heat exchanges minimises the energy consumption. Modern salt plants can have as many as six 'effects' as part of the evaporation system. The salt/brine slurry from the final effect is fed to a centrifuge to separate the salt crystals from their mother liquor. The resulting undried vacuum salt is then stored for supply to the chemical industry. For food and allied industries, a dry salt is required. For these applications the salt from the centrifuges is fed into fluid bed drier-coolers for further drying. After drying, the salt is sieved and graded before being transferred into large storage hoppers prior to packaging and distribution either in bags or bulk tankers (The Salt Manufacturer’s Association, 1999).

Figure 1. Simplified flowsheet of a quadruple effect evaporation plant.
1.3 World Salt Production

The production of common salt is one of the most widely distributed industries in the world. Mined and solar salt each account for roughly 50% of the production. The requirements of Europe and North America are met mostly by mining while in Asia, Africa, Australia and South America, solar evaporation is the main source. The physical and chemical composition of salt produced from the various sources varies widely depending upon the manufacturing techniques, climatic conditions and processes adopted (Venkatesh Mannar, 1995).

<table>
<thead>
<tr>
<th>Country</th>
<th>Production 1997 (Million metric tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>41.5</td>
</tr>
<tr>
<td>China</td>
<td>29.3</td>
</tr>
<tr>
<td>Germany</td>
<td>15.7</td>
</tr>
<tr>
<td>Canada</td>
<td>13.3</td>
</tr>
<tr>
<td>India</td>
<td>9.5</td>
</tr>
<tr>
<td>Australia</td>
<td>8.7</td>
</tr>
<tr>
<td>Mexico</td>
<td>7.9</td>
</tr>
<tr>
<td>France</td>
<td>7.2</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>6.6</td>
</tr>
<tr>
<td>Brazil</td>
<td>5.5</td>
</tr>
<tr>
<td>All Other</td>
<td>55.8</td>
</tr>
<tr>
<td>TOTALS</td>
<td>201</td>
</tr>
</tbody>
</table>

Table I. Approximate world salt production

A distribution of the world salt production is given in Table I and in Figure 2. Some countries depend entirely on rock salt, some on solar salt. In a few countries both forms are produced. Salt manufacturing techniques and product quality vary considerably. Salt is produced in extremely primitive cottage scale units producing a few hundred tons a year to very large fully automated plants producing several million tons a year. Due to its low costs salt is mainly produced for local markets.
Figure 2. World salt production.

The demand for salt increases with the growth of the population as well as with the development of industries. Apart from human consumption and road salt, chemical industry is a large bulk consumer of salt for chlor alkali manufacture. In the developed countries, industrial requirements are several times the edible consumption. In the developing countries, the trend towards increased industrial demand is becoming apparent only during the past few years.

1.4 Aim of this Study

Sodium chloride is produced by evaporative crystallisation in large amounts, which technique is rather energy-consuming. A small reduction in the energy consumption will result in substantial savings in the production of sodium chloride. By using antisolvent crystallisation, i.e. the addition of an organic substance to the brine that reduces the salt solubility by binding the water, the energy intensive water evaporation step is avoided, and therefore the energy consumption in the crystallisation of the salt is reduced. However, in the antisolvent crystallisation process an additional separation step is required, i.e. the recovery of the antisolvent from the spent mother liquor after the crystallisation. To make the antisolvent crystallisation process economically attractive the energy consumption in the recovery of the
antisolvent should be low. Therefore organic substances that are partially miscible with water and salt are suitable antisolvents, because they can be recovered by a temperature induced liquid-liquid separation (see Figure 3).

Figure 3. A partially miscible antisolvent-water-salt system with a Lower Critical Solution Temperature.

The aim of this study is to develop an antisolvent crystallisation process, constituting the antisolvent crystallisation and recovery steps, that provides NaCl crystals with a quality equivalent to the quality of the salt crystals produced by evaporative crystallisation at a reduced energy consumption.

1.5 Outline

Crucial to the viability of the antisolvent crystallisation process is the choice of the antisolvent. The main criteria for the selection of the antisolvent are its effectiveness, i.e. the extent to which its presence reduces the sodium chloride solubility in water, and its separability from the aqueous phase after crystallisation. Other important aspects to the energy household are the enthalpy of mixing and the specific heats of antisolvent-water (-salt) systems. Chapter 2 focuses on the investigation of these properties for the selected antisolvents diisopropylamine, dimethylisopropylamine and 2-isopropoxyethanol.

Antisolvent crystallisation can only be a realistic alternative to evaporative crystallisation if it can provide salt crystals of the required quality. Therefore an experimental setup must be
available for the investigation of the continuous antisolvent crystallisation for a wide variety of temperatures and pressures. The setup must be constructed of corrosion resistant materials, since the antisolvent-water-salt mixtures can be highly corrosive. To visualise the particles inside the crystalliser vessel an in-line image probe needs to be developed. Chapter 3 treats the design of this experimental setup and of the developed in-line image probe.

The size, shape, purity and degree of agglomeration of the particles formed by continuous antisolvent crystallisation needs to be investigated. The antisolvent uptake of the formed salt crystals is particularly important, since both for consumption and electrolysis applications a high uptake of the antisolvent is intolerable. The antisolvent uptake can be reduced if first NaCl.2H₂O is formed by antisolvent crystallisation which is subsequently recrystallised in a purer brine. The purification that can be obtained by applying this recrystallisation step can be studied in small scale batch experiments. The quality of the product, and its antisolvent uptake in particular, formed by continuous antisolvent crystallisation of NaCl or by batchwise antisolvent crystallisation of NaCl.2H₂O followed by a recrystallisation step, is the subject of Chapter 4.

Chapter 5 treats the influence of the antisolvent on the kinetics of nucleation and crystal growth and the effect of the high levels of supersaturation, often encountered in antisolvent crystallisation, on mainly particle size, shape and agglomeration. In the first part of this chapter, the influence of locally increased levels of supersaturation at the crystalliser antisolvent inlet during continuous crystallisation on the NaCl product characteristics is evaluated. Also crystallisation of NaCl in the two liquid phase area is attempted. In the second part the design and calibration of an in-line particle counter for counting fast moving small particles at low concentrations is treated. This tool is intended for the measurement of induction times for crystallisation as well as of nucleation (and growth) rates as a function of the antisolvent concentration at supersaturation levels that prevail in the area of the crystalliser antisolvent inlet. In the third and final part of this chapter the measured primary nucleation rates and the estimated induction times and growth rates are presented.

Finally in Chapter 6, guidelines are formulated for the design of an antisolvent crystallisation process, as well as the energy consumption and costs estimations of the designed processes for the production of NaCl, either via the antisolvent crystallisation of
NaCl or via the antisolvent crystallisation of NaCl.2H₂O followed by a recrystallisation step, are presented.

1.6 Literature Cited


Jongema, P. Optimization of the Fuel Consumption of an Evaporation Salt Plant with the Aid of the Exergy Concept. Sixth Int. Symp. on Salt 1983, 2, 463-469.


CHAPTER 2

2a Liquid-Liquid and Solid-Liquid Equilibria of Amine-\( \text{H}_2\text{O} \)-NaCl Mixtures

2b Specific Heats and Enthalpies of Mixing of Amine-\( \text{H}_2\text{O} \) and Amine-\( \text{H}_2\text{O} \)-NaCl Mixtures

2c Liquid-Liquid and Solid-Liquid Equilibria of 2-Isopropoxyethanol-\( \text{H}_2\text{O} \)-NaCl Mixtures
Chapter 2a

Liquid-Liquid and Solid-Liquid Equilibria of Amine-H₂O-NaCl Mixtures

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Solubility measurements of NaCl in mixtures of diisopropylamine or dimethylisopropylamine and water were performed. At 5 °C the NaCl solubility in dimethylisopropylamine-water and at -12 °C the NaCl.2H₂O solubility in diisopropylamine-water were determined. Both the NaCl and the NaCl.2H₂O solubilities decreased significantly upon the addition of the amines to water. In liquid-liquid equilibrium experiments the influence of the presence of the salt on the shape and the positions of the binary liquid-liquid equilibrium lines was determined. The mutual solubilities of the amines and water in the two liquid phase area decreased upon the addition of the salt. At NaCl saturation the lower critical solution temperatures of the diisopropylamine-water and the dimethylisopropylamine-water systems decreased from 27 to -11.7 °C and from 65 to 6.6 °C respectively.

Keywords: solubility, phase diagram, sodium chloride, water, diisopropylamine, dimethylisopropylamine.

1. Introduction

In industry well soluble inorganic salts with a small solubility temperature dependency like NaCl, are often separated from water by evaporative crystallisation. The evaporation of water in these processes is energy consuming. To reduce the energy consumption in the production of such salts, drowning out crystallisation by the addition of an antisolvent is an interesting alternative.

The addition of an antisolvent however, introduces an additional separation step in which the antisolvent has to be recovered from the spent mother liquor. The energy consumption in the antisolvent recovery must be small in order to make the antisolvent crystallisation process
competitive. Therefore amines are promising antisolvents, because many amine-water systems show lower critical solution temperatures with water due to the formation of nitrogen to hydrogen bonds, which can be broken by heating. Hence such amines can be recovered from a spent motherliquor by a temperature induced liquid-liquid phase split. Davison et al. (1960) established that especially highly branched secondary amines containing 5 or 6 carbon atoms or tertiary amines are suitable solvents for (sea) water desalination purposes. These amines reduce the solubility of sodium chloride significantly and they demix well from the water phase in the two liquid phase area. From his work the amines diisopropylamine and dimethylisopropylamine were selected for the antisolvent crystallisation of NaCl.

In this work the influence of the presence of NaCl on the binary amine-water liquid-liquid equilibrium lines presented by Davison, has been studied by carrying out liquid-liquid equilibrium experiments. Furthermore, to determine the effectiveness of the amines in a crystallisation process, the influence of the amines on the sodium chloride solubility was investigated by doing solid-liquid equilibrium experiments.

2. Experimental Section

2.1 Chemicals

The chemicals were diisopropylamine (or DiPA, C₉H₁₉N, Elf Atochem ≥ 99%), N,N-dimethylisopropylamine (or DMiPA, C₉H₁₉N, Fluka purum ≥ 98%) and pharmaceutical grade sodium chloride (Akzo Nobel). In all experiments demineralised water with a conductivity of less than 4 mS·cm⁻¹ was used. In these experiments the amine concentration is expressed as a salt free weight fraction: 

\[ w_{\text{amine}} = \frac{m_{\text{amine}}}{(m_{\text{amine}} + m_{H₂O})} \]

2.2 Apparatus and Procedures

All experiments were carried out in a jacketed 125 ml glass flask. A magnetic stirrer in combination with a stir bar provided agitation and a Lauda RK-8-KP thermostat was used to control temperature. The temperature of the vessel content was measured with an ASL precision thermometer (0.01 °C accuracy, 0.002 °C repeatability) and a small hole in the vessel cover ensured atmospheric pressure. Figure 1 shows a schematic drawing of the setup.
The sodium chloride solubilities were determined in the single liquid phase region as a function of the amine concentration at a constant temperature. In the case of dimethylisopropylamine, the vessel was filled with known amounts of the amine and water and an excess of sodium chloride. At a temperature of 5 °C the solution was stirred for approximately 30 minutes and liquid samples of the mixture were taken. Tests showed that this period of time was sufficient to reach chemical equilibrium. With the diisopropylamine-water-salt system the solubilities were determined at a temperature of -12 °C. Experiments demonstrated that at this temperature NaCl.2H₂O instead of NaCl is the stable crystal modification. Therefore in this case the amine-water mixtures should not be saturated with NaCl but with NaCl.2H₂O in order to determine the NaCl equilibrium concentrations in the solution. Since it is hard to store NaCl.2H₂O crystals because of their instability at room temperature, these solubilities were determined differently. In these measurements known amounts of a saturated aqueous NaCl solution and diisopropylamine were mixed at a temperature of -12 °C. Upon the addition of the diisopropylamine to the saturated solution the NaCl.2H₂O started to crystallise. After the system had reached thermal equilibrium approximately 60 minutes was waited to allow the system to reach chemical equilibrium. After this period both liquid and solid samples were taken. The sodium chloride
concentrations of the liquid samples were determined, and under a microscope equipped with a polarised light source the crystal modification was established. Since NaCl.2H₂O crystals are birefringent they change the rotation direction of polarised light. Therefore they could easily be distinguished from NaCl crystals.

The liquid-liquid equilibrium experiments with the dimethylisopropylamine-water-salt system were carried out by filling the vessel with known amounts of antisolvent and water at room temperature. Subsequently an excess of sodium chloride was added to ensure NaCl saturation during the experiments. With the diisopropylamine-water-salt system a NaCl.2H₂O saturated amine-water mixture was created by mixing a saturated aqueous sodium chloride solution with the amine at -12 °C, as in the solubility experiments with diisopropylamine. For diisopropylamine-water, points of the liquid-liquid equilibrium line were determined by visual observation of the mixing/demixing temperatures at a given overall diisopropylamine to water ratio. For dimethylisopropylamine-water saturated with NaCl, points of the liquid-liquid equilibrium line were also determined by analysing samples of the organic and the aqueous phases at a fixed temperature in the two liquid phase area. The samples were taken 30 minutes after the solution had reached the selected temperature. When the compositions of both the organic phase and the aqueous phase change strongly with temperature (the horizontal part of the L-L equilibrium line), the points on the liquid-liquid equilibrium line are most reliably determined by the visual method (accuracy 0.05 °C). However, when the mixing/demixing temperature is a very steep function of the amine to water ratio in the mixture (the vertical parts of the L-L equilibrium line), the sampling method is favoured for maximum reliability.

2.3 Analytical Methods

The amine concentration in the liquid samples was determined with a Chrompack CP 9002 gas chromatograph equipped with a CP-Sil-5 CB column. Sodium chloride concentrations were determined gravimetrically. Water concentrations were calculated from the measured amine and sodium chloride concentrations.
3. Results and Discussion

In Figure 2, Table I and Table II the results of the solubility measurements are displayed. For both amines the NaCl or NaCl.2H₂O solubility decreases similarly at an increasing amine concentration. At amine concentrations above 0.85 the salt solubility approaches zero for both systems. In the solubility plot of NaCl.2H₂O in diisopropylamine-water also data points measured by Weingaertner et al. (1991) are displayed. These solubilities, that were measured in the temperature range of -12.5 to -3.9 °C, fall approximately on the same line as the solubilities measured at a constant temperature of -12 °C. This demonstrates that the NaCl solubility in mixtures of diisopropylamine and water is a weak function of temperature and is mainly determined by the diisopropylamine concentration in the mixture. Furthermore, in the entire diisopropylamine concentration range at -12 °C, sodium chloride dihydrate was the crystal modification that was in equilibrium with the water-diisopropylamine mixtures.

Table I. NaCl.2H₂O solubilities in mixtures of diisopropylamine (DiPA) and H₂O at -12°C.

<table>
<thead>
<tr>
<th>[DiPA] m_{DiPA}/(m_{H₂O}+m_{DiPA})</th>
<th>[NaCl]<em>{eq} m</em>{NaCl}/(m_{H₂O}+m_{DiPA})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 (^a)</td>
</tr>
<tr>
<td>0.8308</td>
<td>0.0043</td>
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<tr>
<td>0.7298</td>
<td>0.0258</td>
</tr>
<tr>
<td>0.6251</td>
<td>0.0585</td>
</tr>
<tr>
<td>0.3947</td>
<td>0.1467</td>
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<tr>
<td>0.2060</td>
<td>0.2227</td>
</tr>
<tr>
<td>0.1108</td>
<td>0.2622</td>
</tr>
<tr>
<td>0</td>
<td>0.3280 (^b)</td>
</tr>
</tbody>
</table>

\(^a\) assumed zero

\(^b\) (Kaufmann, 1960)
Table II. NaCl solubilities in mixtures of dimethylisopropylamine (DMiPA) and H₂O at 5 °C.

<table>
<thead>
<tr>
<th>[DMiPA] \ [NaCl]_{eq}</th>
<th>m_{DMiPA}/(m_{H₂O}+m_{DMiPA})</th>
<th>m_{NaCl}/(m_{H₂O}+m_{DMiPA})</th>
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<td>0°</td>
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<td>0.8804</td>
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<td>0.7051</td>
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<td>0</td>
<td>0.3572°</td>
<td></td>
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</table>

* assumed zero

b (Kaufmann, 1960)
Figure 2. Solubility of NaCl in dimethylisopropylamine-H₂O at 5 °C (left) and of NaCl.2H₂O in diisopropylamine-H₂O (right) as a function of amine concentration.

In Figure 3, Table III, Table IV and Table V the results of the liquid-liquid equilibrium experiments are presented. The binary amine-water equilibrium data in Figure 3 were determined by Davison et al. (1960) and also ternary diisopropylamine-water-salt equilibrium data from Weingaertner are displayed in this figure. The lower critical solution temperatures (LCST) of the diisopropylamine-H₂O and the dimethylisopropylamine-H₂O systems were estimated to be 27 and 65 °C respectively. Below these temperatures there is one single liquid phase present regardless of the concentration of the amine. The LCST’s of both systems decrease in the presence of sodium chloride as well as the mutual solubilities of the amines and the water in the two liquid phase area. At lower temperatures however, the amines are sufficiently hydrophilic to be fully miscible with water at NaCl saturation. The LCST’s of the diisopropylamine-H₂O-NaCl.sat and the dimethylisopropylamine-H₂O-NaCl.sat systems were estimated to be -11.7 and 6.6 °C. The LCST of the diisopropylamine-H₂O-NaCl.sat system deviates from the one presented by Weingaertner et al. who estimated the LCST at -7.5 °C. From Figure 3 it can be seen, that the mutual solubilities of diisopropylamine and water increase less with a decreasing NaCl concentration in the mixture than the mutual solubilities of dimethylisopropylamine and water. The reduction in lower critical solution temperature
upon NaCl saturation is 38.7 °C for diisopropylamine-water and 58.4 °C for dimethylisopropylamine-water. With respect to this diisopropylamine is a more suitable antisolvent than dimethylisopropylamine, because with diisopropylamine the temperature difference between the crystallisation and the antisolvent recovery sections in the antisolvent crystallisation process can be smaller. This is a crucial factor, because it reduces the magnitude of the heat streams in the process and with that the required total heat transfer area.

Figure 3. Liquid-liquid equilibria of the binary amine-H₂O and the ternary amine-H₂O-NaCl (saturated) systems (DiPA - diisopropylamine, DMiPA - dimethylisopropylamine).
Table III. Demixing temperatures of diisopropylamine
-\(H_2O\) mixtures at NaCl.2\(H_2O\) saturation.

<table>
<thead>
<tr>
<th>[DiPA] ((m_{DiPA}/(m_{DiPA}+m_{H2O})))</th>
<th>(T_{demix}) ((^{\circ}C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7330</td>
<td>-3.00</td>
</tr>
<tr>
<td>0.6030</td>
<td>-5.50</td>
</tr>
<tr>
<td>0.5010</td>
<td>-8.90</td>
</tr>
<tr>
<td>0.3710</td>
<td>-10.90</td>
</tr>
<tr>
<td>0.2300</td>
<td>-10.90</td>
</tr>
<tr>
<td>0.1994</td>
<td>-11.40</td>
</tr>
<tr>
<td>0.1070</td>
<td>-11.65</td>
</tr>
<tr>
<td>0.0990</td>
<td>-11.30</td>
</tr>
</tbody>
</table>

Table IV. Demixing temperatures of dimethylisopropylamine
-\(H_2O\) mixtures at NaCl saturation.

<table>
<thead>
<tr>
<th>[DMiPA] ((m_{DMiPA}/(m_{DMiPA}+m_{H2O})))</th>
<th>(T_{demix}) ((^{\circ}C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8013</td>
<td>15.45</td>
</tr>
<tr>
<td>0.7051</td>
<td>12.65</td>
</tr>
<tr>
<td>0.6087</td>
<td>9.80</td>
</tr>
<tr>
<td>0.4986</td>
<td>6.85</td>
</tr>
<tr>
<td>0.2987</td>
<td>6.60</td>
</tr>
<tr>
<td>0.2003</td>
<td>6.80</td>
</tr>
<tr>
<td>0.1002</td>
<td>7.90</td>
</tr>
</tbody>
</table>
Table V. Liquid-liquid equilibrium data of
dimethylisopropylamine-H₂O mixtures at NaCl saturation.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Aqueous-phase [DMiPA] ( m_{\text{H}<em>2\text{O}}/(m</em>{\text{DMiPA}}+m_{\text{H}_2\text{O}}) )</th>
<th>organic-phase [DMiPA] ( m_{\text{H}<em>2\text{O}}/(m</em>{\text{DMiPA}}+m_{\text{H}_2\text{O}}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.00</td>
<td>0.0342</td>
<td>0.8340</td>
</tr>
<tr>
<td>25.00</td>
<td>0.0195</td>
<td>0.8612</td>
</tr>
<tr>
<td>35.00</td>
<td>0.0179</td>
<td>0.8923</td>
</tr>
<tr>
<td>45.00</td>
<td>0.0159</td>
<td>0.9452</td>
</tr>
</tbody>
</table>

4. Conclusions

The amines diisopropylamine and dimethylisopropylamine are suitable antisolvents for the crystallisation of NaCl or NaCl₂H₂O. They significantly reduce the solubility of the salt in the water phase and they can be recovered by a temperature induced liquid-liquid phase split. Because the mutual solubilities of diisopropylamine and water increase less upon the removal of NaCl from the mixture than for dimethylisopropylamine, diisopropylamine is more suitable for the antisolvent crystallisation of NaCl than dimethylisopropylamine.

5. Literature Cited


Specific Heats and Enthalpies of Mixing of Amine-H$_2$O and Amine-H$_2$O-NaCl Mixtures

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Laboratory for Process Equipment, Delft University of Technology, Delft, the Netherlands

Specific heats of mixtures of N,N-dimethylisopropylamine or diisopropylamine and water and of N,N-dimethylisopropylamine and water saturated with NaCl were measured. The specific heats of the three systems all obtained maximum values in the amine weight fraction range of 0.1 to 0.4. The enthalpies of mixing of N,N-dimethylisopropylamine or diisopropylamine and water were determined as a function of the amine concentration in the mixture. The mixing of water and the amines was strongly exothermic. The highest measured enthalpies of mixing were -105 J·g$^{-1}$ (mixture) for dimethylisopropylamine-H$_2$O at an amine weight fraction of 0.49 and -81 J·g$^{-1}$ (mixture) for diisopropylamine-H$_2$O at an amine weight fraction of 0.60.

Keywords: specific heat, enthalpy of mixing, dimethylisopropylamine, diisopropylamine, NaCl.

1. Introduction

In industry highly soluble inorganic salts with a small solubility temperature dependency like NaCl, are often separated from water by evaporative crystallisation. The evaporation of water in these processes is rather energy consuming. To reduce the energy consumption in the production of such inorganic salts, drowning out crystallisation by the addition of an organic antisolvent could be an interesting alternative. N,N-dimethylisopropylamine and diisopropylamine are suitable antisolvents for the crystallisation of NaCl, because they reduce the NaCl solubility and they can be separated from the water phase by a temperature induced liquid-liquid phase split (Zijlema, 1995).
To set up an energy balance over the process, specific heats of the binary amine-H₂O mixtures and of the ternary amine-H₂O mixtures saturated with NaCl have to be known. Also the enthalpy of mixing of the amines and water in the crystalliser is of great importance to the overall energy consumption. Since these data are not available in the literature and their values cannot be predicted with great accuracy, they have to be determined experimentally. In this work the specific heats of mixtures of diisopropylamine or dimethylisopropylamine and water and of dimethylisopropylamine and water saturated with NaCl, as well as the enthalpies of mixing of water and diisopropylamine or dimethylisopropylamine are presented.

2. Experimental Section

2.1 Chemicals

The chemicals were N,N-dimethylisopropylamine (or DMiPA, C₆H₁₃N, Fluka purum ≥ 98%), diisopropylamine (or DiPA, C₆H₁₃N, Elf Atochem ≥ 99%) and pharmaceutical grade sodium chloride (Akzo Nobel). Demineralised water with a conductivity of less than 4 mS·cm⁻¹ was used in all the experiments. In these experiments the amine concentration is expressed as a salt free weight fraction: \( w_{\text{amine}} = \frac{m_{\text{amine}}}{m_{\text{amine}} + m_{\text{H₂O}}} \).

2.2 Apparatus and Procedures

All experiments were carried out in a covered stainless steel Dewar vessel (Figure 1). A small hole in the vessel cover ensured atmospheric pressure during the experiments. A magnetic stirrer and a stir bar provided agitation and the temperature of the vessel contents was measured with an ASL-F250 precision thermometer (0.01 K accuracy, 0.002 K repeatability). All experiments were carried out in a thermostated room which was kept at temperatures of -5 to 5 °C, depending upon the temperature of the experiment.
Figure 1. Experimental setup.

The specific heats were determined by heating the amine-water or amine-water-salt solutions with an electrical heating device (Figure 2). The device consisted of a Cr-Ni wire (D=0.4 mm, 11 Ω·m⁻¹) which at both ends was attached to a stainless steel pin (AISI-316SS, D=2 mm). During the experiments the Ni-Cr wire was fully immersed in the solution. The stainless steel pins were attached to copper wire which was connected to a power supply (ES 030-4, Delta Electronics). The electrical heat input was controlled by the power supply. The electrical current through the Cr-Ni wire was kept at a constant value and the potential difference over the wire adjusted itself to the given current set point value. The potential difference over the Ni-Cr wire was measured locally and the electrical power input was calculated from \( P_{el} = V \times I \), in which V is the measured potential difference and I is the current through the Ni-Cr wire. During the experiments the electrical power input was kept at a value between 7 and 9 W, at which solution temperature changes were measurable and yet no insulating gas layer formed at the Ni-Cr wire-solution interface. Experiments showed, that the heat exchange between the Dewar vessel contents and the surroundings could be neglected. An enthalpy balance could be set up for the solution in the vessel during an experiment:
\[
\frac{dH}{dt} = P_{ei} \quad \text{with} \quad dH = mC_{p,m}dT
\]
equation 1

in which \( C_{p,m} \) is the specific heat at constant pressure (\( J \cdot g^{-1} \cdot K^{-1} \)). The following relationship for the calculation of the specific heat from the experimental data can now be derived:

\[
C_{p,m} = \frac{P_{ei}}{m\frac{dT}{dt}}
\]
equation 2

All specific heats were determined in the temperature range of -2 to 6 K (solution temperature).

![Diagram](image)

Figure 2. Heating device.

The enthalpy of mixing experiments were carried out in the same experimental setup, only in these experiments the electrical heating device was removed. At the start of the experiments the Dewar vessel, the amine and the water were in thermal equilibrium with their surroundings. The vessel was filled with the amine first. The temperature of the amine inside the Dewar vessel \( T_1 \), as well as the temperature of the water in the erlenmeyer flask \( T_2 \), were measured. The water was added to the Dewar vessel under stirring and the temperature rise due to mixing was recorded. It took approximately five seconds for the liquid to reach its final constant temperature value, \( T_m \). The enthalpies of mixing were calculated from the following equation:

\[
\Delta H_{mix} = \frac{(m_1C_{p,m1}T_1 + m_2C_{p,m2}T_2) - (m_1 + m_2)C_{p,m(1+2)}T_m - C_{p,D}(T_m - T_1)}{(m_1 + m_2)}
\]
equation 3
in which \(\Delta H_{\text{mix}}\) is the enthalpy of mixing (J·g\(^{-1}\)), \(m\) the component mass (g), \(T\) the temperature (K), \(C_{p,m}\) the specific heat (J·g\(^{-1}·K\(^{-1}\)) and \(C_{p,D}\) the specific heat of the Dewar vessel (J·K\(^{-1}\)). The subscripts 1 and 2 refer to the amine and the water respectively. Since in all experiments the total volume of the mixture in the vessel was kept constant at a value of approximately 400 ml a correction for the heat loss to the Dewar vessel wall could be made. The specific heat of the vessel wall was determined in separate experiments and proved to be 68 J·K\(^{-1}\) (liquid volume inside the vessel ca. 400 ml).

3. Results and Discussion

The results of the specific heat measurements of the binary mixtures of dimethylisopropylamine or diisopropylamine and water are displayed in Figure 3, Figure 4, Table I and Table II. The specific heats of dimethylisopropylamine-H\(_2\)O and diisopropylamine-H\(_2\)O reach maximum values of 4.90 and 5.02 (J·g\(^{-1}·K\(^{-1}\)) at amine fractions of 0.2492 and 0.2015 respectively. The specific heat of pure water was measured at a temperature of 277 K; the measurement deviated +1.2% from a literature value (Lide, 1994). In Figure 3 and Figure 4 also estimated values calculated from the relationship proposed by Jamieson et al. (1978) for aqueous mixtures are displayed:

\[
C_{p,m(1+2)} = (w_1C_{p,m1} + w_2C_{p,m2})(1 + Dw_1w_2)
\] equation 4

In this equation \(w\) is a weight fraction and \(D\) is a constant which is fitted from the experimental data.

Table I. Specific Heats of dimethylisopropylamine-H\(_2\)O mixtures.

<table>
<thead>
<tr>
<th>(w_{\text{DMiPA}}) (\text{(m}<em>{\text{DMiPA}}/(\text{m}</em>{\text{H2O}}+\text{m}_{\text{DMiPA}})))</th>
<th>(T_{\text{range}}) (K)</th>
<th>(C_{p,m}) (J·g(^{-1}·K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>277</td>
<td>4.26</td>
</tr>
<tr>
<td>0.0995</td>
<td>275 - 277</td>
<td>4.80</td>
</tr>
<tr>
<td>0.2492</td>
<td>273 - 274</td>
<td>4.90</td>
</tr>
<tr>
<td>0.4998</td>
<td>272 - 273</td>
<td>4.33</td>
</tr>
<tr>
<td>0.7550</td>
<td>272 - 272</td>
<td>3.55</td>
</tr>
<tr>
<td>1</td>
<td>277 - 279</td>
<td>2.32</td>
</tr>
</tbody>
</table>

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Table II. Specific Heats of diisopropylamine-H₂O mixtures.

<table>
<thead>
<tr>
<th>w_{DIPA} (m_{DIPA}/(m_{H₂O} + m_{DIPA}))</th>
<th>T_{range} (K)</th>
<th>C_{p,m} (J·g⁻¹·K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>277</td>
<td>4.26</td>
</tr>
<tr>
<td>0.2015</td>
<td>276 - 277</td>
<td>5.04</td>
</tr>
<tr>
<td>0.3928</td>
<td>276 - 277</td>
<td>4.55</td>
</tr>
<tr>
<td>0.5996</td>
<td>275 - 276</td>
<td>3.92</td>
</tr>
<tr>
<td>0.8001</td>
<td>275 - 277</td>
<td>3.37</td>
</tr>
<tr>
<td>1</td>
<td>277 - 279</td>
<td>2.63</td>
</tr>
</tbody>
</table>

Figure 3. Experimentally determined and estimated (equation 4) specific heats of dimethylisopropylamine-H₂O mixtures.
Figure 4. Experimentally determined and estimated (equation 4) specific heats of diisopropylamine-H$_2$O mixtures.

The results of the specific heat measurements on mixtures of dimethylisopropylamine and water saturated with sodium chloride are displayed in Table III and in Figure 5. As a result of the presence of NaCl, both the negatively charged stainless steel pin and the connected Cr-Ni wire were subject to corrosion. The measured specific heats reached a maximum value of 4.06 (J·g$^{-1}$·K$^{-1}$) at an amine weight fraction of 0.1998. The specific heats of dimethylisopropylamine-H$_2$O-NaCl were estimated with the relationship of Jamieson by regarding the ternary system as a binary mixture of an (undersaturated) aqueous sodium chloride solution and the amine. The specific heats of the sodium chloride solutions were taken from the literature (Kaufmann, 1960) whereas the specific heat of dimethylisopropylamine was determined experimentally. The relationship of Jamieson was moderately successful in estimating these specific heats (accuracy: ±10%). This is attributed to the strong non-ideal behaviour of the ternary system, in which one of the components is a dissolved inorganic salt.
Figure 5. Experimentally determined and estimated (equation 4) specific heats of dimethylisopropylamine-H₂O mixtures saturated with NaCl.

Table III. Specific heats of mixtures of dimethylisopropylamine and H₂O saturated with NaCl.

<table>
<thead>
<tr>
<th>w_{DMIPA} (m_{DMIPA}/(m_{H₂O}+m_{DMIPA}))</th>
<th>T_{range (K)}</th>
<th>C_{p,m} (J·g⁻¹·K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>278</td>
<td>3.26 a</td>
</tr>
<tr>
<td>0.1998</td>
<td>274 - 276</td>
<td>4.06</td>
</tr>
<tr>
<td>0.3993</td>
<td>277 - 278</td>
<td>4.03</td>
</tr>
<tr>
<td>0.5003</td>
<td>278 - 280</td>
<td>3.92</td>
</tr>
<tr>
<td>0.6565</td>
<td>276 - 277</td>
<td>3.44</td>
</tr>
<tr>
<td>1</td>
<td>277 - 279</td>
<td>2.32</td>
</tr>
</tbody>
</table>

a Literature value Kaufmann, 1960

The results of the enthalpy of mixing measurements are displayed in Figure 6, Table IV and Table V. For the calculation of enthalpies of mixing, the experimentally determined specific heats of the amine and of the amine-H₂O mixtures were used and were considered temperature independent in the temperature range at which the experiments were carried out. The specific heat of pure water was taken from the literature (Lide, 1994). The results show that the mixing process is strongly exothermic. This indicates that the amine-water
interactions are strong compared to the water-water and amine-amine interactions. For dimethylisopropylamine-H₂O, the highest measured enthalpy of mixing was -105 J·g⁻¹ (mixture) at an amine weight fraction of 0.4916, corresponding to a temperature rise of approximately 23 K. For diisopropylamine-H₂O the highest enthalpy of mixing was -81 J·g⁻¹ (mixture) measured at an amine weight fraction of 0.5990, corresponding to a temperature rise of approximately 19 K. The molar enthalpy of mixing (kJ·mole⁻¹ amine) decreased strongly with the amine mole fraction at low mole fractions and decreased more gradually in the mole fraction range of 0.4 to 1.0.

![Graph showing enthalpies of mixing for DiPA-H₂O and DMiPA-H₂O](image)

Figure 6. Enthalpies of mixing of the dimethylisopropylamine-H₂O and the diisopropylamine-H₂O systems in J·g⁻¹ mixture against the weight fraction amine (left) and in kJ·mole⁻¹ amine against the mole fraction amine (right).

<table>
<thead>
<tr>
<th>w_{DMiPA} \ (m_{DMiPA}/(m_{H_2O}+m_{DMiPA}))</th>
<th>T_{range} \ (K)</th>
<th>\Delta H_{mix} \ (J·g⁻¹ mixture)</th>
<th>\Delta H'_{mix} \ (kJ·mole⁻¹ DMiPA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2579</td>
<td>275 - 291</td>
<td>-85.6</td>
<td>-28.9</td>
</tr>
<tr>
<td>0.4916</td>
<td>275 - 298</td>
<td>-105.0</td>
<td>-18.5</td>
</tr>
<tr>
<td>0.7533</td>
<td>275 - 297</td>
<td>-84.5</td>
<td>-9.8</td>
</tr>
</tbody>
</table>

Table IV. Enthalpies of mixing of dimethylisopropylamine and H₂O.
Table V. Enthalpies of mixing of diisopropylamine and H₂O.

<table>
<thead>
<tr>
<th>( \text{w}<em>{\text{DiPA}} ) (( \text{m}</em>{\text{DiPA}}/\text{m}<em>{\text{H₂O}} + \text{m}</em>{\text{DiPA}} ))</th>
<th>( T_{\text{range}} ) (K)</th>
<th>( \Delta H'_{\text{mix}} ) (J·g⁻¹ mixture)</th>
<th>( \Delta H_{\text{mix}}^* ) (kJ·mole⁻¹ DiPA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1986</td>
<td>276-288</td>
<td>-63.2</td>
<td>-32.2</td>
</tr>
<tr>
<td>0.3964</td>
<td>277-293</td>
<td>-79.6</td>
<td>-20.3</td>
</tr>
<tr>
<td>0.5990</td>
<td>277-296</td>
<td>-81.5</td>
<td>-13.8</td>
</tr>
<tr>
<td>0.7894</td>
<td>277-295</td>
<td>-66.5</td>
<td>-8.5</td>
</tr>
</tbody>
</table>

4. Conclusions

Specific heats of the binary dimethylisopropylamine-H₂O and diisopropylamine-H₂O systems and of the ternary dimethylisopropylamine-H₂O system saturated with NaCl have been measured as a function of the amine concentration. The specific heats of the three systems obtained maximum values in the amine weight fraction range of 0.1-0.4. The enthalpies of mixing of the amines and water were determined as a function of the mixing ratio. The mixing process was strongly exothermic, demonstrating the non-ideal behaviour of the amine-H₂O mixtures. The highest measured enthalpies of mixing were -105 J·g⁻¹ (mixture) for dimethylisopropylamine-H₂O at an amine weight fraction of 0.4916 and -81 J·g⁻¹ (mixture) for diisopropylamine-H₂O at an amine weight fraction of 0.5990. The molar enthalpy of mixing (kJ·mole⁻¹ amine) decreased strongly with the amine mole fraction at low mole fractions and decreased more gradually in the mole fraction range of 0.4 to 1.0.

5. Literature Cited


Chapter 2c


Liquid-Liquid and Solid-Liquid Equilibria of 2-Isopropoxyethanol-H₂O-NaCl Mixtures

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Laboratory for Process Equipment, Delft University of Technology, Delft, the Netherlands

Liquid-liquid equilibria experiments demonstrated that mixtures of 2-isopropoxyethanol and water saturated with NaCl are partially miscible. The lower critical solution temperature was estimated at 29.2 °C at a 2-isopropoxyethanol (or IPE) concentration of 0.399 (m_{IPE}/(m_{IPE}+m_{H₂O})). Solid-liquid equilibria experiments showed that the solubility of NaCl in water is reduced significantly by the presence of 2-isopropoxyethanol. As in pure water the NaCl solubility in 2-isopropoxyethanol-H₂O mixtures increases weakly with temperature.

Keywords: solubility, phase diagram, sodium chloride, water, 2-isopropoxyethanol.

1. Introduction

In industry well soluble inorganic salts with a small solubility temperature dependency like NaCl, are often separated from water by evaporative crystallisation. The evaporation of water in these processes is energy consuming. To reduce energy costs in the production of such inorganic salts, drowning out crystallisation by the addition of an organic antisolvent could be an interesting alternative. The addition of an antisolvent crystallisation however, introduces an additional separation step in which the antisolvent has to be recovered from the spent mother liquor. The antisolvent recovery must be carried out with little energy consumption in order to make the entire process economically attractive. Therefore 2-isopropoxyethanol is a promising candidate for the crystallisation of NaCl, since Chiavone-Filho et al. (1993) demonstrated that it reduces the KCl solubility in water and that the 2-isopropoxyethanol-H₂O-KCl system shows a double liquid phase area close to room temperature. This enables

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antisolvent recovery from the spent mother liquor after crystallisation by a temperature induced liquid-liquid phase split.

In this work the results of the experimentally determined liquid-liquid and solid-liquid equilibria of the 2-isopropanol-\textit{H}_2\textit{O}-\textit{NaCl} system are presented.

2. Experimental Section

2.1 Chemicals

The chemicals were 2-isopropanol ((CH$_3$)$_3$CHOCH$_2$CH$_2$OH, Fluka Chemie AG ≥ 99.7% (GC)) and pharmaceutical grade sodium chloride (Akzo Nobel). Demineralised water with a conductivity of less than 4 mS·cm$^{-1}$ was used in all experiments. In these experiments the 2-isopropanol concentration is expressed as a salt free weight fraction: \( w_{\text{IP}} = \frac{m_{\text{IP}}}{(m_{\text{IP}}+m_{\text{H}_2\text{O}})} \).

2.2 Apparatus and Procedures

All experiments were carried out in a jacketed 125 ml glass flask. A magnetic stirrer in combination with a stir bar provided agitation and a Lauda RK-8-KP thermostat was used to control the temperature. The temperature of the vessel content was measured with an ASL precision thermometer (0.01 °C accuracy, 0.002 °C repeatability) and a small hole in the vessel cover ensured atmospheric pressure. Figure 1 shows a schematic drawing of the setup.

The liquid-liquid equilibria experiments were carried out by filling the vessel with known amounts of antisolvent and water at room temperature. Subsequently an excess of sodium chloride was added to ensure NaCl saturation during the experiments. Points on the liquid-liquid equilibrium line were determined in two different ways: either by visual observation of the mixing/demixing temperatures at a given overall 2-isopropanol to water ratio, or by determining the compositions of both the organic and the aqueous phases at a fixed temperature in the two liquid phase area. In the second case the samples were taken 30 minutes after the solution had reached the selected temperature. Experiments had shown that this period of time was sufficient to reach chemical equilibrium. When the compositions of both the organic phase and the aqueous phase vary strongly with temperature (the horizontal part of the L-L equilibrium line), points of the liquid-liquid equilibrium line are most reliably
determined by using the first method (accuracy 0.05 °C). However, when the mixing/demixing temperature is a very steep function of the 2-isopropoxyethanol to water ratio in the mixture (the vertical sides of the L-L equilibrium line), the second method is favoured for maximum reliability.

![Diagram](image)

Figure 1. Experimental setup used for determining the liquid-liquid and solid-liquid equilibria.

The sodium chloride solubilities were determined in the single liquid phase region as a function of the 2-isopropoxyethanol concentration at a temperature of 15 °C and as a function of temperature at 2-isopropoxyethanol concentrations of 0.25, 0.50 and 0.75. The vessel was filled with known amounts of 2-isopropoxyethanol and water and an excess of sodium chloride. At the selected temperature the solution was stirred for 30 minutes and clear liquid samples of the mixture were taken for the determination of the sodium chloride concentration.

### 2.3 Analytical Methods

The 2-isopropoxyethanol concentration of the liquid samples was determined with a Chrompack CP 9002 gas chromatograph equipped with a CP-Sil-5 CB column. Sodium chloride concentrations concentration were determined gravimetrically. Water concentrations were calculated from the measured 2-isopropoxyethanol and sodium chloride concentrations.
3. Results and Discussion

In Figure 2, Table I and Table II the results of the liquid-liquid equilibria experiments are displayed. From these data it can be seen that 2-isopropoxyethanol, which is completely miscible with pure water, shows a two liquid phase area in the presence of NaCl. The lower critical solution temperature of the 2-isopropoxyethanol-H₂O system at NaCl saturation is approximately 29.2 °C at an 2-isopropoxyethanol concentration of 0.399. Similar observations were made by Chiavone-Filho et al. (1993), who demonstrated that water and 2-isopropoxyethanol are no longer completely miscible in the presence of KCl. In Figure 2 it can be seen that the mutual solubilities of water and 2-isopropoxyethanol in the two liquid phase region are still quite large. Therefore the 2-isopropoxyethanol recovery by a temperature induced liquid-liquid phase split can be used as a first separation step but the remaining water phase will need further treatment.

![Graph](image)

**Figure 2.** LLE data of 2-isopropoxyethanol-H₂O mixtures at NaCl saturation. The ◇-marks were collected by visual determination of the mixing/demixing temperature and the □-marks by analysing samples of both phases.
Table I. Liquid-liquid equilibrium data of 2-isopropanoylethanol-H₂O mixtures at NaCl saturation.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>[2-IsoPropoxyEthanol]</th>
<th>[NaCl]</th>
<th>organic-phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m_{PE}/(m_{PE}+m_{H₂O})</td>
<td>m_{NaCl}/(m_{PE}+m_{H₂O})</td>
<td>[2-IsoPropoxyEthanol]</td>
</tr>
<tr>
<td>49.88</td>
<td>0.0988</td>
<td>0.3200</td>
<td>0.8030</td>
</tr>
<tr>
<td>59.55</td>
<td>0.0826</td>
<td>0.3337</td>
<td>0.8309</td>
</tr>
<tr>
<td>79.97</td>
<td>0.0631</td>
<td>0.3524</td>
<td>0.8582</td>
</tr>
</tbody>
</table>

Table II. Demixing temperatures of 2-isopropanoylethanol-H₂O mixtures at NaCl saturation.

<table>
<thead>
<tr>
<th>[2-IsoPropoxyEthanol]</th>
<th>T_{emix} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m_{PE}/(m_{PE}+m_{H₂O})</td>
<td></td>
</tr>
<tr>
<td>0.1012</td>
<td>44.00</td>
</tr>
<tr>
<td>0.1267</td>
<td>38.05</td>
</tr>
<tr>
<td>0.1496</td>
<td>34.65</td>
</tr>
<tr>
<td>0.1998</td>
<td>30.70</td>
</tr>
<tr>
<td>0.2999</td>
<td>29.40</td>
</tr>
<tr>
<td>0.3020</td>
<td>29.30</td>
</tr>
<tr>
<td>0.3992</td>
<td>29.20</td>
</tr>
<tr>
<td>0.3996</td>
<td>29.35</td>
</tr>
<tr>
<td>0.4984</td>
<td>29.35</td>
</tr>
<tr>
<td>0.4998</td>
<td>29.40</td>
</tr>
<tr>
<td>0.5998</td>
<td>30.65</td>
</tr>
<tr>
<td>0.6068</td>
<td>32.30</td>
</tr>
<tr>
<td>0.6892</td>
<td>35.30</td>
</tr>
<tr>
<td>0.6994</td>
<td>36.45</td>
</tr>
<tr>
<td>0.7496</td>
<td>42.15</td>
</tr>
</tbody>
</table>
In Figure 3, Figure 4 and Table III the NaCl solubilities in mixtures of 2-isopropoxyethanol and water at 15 °C are presented. In Figure 3 the NaCl concentrations are expressed as \( m_{\text{NaCl}}/(m_{\text{IPE}}+m_{\text{H}_2\text{O}}) \). The solid line represents the NaCl equilibrium concentrations and the dotted line the NaCl concentrations, that would arise if a saturated sodium chloride solution is mixed instantaneously with pure 2-isopropoxyethanol in an arbitrary mixing ratio. Therefore, the difference between the dotted line and the solid line is representative for the total amount of NaCl that crystallises as a result of this mixing. Figure 4 displays the NaCl solubility expressed as \( m_{\text{NaCl}}/m_{\text{H}_2\text{O}} \). It shows the extent to which the antisolvent reduces the NaCl solubility in the water volume present in the mixture.

![Graph](image_url)

**Figure 3.** NaCl solid-liquid equilibria expressed as \( m_{\text{NaCl}}/(m_{\text{H}_2\text{O}}+m_{\text{IPE}}) \) in mixtures of 2-isopropoxyethanol and H\(_2\)O at 15°C.
Table III. NaCl solubility in mixtures of 2-isopropoxyethanol and H₂O at 15°C.

<table>
<thead>
<tr>
<th>[2-IsopropoxyEthanol]</th>
<th>[NaCl]_{eq}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.3576 a</td>
</tr>
<tr>
<td>0.0996</td>
<td>0.3002</td>
</tr>
<tr>
<td>0.1310</td>
<td>0.2821</td>
</tr>
<tr>
<td>0.1994</td>
<td>0.2477</td>
</tr>
<tr>
<td>0.2080</td>
<td>0.2297</td>
</tr>
<tr>
<td>0.2500</td>
<td>0.2262</td>
</tr>
<tr>
<td>0.2999</td>
<td>0.2024</td>
</tr>
<tr>
<td>0.3010</td>
<td>0.2050</td>
</tr>
<tr>
<td>0.3986</td>
<td>0.1652</td>
</tr>
<tr>
<td>0.4010</td>
<td>0.1631</td>
</tr>
<tr>
<td>0.4998</td>
<td>0.1241</td>
</tr>
<tr>
<td>0.5000</td>
<td>0.1257</td>
</tr>
<tr>
<td>0.5010</td>
<td>0.1250</td>
</tr>
<tr>
<td>0.5990</td>
<td>0.0890</td>
</tr>
<tr>
<td>0.5998</td>
<td>0.0899</td>
</tr>
<tr>
<td>0.7000</td>
<td>0.0570</td>
</tr>
<tr>
<td>0.7090</td>
<td>0.0500</td>
</tr>
<tr>
<td>0.7500</td>
<td>0.0390</td>
</tr>
<tr>
<td>0.7990</td>
<td>0.0250</td>
</tr>
<tr>
<td>0.9000</td>
<td>0.0060</td>
</tr>
<tr>
<td>1</td>
<td>0 b</td>
</tr>
</tbody>
</table>

\( a \) Mullin, 1993
\( b \) assumed zero

In Figure 5 and Table IV the NaCl solubilities in pure water (Mullin, 1993) and in 2-isopropoxyethanol-H₂O mixtures as a function of temperature are displayed. At all 2-isopropoxyethanol concentrations the solubility increases weakly with temperature. The NaCl solubility has the largest slope with temperature at the 2-isopropoxyethanol concentrations of 0.25 and 0.50 (\( \sim 5 \times 10^{-4} \) °C⁻¹) and is smaller in pure water (\( \sim 1 \times 10^{-4} \) °C⁻¹) and in 0.75 2-isopropoxyethanol (\( \sim 6 \times 10^{-5} \) °C⁻¹).
Figure 4. NaCl solubilities expressed as \( \text{m}_{\text{NaCl}} / \text{m}_{\text{H}_2\text{O}} \) in mixtures of 2-isopropoxyethanol and \( \text{H}_2\text{O} \) at 15°C.

Figure 5. NaCl solid-liquid equilibrium lines in pure water and in mixtures of 2-isopropoxyethanol and \( \text{H}_2\text{O} \) as a function of temperature; 2-isopropoxyethanol concentrations (\( \text{m}_{\text{IPE}} / (\text{m}_{\text{IPE}} + \text{m}_{\text{H}_2\text{O}}) \)): ○ - 0.00; □ - 0.25; ◇ - 0.50; △ - 0.75.
Table IV. NaCl solubility in mixtures of 2-isoproxyethanol and H₂O as a function of temperature.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>[2-IsoproxyEthanol] (m_{NaCl}/(m_{NaCl}+m_{H₂O}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.3560</td>
</tr>
<tr>
<td>1.00</td>
<td>0.2185 0.1191</td>
</tr>
<tr>
<td>2.50</td>
<td>0.2194 0.1212 0.0383</td>
</tr>
<tr>
<td>5.00</td>
<td>0.2207 0.1223 0.0383</td>
</tr>
<tr>
<td>7.50</td>
<td>0.2226 0.1228 0.0390</td>
</tr>
<tr>
<td>10.00</td>
<td>0.3570 0.2232 0.1237 0.0391</td>
</tr>
<tr>
<td>12.50</td>
<td>0.2235 0.1254 0.0393</td>
</tr>
<tr>
<td>15.00</td>
<td>0.2262 0.1257 0.0390</td>
</tr>
<tr>
<td>17.50</td>
<td>0.2263 0.1260 0.0395</td>
</tr>
<tr>
<td>20.00</td>
<td>0.3580 0.2289 0.1299 0.0395</td>
</tr>
<tr>
<td>22.50</td>
<td>0.2300 0.1292 0.0395</td>
</tr>
<tr>
<td>25.00</td>
<td>0.2296 0.1331 0.0397</td>
</tr>
</tbody>
</table>

* Mullin, 1993

4. Conclusions

2-Isoproxyethanol is a suitable antisolvent for the crystallisation of NaCl since it reduces the solubility of NaCl in water significantly and it obtains a two liquid phase area close to room temperature with water saturated with NaCl. Because the mutual solubilities of water and 2-isoproxyethanol in the two liquid phase region are still quite large, a temperature induced liquid-liquid phase split can be used as a first separation step in the recovery of the 2-isoproxyethanol, but the remaining aqueous phase will need further treatment.

5. Literature Cited


Pilot Plant for Continuous Crystallisation Experiments

CHAPTER 3

3 a Experimental Setup for Antisolvent Crystallisation Experiments

3 b In-Line Image Probe for the Visualisation of Fast Flowing Small Particles
Chapter 3a

Experimental Setup for
Antisolvent Crystallisation Experiments

Tjakko G. Zijlema, Harald Oosterhof, Geert-Jan Witkamp
and Gerda M. van Rosmalen

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An experimental setup has been built that can be used for continuous or (semi-) batch antisolvent crystallisation experiments. The 1 liter crystalliser can be used at temperatures of -20 to 200 °C and at pressures of up to 20 bar. To prevent corrosion Hastelloy-C has been used as the main material of construction. Solid as well as liquid samples can be taken and the crystalliser is equipped with an in-line image probe for the visualisation of the crystals inside the vessel.

Keywords: crystallisation, antisolvent, crystalliser, design.

1. Introduction

An experimental setup for the investigation of antisolvent crystallisation processes has been built. The crystallisation experiments can be carried out continuously or (semi-) batch wise. The setup can be operated at temperatures of -20 to 200 °C and at pressures of up to 20 bar. This enables the use of volatile organic antisolvents above their atmospheric boiling points. Since the main material of construction is Hastelloy-C and most of the packings and o-rings are of Kalrez, a wide range of combinations of solute, solvent and antisolvent can be studied in the experimental setup. During the experiments liquid and solid samples can be taken and the crystals inside the crystalliser can be observed with an in-line image probe. Furthermore the setup is almost completely automated, because it is too complicated to be controlled manually during a continuous crystallisation experiment. Finally, for safety reasons the setup is built up in a isolated and ventilated area, and it is provided with a sprinkler system.

In Figure 1 a schematic drawing of the setup is displayed. The setup can be divided into three sections, i.e. the crystalliser, an upstream and a downstream part. The upstream part
focuses on the storage of the feeds and their transportation to the crystalliser. The downstream part concentrates on solid and liquid sampling and waste stream handling.

Figure 1. Scheme of the continuous crystalliser setup.

2. Upstream Part

In Figure 2 a detailed drawing of the upstream part of the experimental setup is displayed. Vessels 21 and 31 are used for the storage of the brine and the antisolvent respectively. Vessel 31 is jacketed and vessel 21 is provided with a spiral that can be connected to a circulation thermostat. Both vessels are stored on separate balances which are connected to midilab dosage controllers (Systach; DC21 and DC31). Lewa membrane pumps (P21 and P31) are used to transport both feeds to the crystalliser. Filters are installed in the pipes before the pumps to protect their teflon membranes. The feed mass flow rates can be controlled by varying the pump frequencies or by altering the amplitudes of the plungers of the pumps, allowing a wide range flow rates. The pump frequencies are controlled by the midilabs and the plunger amplitudes are put at a fixed position at the start of an experiment. Furthermore, no-return valves are installed in the feed pipes to prevent reverse flows. Almost all the other valves in the experimental setup are pneumatically controlled plug valves, that are free of dead space and are equipped with self-lubricating PTFE packing bushes.
The reactor entrance temperature of the feed streams can be controlled by cooling or heating the feed streams in shell and tube type heat exchangers E22 and E32. The reactor entrance temperatures are measured by the PT-100’s T22 and T32. These temperatures are used to control the positions of the metering valves CV22 and CV32, that determine the thermostat liquid feed flow rates to heat exchangers E22 and E32. The heat exchangers E22 and E32 make use of a collective thermostation system, as is drawn in Figure 2. It consists of a circulation pump, plate heat exchangers and two circulation thermostats, i.e. one for heating and the other for cooling. Depending on the required crystalliser temperature one of the two will be selected by putting valve V91/92H in the required position.
3. Crystalliser

The crystalliser is a 1 liter (~effective volume) jacketed vessel. A technical drawing of the crystalliser is depicted in Figure 3. The parts of the crystalliser that come into contact with its contents are constructed of Hastelloy-C and its sealings are of Kalrez. It is equipped with a Buchi magnetic stirrer. The vessel is equipped with 4 (removable) baffles of 9.7 cm long and 1.2 cm wide. The antisolvent and the brine feeds are continuously introduced into the crystalliser ca. 10 mm above the stirrer blades and the inlets have an inner diameter of 4 mm. The suspension is withdrawn from the crystalliser intermittently. For this three conductivity electrodes are installed in the crystalliser depicted as I.41 in Figure 2 and Figure 4: a reference electrode (long), a low level electrode (middle) and a high level electrode (short). If all three electrodes make contact with the solution inside the crystalliser, a high level is

![Figure 3. A technical drawing of the crystalliser.](image-url)
detected and suspension will be withdrawn until both the high and the low level electrodes are above the liquid level. The exact positions of the high and the low level electrodes will determine the actual (average) crystalliser volume. The crystalliser is put under pressure by a 50 liter cylinder containing nitrogen (N₂, 200 bar). The maximum crystalliser pressure is approximately 20 bar at a temperature of 200 °C. The minimum operating pressure is ca. 3 bar.

The crystalliser contains two windows. One is used for the observation of the crystalliser liquid level and the other for the in-line image probe. The probe enables the visualisation of fast moving small particles inside the crystalliser. The system consists of an Optem Zoom 70 lens attached to a CCD camera, a video recorder and a monitor. It uses a stroboscope for illumination to minimise motion blur. The stroboscope light transmission device for diascopic illumination can be distinguished in Figure 3. A detailed description of the design and operation of the visualisation probe can be found in the second part of this chapter.

The crystalliser contents can be kept at a constant temperature between -20 and 200 °C. This is achieved by circulating the thermostat oil of the crystalliser jacket over heat exchanger E41 with centrifugal pump P41 (see Figure 2). In E41 heat is exchanged between the thermostat oil of the crystalliser jacket and the thermostat oil of the collective thermostatation system. The amount of heat that is exchanged is determined by the position of metering valve CV41. The position of this valve is controlled by the temperature readings of PT-100 T41, which is submerged in the suspension in the crystalliser.

The experimental setup has been designed in such a way that it is very easy to increase the crystalliser volume from 1 to 10 liter. The most important modification of the setup besides the replacement of the crystalliser is that the volumes of the storage and the waste vessels need to be increased by a factor of 10.

4. Downstream Part

In Figure 4 a detailed drawing and in Figure 5 a picture of the downstream part are displayed. The downstream part is concerned with the removal of the suspension from the crystalliser. This is done in three different ways, i.e. by taking a solid or a liquid sample or by transferring
the suspension to the waste vessel. These three options are discussed separately in the following.

Figure 4. Detailed drawing of the experimental setup - downstream part.

4.1 Solid Sample

Before taking the solid sample the pressure in the solid sample section is increased from atmospheric to the crystalliser pressure. Then valves V50, V60 and V65 are opened and suspension is transferred from the crystalliser to the filter in the solid sampling section. The tubing from the crystalliser to the sampling vessel is traced to ensure a constant temperature during sampling. The sampling time, i.e. the time that the three valves are open, can be varied in order to control the amount of suspension that is transferred and with that the amount of solids on the filter. In the filter house a stainless steel (AISI316L) filter is installed with a pore size of 8 μm. The mother liquor is removed from the solids by using pressurised nitrogen by opening V59, V64 and V65. Subsequently the crystals can be washed with the
selected medium by opening V66 and V65 and dried again with nitrogen. After this the crystals are removed from the filter by opening the filter house and stored, or dried in a stove. The tubes that still contain (super-) saturated suspension are emptied into the waste vessel and washed with demi-water and dried with compressed nitrogen.

Figure 5. Picture of the crystalliser and the key items of the downstream part.

4.2 Liquid Sample

Before taking the liquid sample the tubing of the liquid sample section is dried with compressed nitrogen and its pressure is increased to the crystalliser pressure. Then valve V69 is put in position 1 and valves V50, V61A, V61B, V62 are opened, and the suspension is transported from the crystalliser to the liquid sample section. When F61 detects a flow (through conductivity measurements) or after maximally 3 seconds V62 is closed again. Then V61B is closed and V62 is opened and V69 is put in position 2. The liquid sample is brought to room temperature in the thermostated liquid sample vessel. Then valve V63 and V57 are opened and the liquid sample is released. Finally the tubes that still contain (super-) saturated
suspension are emptied into the waste vessel, washed with demi-water and dried with compressed nitrogen.

4.3 Transfer to Waste

If a high liquid level is detected in the crystalliser, the level control vessel is brought at the pressure of the crystalliser. When this action is completed a connection is made between the crystalliser and the level control vessel by opening valves V50 and V51. Then V55 and V57 are opened and suspension is transferred from the crystalliser to the level control vessel. At the moment that a low level is detected in the crystalliser valves V50, V51, V55 and V57 are closed and the suspension is brought to room temperature in the transfer vessel. After this valve V55, V57 and V52 are opened and the suspension is released into the waste vessel. Finally, the tubes filled with suspension are emptied, washed and dried. This procedure is repeated as soon as a new high level is detected.

5. Automation of the Setup

The setup is almost completely automated, because it is too complicated to be controlled manually during continuous crystallisation experiments. The heart of the automation is the Mistic Opto 22 industrial controller. It controls all digital and analogue in- and output modules of the setup automation. The feed flow rates however, are controlled separately by midilab dosage controllers. The Mistic processor has been programmed with the process computer with the flow chart program ‘Cyrano’. This can only be done off-line. While experimenting this program runs in the background. During the experiments the program Intellution FIX/MMI serves as the user interface for the operator. With this program both the Mistic and the midilabs are controlled. It displays important information such as valve positions, liquid levels, pressures, temperatures, alarms etc., and it is used for data acquisition. The standard screen of the Intellution FIX/MMI automation software is displayed in Figure 6. It represents a schematic drawing of the setup (upstream, crystalliser, downstream), an alarm window and control buttons. Under these control buttons there are separate windows in which set points can be given or data are displayed. More information on automation of the setup can be found in ‘Automatisierung eines Energie sparenden Kristallisationsverfahrens’ by Perriard et al..
6. Discussion

The experimental setup has been used for the crystallisation of sodium chloride with the antisolvents diisopropylamine, dimethylisopropylamine or ethanol and for the crystallisation of sodium carbonate with 1-propanol or 1-butanol. Generally the setup functioned well.

With sodium chloride the crystalliser temperature was between 0 and 20 °C and the crystalliser pressure was approximately 3 bar. The only problem remaining in this case is that even the highly corrosion resistant o-rings and packings of Kelrez were not resistant to the used salt-water-amine mixtures. They had to be replaced quite frequently which is a costly matter. The advantage of using this setup for these experiments above a simple (glass) jacketed crystalliser and (glass) storage vessels and peristaltic pumps is that it is equipped with the in-line image probe. The setup is however, quite complicated for the simple
experiments with NaCl that are carried out at atmospheric pressure and at temperatures close to ambient temperature.

With sodium carbonate crystalliser temperatures of up to 200 °C and pressures of up to 20 bars were used. In these experiments the setup was pushed to its limits. It proved to be quite difficult to completely seal off the crystalliser at these temperatures and pressures. Also here the o-rings and packings had to be replaced quite frequently. Furthermore it appeared that the sodium carbonate slowly dissolved the quartz windows of the crystalliser. This reduced the quality of the pictures obtained with the in-line image probe significantly.

7. Acknowledgements

The authors would like to thank NOVEM and Akzo Nobel for their support and Aad Rooymans and Sander Nijssen for their contribution to the design and construction of the setup.

8. Literature Cited

Chapter 3b

In-line Image Probe for Visualisation of Fast Flowing Small Particles

Tjakko G. Zijlema, Geert-Jan Witkamp, Gerda M. van Rosmalen

Laboratory for Process Equipment, Delft University of Technology, Delft, the Netherlands

An in-line image probe for the visualisation of fast flowing small particles has been developed. The probe is integrated in a crystalliser that is operated at temperatures of -20 to 200 °C and pressures of up to 20 bar. The crystalliser contents are generally highly corrosive. Therefore the parts of the probe that come into contact with the reactor contents are constructed of Hastelloy-C as is the vessel. The probe uses a stroboscope as a light source. The flashes produced by the stroboscope are transported to an annular fiber optic illuminator mounted on a zoom lens for episcopic illumination, or to a position behind a looking glass inside the crystalliser for diascopic illumination. The zoom lens, which is positioned in front of the looking glass, magnifies the collected images 1.1X to 7.9X. It is attached to a CCD camera which is connected to a video recorder and a 12” monitor. The combined electronic and optical magnifications on the monitor vary between 43X and 300X.

Keywords: visualisation, in-line, probe, stroboscope, crystallisation.

1. Introduction

In processes where particles are formed such as crystallisation or precipitation, the quality of the formed product is primarily determined by the size distribution and the shape of the particles, and the presence of liquid inclusions. These properties can be measured off-line, on-line or in-line. For off- and on-line analyses sampling is required, which generally imposes many difficulties such as temperature or pressure control during the sampling procedure. In-line measurement techniques offer the distinct advantages, that data can be collected on a real time basis and that local (reactor) conditions can be studied. This will help to improve the understanding and the controllability of the processes studied.
To study particle shape, size and inclusion formation commercially available in-line visualisation equipment such as the Lasentech PVM probe can be used. This probe can be installed easily in a vessel and it is built up of a special configured bundle of lasers. The resolution is ca. 20 microns and, depending on the particle size and shape distributions, good images can be obtained at solids concentrations of up to approximately 50%. This probe can be used to visualise fast flowing small particles, since the light source emits intense short laser light pulses with a half-life time of 5 ms to 300 ns. The disadvantage of this probe is however, that it is costly and that it uses episcopic instead of diascopic illumination. With diascopic illumination higher contrast pictures can be obtained.

Therefore an in-line image probe for the visualisation of fast flowing small particles has been developed, which is equipped for the use of either diascopic or episcopic illumination. It is integrated in a 1 litre continuous crystalliser, which is operated at temperatures of -20 to 200 °C and at pressures of up to 20 bar. The crystalliser is used for the crystallisation of sodium chloride with organic antisolvents such as amines or alcohols. Since these mixtures are highly corrosive the metal parts of the crystalliser and the probe that come into contact with the organic-water-salt mixtures are constructed of Hastelloy-C, and the sealings are of Kalrez. In this chapter the design and the performance of the image probe are discussed.

2. In-line Image Probe

The image probe consists of a light source and light transmitters, a zoom lens, a CCD camera, a video recorder and a monitor. A schematic representation of the image probe integrated in the crystalliser is displayed in Figure 1. The zoom lens is positioned in front of the looking glass in the crystalliser. The zoom lens is connected to a CCD camera, which is attached to a super VHS video recorder and a 12” monitor. As a light source a stroboscope is used, which is triggered by the CCD camera. The light pulses emitted by the stroboscope are transmitted by fiber optics to the desired positions. A unique feature of this in-line image probe is that a choice can be made between either episcopic or diascopic illumination.
Figure 1. Schematic representation of the image probe integrated in the crystalliser.

2.1 Light Source

A modified Drello 244 point flash stroboscope was used as a light source. A stroboscope was selected for illumination purposes in order to minimise motion blur in pictures of fast flowing small particles. The stroboscope has a built in video-synchroniser. It enables the stroboscope to be triggered 25 times per second by the CCD camera. Under these circumstances the flash intensity is approximately 0.5 J/flash and the half width of the flash is approximately 4 μs. Therefore a particle that moves with a velocity of 1 m s⁻¹ will move approximately 4 μm during the time that an image is collected by the CCD camera. The Drello 244 was equipped with a white shining plug-in type Xenon flash tube with a point-shaped discharge gap, mounted in a point flash lamp. With mechanical adapters fiber optics were attached to the point flash lamp and positioned in the focal point of the converging light flashes.

2.2 Diascopic and Episcopic Illumination

With the image probe described here both diascopic and episcopic illumination can be used. For episcopic illumination an annular fiber optic illuminator was used, which could be mounted on the zoom lens. An annular illuminator was selected, because it ensures a homogeneous light distribution over the particles inside the crystalliser. For the diascopic illumination the stroboscope pulses had to be transported to a position inside the crystalliser. To do this a special stroboscope flash transmission device was designed. A drawing of this device is displayed in Figure 2. The parts of the device that come into contact with the crystalliser contents are constructed of Hastelloy-C.
Figure 2. Drawing of crystalliser fiber optic transmission device for diascopic illumination.

Part 16 is the tube that conducts a fiber optic which is connected to the point flash lamp of the stroboscope. The proximal tip of the fibre optic was shortened, in order to be able to move the fiber optic through the bend in the tube. The fiber optic was inserted in this tube until it reached part 6A. In part 6A a quartz mirror was installed that changed the direction of the light (see Figure 3). An opaline window was placed at the end of the quartz mirror in order to provide a homogeneous distribution of the light. The light transmission tube was sealed off with a sapphire window (17). This window was pressed against the end of the quartz mirror holder (6A), which contained a Kalrez O-ring, with clamping nut 18. Sapphire was used instead of quartz or borosilicate glass, because of its excellent corrosion resistance and mechanical properties. Part 10 in Figure 2 represents the crystalliser wall and part 11 is the holder through which the transmission device slides. The distance between the diascopic light source and the looking glass of the crystalliser can be varied within a range of 4 mm by rotating adjustment nut 15. By varying this distance the thickness of the liquid layer and with that the amount of solids present between the light source and the looking glass can be influenced in order to optimise the quality of the pictures collected. However, care should be taken that this distance is not chosen too small, since then problems with scaling or classification might arise. At position 13 a pen is inserted in order to fix the vertical position of the transmission device, so that it cannot be moved away from the looking glass during the experiments. Finally, parts 12 and 14 conduct the fiber optic transmission device as it moves towards or away from the crystalliser wall.
Figure 3. Drawing of end tip crystalliser fiber optic transmission tube.

2.3 Visualisation Equipment

In front of the crystalliser an Optem 7-to-1 zoom 70 optical system (0.75X to 5.25X) with internal focus is positioned. It is equipped with an auxiliary lens (0.75X), a TV tube (2X) and an iris diaphragm. With this system optical magnifications of approximately 1.1X to 7.9X can be obtained at working distances of 79 to 115 mm. With the iris diaphragm the amount of light that reaches the CCD chip and with that the exposure time of the chip can be influenced. If the aperture of the diaphragm is decreased both the light energy that reaches the CCD chip and the half width of the flash are reduced. However, a reduction in diaphragm aperture increases the depth of focus. The zoom system is attached to a Hitachi KP-C550 CCD colour camera which is connected to a 12" monitor. The linear electronic magnification from camera to monitor is 38.1X. Therefore the total magnification, both optical and electronic, is approximately 43X to 300X. Consequently at the maximum magnification a particle of 10 μm in diameter appears on the monitor as a particle of 3 mm. During the experiments the images produced by the probe can be taped on a S-VHS video recorder.

3. Results and Discussion

The developed in-line image probe was tested with NaCl crystals suspended in a saturated brine. In Figure 4 two digitised images of pictures of the NaCl crystals with dioscopic illumination are displayed. The approximate magnifications are 17X and 55X respectively. In this particular case the stirring rate was 750 rpm and the mass weighted mean size of the crystals is approximately 380 μm. In the picture with the lowest magnification (left), the circular opaline window of the dioscopic light source can still be distinguished (real diameter 6 mm) whereas in the right picture this is no longer the case. The right picture gives a very good impression of the sizes and shapes of the crystals
inside the vessel. At higher magnifications good pictures can still be obtained. Also tests were performed with episcopic illumination. The quality of the pictures obtained this way was also good. However, these pictures can be improved by increasing the amount of light that reaches the CCD chip by using different annular fiber optic illuminators.

Figure 4. Images of NaCl crystals with a mass weighted mean size of ca. 380 μm at approximate magnifications of 17X and 55X with diascopic illumination.

4. Conclusions and Recommendations

An in-line image probe for monitoring particulate processes, such as crystallisation, has been developed. With the image probe sharp pictures of fast flowing small particles can be obtained. On a continuous basis images can be recorded on a video recorder and displayed on a monitor with magnifications varying between 43X and 300X. With this image probe either episcopic or diascopic illumination can be used, so that the information obtained on the particles is maximal.

A disadvantage of this image probe is that it is not very flexible, i.e. it is a part of the crystalliser. A flexible image probe, based on the same principles, has already been designed.

5. Acknowledgements

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Antisolvent Crystallisation with Amines: Product Purity

CHAPTER 4

4 a Crystallisation of Sodium Chloride with Amines as Antisolvents
4 b The Production of Pure NaCl by the Antisolvent Crystallisation of NaCl.H2O and a Consecutive Recrystallisation Step
Chapter 4a


Crystallisation of Sodium Chloride
with Amines as Antisolvents

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The antisolvent crystallisation of NaCl with diisopropylamine and dimethylisopropylamine has been studied in order to determine whether this energy saving crystallisation technique can provide crystals with the required properties. In continuous crystallisation experiments the influence of the amine concentration on the purity, the size and the shape of the formed particles was investigated. The experiments demonstrated that the amine uptake of the crystals varied between 40 and 630 ppm and that the product generally consisted of small and agglomerated crystals. Measures have to be taken to improve product purity in order to make the antisolvent crystallisation of NaCl with amines a realistic alternative to evaporative crystallisation.

Keywords: crystallisation, impurity, sodium chloride, amines, antisolvent.

1. Introduction

In industry well soluble inorganic salts with a small solubility temperature dependence like NaCl, are often separated from water by evaporative crystallisation. The evaporation of water in these processes is energy consuming. To reduce the energy costs in the production of such inorganic salts, crystallisation with an organic antisolvent could be an interesting alternative. The application of antisolvent crystallisation however, introduces an additional separation step in which the antisolvent has to be recovered from the remaining mother liquor after crystallisation. The energy consumption in this separation step must be small in order to make the antisolvent crystallisation process economically attractive. With respect to this the amines diisopropylamine (DiPA) and dimethylisopropylamine (DMiPA) are suitable antisolvents for
the crystallisation of NaCl. They reduce the NaCl solubility significantly and they can be separated from the water phase by a temperature induced liquid-liquid phase split. A simplified block scheme of the antisolvent crystallisation of sodium chloride with these amines is displayed in Figure 1.

![Block scheme for the antisolvent crystallisation of NaCl.](image)

Figure 1. Block scheme for the antisolvent crystallisation of NaCl.

In a viable antisolvent crystallisation process the salt is produced at costs that are low compared to the evaporative crystallisation process, and with a quality preferably equivalent to the quality of the salt produced by evaporative crystallisation. The quality of the product is determined by the shape, size and purity of the particles. In this particular case the purity of the product is most important, since the salt is used for consumption and in electrolysis plants for the production of chlorine. Because these amines form the explosive compound NCl, during electrolysis, the amine uptake in the formed salt crystals must be very low. The maximum allowable amine uptake is 10 ppm. Furthermore, the formed particles should preferably consist of single crystals with an average size equal to the average size of the salt crystals produced by evaporative crystallisation (L₄₁ ~ 350 μm).

To determine whether the antisolvent crystallisation of NaCl with DiPA or DMiPA can provide crystals of the required quality, continuous crystallisation experiments have been carried out. In these experiments the influence of the amine concentration on the purity, size and shape of the formed crystals has been investigated.
1.1 Sodium Chloride Solubilities in Amine-Water Mixtures

The addition of the amines to a (saturated) salt solution influences the salt concentration in two different ways. In the first place the amines reduce the salt concentration through dilution as would be the case if pure water were added to the solution. Secondly, they bind the water molecules resulting in a reduced NaCl solubility in the water volume present in the mixture. This provides the driving force for crystallisation. The influences of both dilution and water binding are demonstrated in Figure 2. The experimental details of these solubility measurements are described in chapter 2. The solid line represents the NaCl solubilities in mixtures of water and dimethylisopropylamine at 5 °C and the dotted line demonstrates the influence of dilution on the salt concentration. The concentration difference between these lines is representative for the amount of NaCl that crystallises as a result of the addition of the antisolvent. This concentration difference therefore equals the NaCl solids concentration in the mixture at chemical equilibrium. As can be seen from Figure 2 the equilibrium solids concentration is generally low for this crystallisation technique. This lack of crystal surface area will keep the supersaturation high during crystallisation.

![Graph 1](image1.png)  ![Graph 2](image2.png)

**Figure 2.** Solubility of NaCl (in kg salt / kg mixed solvent) in DMI PA-water at 5 °C (left) and the equilibrium solids concentration (right).

At antisolvent fractions exceeding 0.85 the NaCl solubility approaches zero. Therefore if a high yield is important the crystallisation is preferably carried out at antisolvent fractions
exceeding 0.85. However due to the low salt solubilities and the very low solids concentrations, the relative supersaturation will be very high at these antisolvent fractions. This will have a profound effect on the size and on the antisolvent uptake of the formed crystals.

1.2 Liquid-Liquid Equilibria of the Amine-Water Mixtures Saturated with Salt

The amines DiPA and DMiPA are particularly suitable for the crystallisation of NaCl because they are partially miscible with water. They form two liquid phase areas, where the amines can be (partly) separated from the water at a low energy consumption. The liquid-liquid equilibria of the DiPA-H₂O and the DMiPA-H₂O systems saturated with NaCl are displayed in Figure 3. The Lower Critical Solution Temperatures of the DiPA-H₂O-NaCl<sub>sat</sub> and the DMiPA-H₂O-NaCl<sub>sat</sub> systems were estimated at -11.7 °C and 6.6 °C (see chapter 2). Below these temperatures there is one single liquid phase present regardless of the concentration of the amine.

![Figure 3](image)

**Figure 3.** Liquid-liquid equilibria of the amine-H₂O systems saturated with NaCl. The ○-marks on the DiPA-H₂O-NaCl equilibrium line were measured by Weingaertner et al. (1991).
The crystallisation is preferably carried out in the single liquid phase area. This is because the NaCl solubility reduction as a result of the addition of the antisolvent is higher in the single liquid phase area than in the double liquid phase area. After the crystallisation, the amines can be recovered from the spent mother liquor by increasing the temperature to an arbitrary value in the double liquid phase area.

2. Experimental

Continuous experiments were carried out at temperatures in the single liquid phase region at several brine to amine feed ratios in a 1 liter crystalliser. A schematic drawing of the experimental setup can be found in Figure 4. The residence time was 30 minutes and each experiment lasted for at least 8 residence times. The brine and the antisolvent were stored in two 10 l vessels. The vessels were positioned on balances, which were connected to Midilab dosage controllers. The antisolvent and the brine were transported towards the crystalliser by Lewa membrane pumps. To ensure constant feed mass flow rates the pump frequencies were controlled by the Midilabs. The feed streams were continuously introduced into the thermostated baffled crystalliser (4 baffles) directly above a pitched blade stirrer \( N = 750 \) rpm. With 30 minutes intervals solid samples were taken from the crystalliser outlet. The crystals were filtered with pressurised nitrogen and washed with ethanol. The amine uptake of the sodium chloride product was determined by TOC (total organic carbon) and gas chromatography, and scanning electron microscopic pictures of the crystals were taken. The remaining part of the crystalliser outlet stream was discarded into a waste vessel. During the experiments the crystalliser contents were recorded continuously with an in-line image probe. The probe enabled the visualisation of fast moving small particles inside the crystalliser. The system consisted of an Optem Zoom 70 lens attached to a CCD camera, a video recorder and a monitor. The zoom lens was positioned in front of a looking glass of the crystalliser and a stroboscope was used for illumination purposes (see chapter 3). The experimental setup is fully automated (Intellution FIX/MMI) and can be operated at temperatures of -20 to 200 °C and at pressures up to 20 bars. Here the crystalliser temperature was 5 °C for the experiments with DMiPA and 1 °C for DiPA and the crystalliser pressure was 3 bar (minimum operating pressure). To prevent corrosion hastelloy-C has been used as the main construction material
for the crystalliser and most of the piping. The antisolvent recovery step is not integrated in this experimental setup, but has been investigated separately. A detailed description of the experimental setup is given in chapter 3.

Figure 4  Schematic drawing of the experimental setup used for the continuous crystallisation experiments.

3. Results and Discussion

Continuous crystallisation experiments were conducted in the single liquid phase area with DiPA and DMiPA as antisolvents. The size, shape and purity of the sodium chloride crystals formed in these experiments were studied. To investigate the influence of the antisolvent concentration on these product characteristics, experiments were performed at several amine to brine feed ratios. All crystallisation experiments were carried out in duplicate and the reproducibility was good.

With DMiPA continuous crystallisation experiments were conducted at four different amine to brine (26 g NaCl / 100 solution) feed ratios at a temperature of 5 °C. The results of
these experiments are listed in Table I. In each experiment agglomerated cubic NaCl crystals were formed and the agglomerates generally contained considerable amounts of the antisolvent. The degree of agglomeration increased with the amine fraction at which the experiments were conducted and at the lower antisolvent fractions hopper shaped crystals were formed.

Table I. Results of the Continuous Crystallisation Experiments with DMiPA.

<table>
<thead>
<tr>
<th>$W_{\text{DMiPA}}$ (\text{ppm})</th>
<th>DMiPA uptake (ppm)</th>
<th>Maximum primary particle size ((\mu\text{m}))</th>
<th>Maximum agglomerate size ((\mu\text{m}))</th>
<th>Degree of agglomeration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>240</td>
<td>50</td>
<td>150</td>
<td>slightly agglomerated</td>
</tr>
<tr>
<td>0.3</td>
<td>40</td>
<td>70</td>
<td>200</td>
<td>agglomerated</td>
</tr>
<tr>
<td>0.6</td>
<td>220</td>
<td>60</td>
<td>150</td>
<td>agglomerated</td>
</tr>
<tr>
<td>0.9</td>
<td>630</td>
<td>10</td>
<td>100</td>
<td>strongly agglomerated</td>
</tr>
</tbody>
</table>

$^a$ $m_{\text{DMiPA}} / (m_{\text{DMiPA}} + m_{\text{H2O}})$

In the area of the antisolvent inlet the antisolvent concentration is high and therefore the NaCl solubility low. This leads to locally high relative supersaturations and consequently to high primary nucleation rates, giving rise to the formation of many small particles. These particles agglomerate easily if also the bulk supersaturation is high. This was in particular the case in the experiment at an antisolvent fraction of 0.9 (see Figure 5). High bulk supersaturations also contribute to the formation of morphological instabilities such as hopper shaped crystals. The formation of such unstable growth forms can however, occur only if the crystals surpass a certain critical length. In the experiment at $w_{\text{DMiPA}} = 0.9$ the primary crystals were too small to develop such morphological instabilities. In the experiment at $w_{\text{DMiPA}} = 0.1$ however, the conditions required for the formation of hopper shaped crystals were met. At the antisolvent fractions of 0.3 and 0.6 fewer hopper shaped crystals were observed.
Figure 5. SEM picture of the strongly agglomerated NaCl crystals formed at $w_{DMiPA} = 0.9$ (NaCl free) and $T = 5$ °C.

In Figure 6 the sodium chloride DMiPA uptakes and the maximum primary particle and agglomerate sizes are plotted against the crystalliser DMiPA concentration. From this figure it follows that beyond $w_{DMiPA} = 0.3$ the amine uptake increases with the antisolvent concentration. This can be attributed to the entrapment of mother liquor in the voids between the primary particles of the agglomerates, that contains more of the amine at higher amine concentrations. Since the particles formed at a DMiPA fraction of 0.9 have a much higher degree of agglomeration (i.e. more primary particles per agglomerate) and were formed in a very DMiPA rich environment, they have the highest DMiPA uptake. The particles formed at an antisolvent fraction of 0.1 form an exception to this rule. These particles are only slightly agglomerated but the hopper shaped crystals, that were frequently observed at this antisolvent fraction, are very prone to inclusion formation due to the overgrowth of macrosteps (see Figure 7).
Figure 6. Sodium chloride DMiPA uptakes, maximum primary particle and maximum agglomerate sizes as a function of the crystalliser DMiPA concentration.

With DiPA continuous crystallisation experiments were carried out at a DiPA fraction of 0.9 at T = 1 °C. Similarly to the experiments carried out at $w_{DMiPA} = 0.9$, the crystals formed at $w_{DiPA} = 0.9$ were strongly agglomerated. The maximum agglomerate and primary particle sizes were 200 μm and 20 μm, respectively. The DiPA concentration in the product was 590 ppm, which is comparable with the DMiPA uptake in the sodium chloride crystals produced at $w_{DMiPA} = 0.9$. With DiPA no crystallisation experiments were performed at the antisolvent fractions of 0.1, 0.3 and 0.6, because at a temperature of 1 °C these compositions form two liquid phases instead of one. At temperatures below zero the crystallisation can be carried out in the single liquid phase with these DiPA fractions. However NaCl.2H₂O instead of NaCl is then formed, which is unstable at room temperature.
4. Conclusions

The sodium chloride crystals formed by antisolvent crystallisation with diisopropylamine or dimethylisopropylamine did not satisfy the product quality requirements. The product generally consisted of small and agglomerated crystals with amine uptakes of 40 to 630 ppm, which is too high. In order to make the antisolvent crystallisation of NaCl a realistic alternative to evaporative crystallisation, measures have to be taken to reduce the antisolvent uptake and to increase the average crystal size.

5. Acknowledgments

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6. Literature Cited

Chapter 4b


The Production of Pure NaCl by the Antisolvent Crystallisation of NaCl.2H₂O and a Consecutive Recrystallisation Step

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NaCl.2H₂O crystals formed by antisolvent crystallisation with N,N-dimethylisopropylamine (DMiPA), were recrystallised batch-wise into NaCl at 0.2 and 0.5 °C in pure brines and in brines containing 5 wt% DMiPA. In all experiments the recrystallisation brought about a strong purification of the solid phase. The average DMiPA concentration in the NaCl.2H₂O crystals was approximately 1000 ppm, whereas the DMiPA concentration in the NaCl product was between 1 and 6 ppm. Both the DMiPA concentration in the mother liquor and the recrystallisation temperature influenced the average NaCl crystal size and the rate at which the recrystallisation took place significantly.

Keywords: sodium chloride, impurity, antisolvent, recrystallisation, purification, N,N-dimethylisopropylamine.

1. Introduction

In industry sodium chloride is produced by evaporative crystallisation, because it is well soluble and has a weak solubility temperature dependence. Since the evaporation of water is energy intensive, the antisolvent crystallisation of NaCl with N,N-dimethylisopropylamine (DMiPA) is investigated as an alternative. DMiPA reduces the solubility of the salt significantly and can be recovered at low energy costs by a temperature induced liquid-liquid phase split (Zijlma, 1995). Depending on the crystallisation temperature either NaCl or NaCl.2H₂O can be formed. Weingaertner et al. (1991) showed that the reduction in energy
costs by applying antisolvent (or extractive) crystallisation can be as high as 63% compared to a three-effect evaporation plant.

However if a salt is crystallised by antisolvent crystallisation it will inevitably contain small amounts of the antisolvent. In continuous crystallisation experiments of NaCl with DMiPA the antisolvent uptake of the sodium chloride crystals varied between 40 and 630 ppm (Zijlema, 1995). To improve the purity of the product a new route for the production of sodium chloride with organic antisolvents has been investigated. In a first step not NaCl but NaCl.2H₂O is formed by antisolvent crystallisation below the NaCl-NaCl.2H₂O transition temperature. In a second step the NaCl.2H₂O crystals are recrystallised in a purer brine at a temperature above the transition point, where the metastable NaCl.2H₂O will dissolve and the solution will become supersaturated with respect to NaCl (Figure 1). Consequently the NaCl will nucleate and grow, and the NaCl.2H₂O will dissolve further. Since the recrystallisation is solution mediated the impurity enclosed in the NaCl.2H₂O crystals is redistributed over the mother liquor and the newly formed solid phase.

![Figure 1](image)

Figure 1. Solubility of NaCl in pure water as a function of temperature.

In this work the influence of such a recrystallisation step on the product purity has been studied in batch recrystallisation experiments. Impure NaCl.2H₂O crystals were recrystallised batch-wise into NaCl in brines containing 0 and 5 wt% DMiPA at various recrystallisation temperatures. The NaCl impurity uptake and the size distribution of the formed crystals were

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determined. In addition the effect of 5 wt% DMiPA on the NaCl-NaCl.2H₂O transition temperature was determined.

2. Thermodynamics

The NaCl-NaCl.2H₂O transition temperature will change in the presence of the antisolvent. The chemical potentials of NaCl and NaCl.2H₂O in the solution are:

\[
\begin{align*}
\mu_{\text{NaCl}} &= \mu_0 + RT \ln(a_{\text{Na}^+} a_{\text{Cl}^-}) \\
\mu_{\text{NaCl.2H₂O}} &= \mu_0 + RT \ln(a_{\text{Na}^+} a_{\text{Cl}^-} a_{\text{H₂O}^2})
\end{align*}
\]

In these equations \(a_{\text{Na}^+}\), \(a_{\text{Cl}^-}\) and \(a_{\text{H₂O}}\) are the activities of the species present in the solution and \(\mu_0\) is the chemical potential of a hypothetical solution at 25 °C and 1 bar with all activities equal to one. At the solubility concentration of NaCl the chemical potential of the solid phase equals the chemical potential of the ions in the solution, and can therefore be written in terms of the thermodynamical solubility product \(K_{\text{sp}}\), given by \(a_{\text{Na}^+} a_{\text{Cl}^-}\) at equilibrium:

\[
\mu_{\text{NaCl}} = \mu_0 + RT \ln(K_{\text{sp,NaCl}})
\]

A similar equation can be written for NaCl.2H₂O. The thermodynamical solubility products of the two crystal modifications can be calculated from their solubilities in pure water (Kaufmann, 1960) and the activity coefficients, which can be calculated by the Pitzer model for electrolyte solutions (Pitzer, 1991).

In pure water the NaCl-NaCl.2H₂O transition temperature is 0.1 °C, which corresponds to a water activity of approximately 0.756. DMiPA reduces the water activity, because the water is coordinated by the amine resulting in a reduced “free water content” of the solution. Therefore the NaCl-NaCl.2H₂O transition temperature decreases in the presence of DMiPA, which can be determined from the following equations:

\[
\begin{align*}
\mu_{\text{NaCl}} &= \mu_{\text{NaClJ}} \\
\mu_{\text{NaCl.2H₂O}} &= \mu_{\text{NaCl.2H₂OJ}}
\end{align*}
\]
Substitution of equation 1 and equation 2 in equation 3 leads to:

\[
\begin{align*}
\mu_0 + RT \ln (K_{sp,NaCl}) &= \mu_0 + RT \ln (a_{Na} a_{Cl}^{-1})_{eq} \\
\mu_0 + RT \ln (K_{sp,NaCl\cdot2H_2O}) &= \mu_0 + RT \ln (a_{Na} a_{Cl} a_{H_2O}^{2})_{eq}
\end{align*}
\]

This set of equations can be simplified to:

\[
\frac{K_{sp,NaCl\cdot2H_2O}(T)}{K_{sp,NaCl}(T)} = a_{H_2O}^{2} \quad \text{(at the transition points)}
\]

Because the solubility products of both phases are only a function of temperature, equation 5 shows that the phase transition temperature is exclusively determined by the water activity. Figure 2 shows the dependency of the phase transition temperature on the water activity calculated from equation 5. In Figure 2 also the NaCl\cdot2H_2O-NaCl transition temperatures in pure water (Kaufmann, 1960) and in 5 wt% DMiPA (see section 4.1) are displayed.

![Figure 2](image_url)

**Figure 2.** The NaCl\cdot2H_2O-NaCl transition temperature as a function of the water activity. The □-mark is in pure water and the ◊-mark is in 5 wt% DMiPA.
3. Experimental

All experiments were carried out in a thermostated room at temperatures between 0 and -5 °C. The used chemicals are N,N-dimethylisopropylamine (C₆H₁₃N, Fluka purum ≥ 98%), demineralised water (conductivity: 4 mS·cm⁻¹) and pharmaceutical grade sodium chloride (Akzo Nobel). The NaCl·2H₂O crystals were produced by batch antisolvent crystallisation with DMiPA at -5 °C in a thermostated 1.7 liter vessel in which agitation was provided by a marine type propeller (250 rpm). At the beginning of the experiment the vessel was filled with 635 g of saturated brine and subsequently 715 g of DMiPA was added at a rate of approximately 6 g/min. Finally the crystals were separated from their mother liquor by filtration and the crystals were washed three times with pure saturated brine. The wet crystals were centrifuged for 5 minutes at 2500 rpm (ca. 750 g).

3.1 In-Situ Determination of the NaCl-NaCl·2H₂O Transition Temperature in a Brine Containing 5 wt% DMiPA

The NaCl-NaCl·2H₂O transition temperature in a brine containing 5 wt% DMiPA was determined in a jacketed glass cell placed under a microscope with a polarised light source. The cell was thermostated with a Lauda RK8-KP cooling thermostat and the temperature in the cell was measured by an ASL-F250 precision thermometer (0.01 °C accuracy, 0.002 °C repeatability). The experiments were started by filling the cell with 20 g of the NaCl saturated amine-water mixture at the desired temperature. Subsequently 0.1 g NaCl and 0.1 g NaCl·2H₂O crystals were added to the solution and the lid was closed. The cell was placed under the microscope and the growth and dissolution of the crystals were observed at a constant temperature. The NaCl·2H₂O crystals (monoclinic) could easily be distinguished from the NaCl crystals (cubic) because of their different morphology and their birefringence. At temperatures above the NaCl-NaCl·2H₂O transition point the NaCl·2H₂O dissolves and the NaCl grows and at temperatures below the transition point the opposite occurs.

3.2 Batch Recrystallisation Experiments

The batch recrystallisations were carried out at temperatures of 0.2 and 0.5 °C and at DMiPA concentrations of 0 and 5 wt% (NaCl free weight percentage). The experiments were conducted in a 500 ml thermostated vessel in which the solids were suspended with a marine
type propeller (250 rpm). At the beginning of each experiment the vessel was filled with approximately 400 g of a clear NaCl saturated solution with or without DMiPA at -2 °C, which is below the NaCl-NaCl,2H₂O transition temperature. Subsequently the NaCl,2H₂O crystals, with an average size of approximately \( L_{43} = 650 \) micron (\( L_{43} = \frac{m_t}{m_s} = \frac{\int_0^\infty l^4 n(l) dl}{\int_0^\infty l^3 n(l) dl} \), with \( l \) as the particle size and \( n(l) \) as the population density), were added to the solution up to a solids concentration of 19.6 wt%. Thereafter the temperature of the suspension was raised to the recrystallisation temperature in a period of 30 minutes, during which no NaCl crystals were formed. At this point the NaCl seeds consisting of pharmaceutical pure sodium chloride crystals that were washed with a slightly undersaturated brine, were added to the solution. The average size of the washed NaCl seeds was \( L_{43} = 380 \) micron. The NaCl solids concentration was 1 wt% at the beginning of the experiment, which is approximately 10 wt% of the total amount of NaCl crystals in the reactor at the end of the recrystallisation. During the recrystallisation process samples were taken from the suspension. The crystals were separated from the mother liquor in a centrifuge (5 minutes at 2500 rpm, ca. 750 g) and light microscopic pictures were made. Part of the solid sample was weighed and dried in an oven at 150 °C for 12 hours. In the oven the NaCl,2H₂O fraction within the solid sample lost its crystal water and the water in the adhering mother liquor was evaporated as well. The decrease in weight of the solid sample was a measure for the fraction of NaCl,2H₂O crystals in the solid sample. The measured solid sample weight losses were used to follow the NaCl,2H₂O conversion during the recrystallisation process. After the recrystallisation crystal size distributions were determined from the formed NaCl crystals with a Coulter Multisizer. Furthermore the DMiPA uptake in the NaCl product was measured by gas chromatography. For this purpose the NaCl crystals were dissolved in water and the amine was extracted from the aqueous solution with pentane. Subsequently the DMiPA concentration in the pentane phase was determined by a gas chromatograph equipped with a Poraplot column and a NPD detector. The average DMiPA concentration in the NaCl,2H₂O crystals was approximately 1000 ppm.
4. Results and Discussion

4.1 In-Situ Determination of the NaCl-NaCl.2H₂O Transition Temperature in a Brine Containing 5 wt% DMiPA

The in-situ recrystallisation experiments in a brine containing 5 wt% DMiPA (NaCl free weight percentage) showed that at temperatures of -1.00 and -0.70 °C the NaCl dissolved and the NaCl.2H₂O grew (Table I). At -0.60 °C the NaCl was stable and the NaCl.2H₂O grew. At -0.50 °C however the NaCl.2H₂O dissolved and the NaCl was again stable, indicating that the NaCl-NaCl.2H₂O transition temperature lies somewhere between -0.50 and -0.60 °C. At -0.20 and 0.00 °C the NaCl grew and the NaCl.2H₂O dissolved. If the transition temperature is assumed to be -0.55 °C, than the water activity decreased from ca. 0.756 in a pure brine to ca. 0.752 in a brine containing 5 wt% DMiPA according to Figure 2. In Figure 3 two light microscopic pictures of the in-situ recrystallisation experiment at -0.70 °C are displayed. The NaCl.2H₂O crystal indicated in the pictures, grew to a bigger size in about three hours and the size of the NaCl crystal decreased due to dissolution.

![NaCl.2H₂O](image1.png)  
experiment time: 3:55 (h:mm)

![NaCl.2H₂O](image2.png)  
experiment time: 7:10 (h:mm)

Figure 3. Light microscopic pictures of an in-situ recrystallisation at T = -0.70 °C in a brine containing 5 wt% DMiPA: NaCl.2H₂O grows and NaCl dissolves (width pictures: 1000 micron).
Table 1. Results of the In-situ Determination of the NaCl-NaCl.2H₂O

Transition Temperature in a Brine Containing 5 wt% DMiPA.

<table>
<thead>
<tr>
<th>solution temperature (°C)</th>
<th>NaCl(s)</th>
<th>NaCl.2H₂O(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.00 and -0.70</td>
<td>dissolves</td>
<td>grows</td>
</tr>
<tr>
<td>-0.60</td>
<td>stable</td>
<td>grows</td>
</tr>
<tr>
<td>-0.50</td>
<td>stable</td>
<td>dissolves</td>
</tr>
<tr>
<td>-0.20 and 0.00</td>
<td>grows</td>
<td>dissolves</td>
</tr>
</tbody>
</table>

4.2 Batch Recrystallisation Experiments

The water fractions in the solid samples of the recrystallisation experiments are displayed in Figures 4 and 5. The solid sample water fractions that remain after all NaCl.2H₂O has been converted, originate from the water present in the adhering mother liquor surrounding the crystals. The average error bound on the recrystallisation temperature values is approximately ±0.06 °C. This is caused by small fluctuations in the thermostat liquid temperature during the experiments. During the conversion in a pure brine at 0.5 °C all NaCl.2H₂O was dissolved after a period of approximately 170 minutes, whereas at a temperature of 0.2 °C it took 570 minutes for all NaCl.2H₂O to dissolve. At a temperature of 0.2 °C in a mother liquor containing 5 wt% DMiPA all the NaCl.2H₂O was converted after a period of approximately 100 minutes and at 0.5 °C after only 50 minutes. From Figures 4 and 5 it can be seen that the time needed for all NaCl.2H₂O to dissolve decreases at an increasing recrystallisation temperature. This is attributed to an increased difference in solubility between the metastable NaCl.2H₂O and the stable NaCl phases at a higher temperature and thus an increased driving force (see Figure 1). Furthermore the time needed for all NaCl.2H₂O to dissolve is also reduced if the recrystallisation is carried out in the presence of 5 wt% DMiPA, because also in this case the solubility difference between both phases increases since the presence of the amine reduces NaCl-NaCl.2H₂O transition temperature.

In Figure 6 the NaCl crystals formed by recrystallisation at 0.2 °C (left) and at 0.5 °C (right) in a pure brine are depicted. Due to an increased supersaturation and consequently an increased nucleation rate during the recrystallisation, the particles formed at 0.5 °C are much smaller (L₄₃ = 210 micron, Table II) than the particles formed at 0.2 °C (L₄₃ = 430 ± 30
micron) and slightly agglomerated. The experiments carried out in a mother liquor containing 5 wt% DMiPA showed similar behavior. Furthermore the particles formed at 0.2 °C in a pure brine have been more subject to abrasion, because of their long residence time in the crystalliser (see Table II) and their relatively large sizes. In the SEM picture of the experiment at 0.5 °C in a pure brine (Figure 6) the seed crystals can clearly be distinguished from the newly formed particles. This bimodal character was also observed in the size distribution of the product crystals, and was present in the product crystal size distributions of all the recrystallisation experiments.

![Graphs showing water fraction in solid samples as a function of time for recrystallisation in pure water at 0.2 and 0.5 °C.]

Figure 4. Water fraction in solid samples as a function of time for the recrystallisation in pure water at 0.2 and 0.5 °C.

Table II. Results of the Batch Recrystallisation Experiments.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>[DMiPA] (wt%)</th>
<th>NaCl.2H₂O dissolution time (min)</th>
<th>NaCl.2H₂O DMIPA uptake (ppm)</th>
<th>NaCl DMiPA uptake (ppm)</th>
<th>L₄₃ NaCl (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0</td>
<td>570</td>
<td>850 ± 20</td>
<td>2 ± 1</td>
<td>430 ± 30</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
<td>170</td>
<td>810</td>
<td>3</td>
<td>210</td>
</tr>
<tr>
<td>0.2</td>
<td>5</td>
<td>100</td>
<td>890 ± 230</td>
<td>6</td>
<td>330 ± 20</td>
</tr>
<tr>
<td>0.5</td>
<td>5</td>
<td>50</td>
<td>1300 ± 140</td>
<td>4 ± 1</td>
<td>230 ± 20</td>
</tr>
</tbody>
</table>
Figure 5. Water fraction in solid samples as a function of time for the recrystallisation in water containing 5 wt% DMiPA at 0.2 and 0.5 °C.

In all recrystallisation experiments the recrystallisation brought about a strong purification of the solid phase. Although the DMiPA addition rate was constant during all the batch NaCl.2H₂O crystallisation experiments the NaCl.2H₂O DMiPA uptake varied between 600 and 1500 ppm (Table II). These high DMiPA uptakes are considered to be the result of the formation of inclusions, which were present to large extents in the NaCl.2H₂O crystals. The

Figure 6. SEM pictures of the NaCl product formed in the recrystallisation experiments at 0.2 (left) and 0.5 °C (right) in a pure brine (magnification: 35).
DMiPA concentration in the formed NaCl crystals varied between 1 and 6 ppm for all recrystallisation experiments and did not show a strong dependency on the NaCl.2H₂O DMiPA uptake, the recrystallisation temperature nor on the DMiPA concentration in the mother liquor.

5. Conclusions

Recrystallisation of NaCl.2H₂O into NaCl gives a 100 to 900 fold purity increase of the solid phase. The average DMiPA concentration in the NaCl.2H₂O was approximately 1000 ppm, whereas the DMiPA concentration in the NaCl product was between 1 and 6 ppm. The recrystallisation rate was higher at an increased recrystallisation temperature and in the presence of DMiPA, because of a greater difference in the solubility between the metastable NaCl.2H₂O and the stable NaCl phases, leading to a higher supersaturation. This higher supersaturation causes more nucleation and agglomeration. The presence of 5 wt% DMiPA increases the solubility difference between the NaCl and the NaCl.2H₂O, because it reduces the transition temperature from 0.10 °C in a pure brine to -0.55 °C.

6. Literature Cited

Antisolvent Crystallisation with 2-Isopropoxyethanol: Crystal Size and Morphology

CHAPTER 5

5 a Control of Particle Size in Continuous Antisolvent Crystallisation
5 b In-line Particle Counter for Counting Fast Moving Small Particles at Low Concentrations
5 c Primary Nucleation in the Antisolvent Crystallisation of NaCl with 2-Isopropoxyethanol
Chapter 5a


Control of Particle Size in Continuous Antisolvent Crystallisation

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Continuous crystallisation experiments demonstrated that NaCl crystals formed by antisolvent crystallisation are generally small and agglomerated. This results from extensive primary nucleation at the antisolvent inlet in the crystalliser. The supersaturation at the antisolvent inlet and with that the primary nucleation rate can be reduced by adding water to the antisolvent. This however, reduces the yield. Another option to reduce primary nucleation and suppress agglomeration is to crystallise the salt in the two liquid phase area, provided that the antisolvent-water-NaCl system is partially miscible. In the double liquid phase area the yield is lower than in the single liquid phase area.

Keywords: crystallisation, antisolvent, NaCl, extraction.

1. Introduction

Well soluble inorganic salts with a weak solubility temperature dependence like sodium chloride are usually separated from their solutions by evaporative crystallisation. The energy consumption in the production of these salts can be reduced by applying antisolvent crystallisation with antisolvents that demix from water upon a temperature variation (Weingaertner, 1991). With respect to this 2-isoproxyethanol is a suitable antisolvent (see chapter 2), because its presence reduces the solubility of NaCl (Figure 1) and it has a two liquid phase area with a brine close to room temperature (Figure 2).
Figure 1. NaCl solubilities in mixtures of IPE and water at 15 °C.

If an antisolvent is added to a brine the salt concentration is influenced in two different ways. The addition of the antisolvent dilutes the mixture and with that reduces the concentration of the salt. In addition, the antisolvent molecules bind the water molecules and with that reduce the amount of free water available for the ions present in the solution. Thus, the solubility of the sodium chloride in the water phase decreases. The effects of dilution and water binding are demonstrated in Figure 1 for the addition of 2-isopropoxyethanol to a

Figure 2. Liquid-liquid equilibrium line of IPE-H₂O mixtures at NaCl saturation.
saturated brine. The mixing line (dotted) depicts the NaCl concentrations that arise if a saturated brine is mixed with an antisolvent in the absence of crystallisation, and thus represents the effect dilution. As a result of a reduced free water content, the NaCl concentration in the mixture decreases to a value on the equilibrium line (solid) due to crystallisation.

The concentration difference between the dilution and the solubility lines is representative for the amount of salt that crystallises as a result of the mixing of the brine and 2-isopropanol. If instantaneous mixing were possible the NaCl concentration in the mixture would be on the mixing line and the driving force for crystallisation, i.e. the relative supersaturation \((\sigma = (C-C_{eq})/C_{eq})\), maximal. These maximum concentration differences and relative supersaturations are presented in Figure 3. This figure demonstrates that in antisolvent crystallisation, especially in the high 2-isopropanol concentration range, very high relative supersaturations can be obtained.

![Graph](image)

Figure 3. The maximum relative supersaturations \((\sigma = \Delta c/c_{eq})\) and concentration differences that can be obtained.

High supersaturations lead to extensive primary nucleation and consequently to the formation of small crystals that easily agglomerate if also the supersaturation in the bulk is
high. The fact that the crystals formed by continuous antisolvent crystallisation are generally small and agglomerated (Zijlema, 1995), confirms the occurrence of high relative supersaturations in antisolvent crystallisation.

To suppress agglomeration and to increase the average crystal size, the supersaturation in the area of the antisolvent inlet and in the bulk should be reduced. Methods to reduce these high local and bulk supersaturations are:

I. Diluting the antisolvent or the brine with water to reduce the supersaturation in the inlet areas.

II. Improving the mixing in the crystalliser. This influences the mixing intensity in the area of the reactor inlets and with that supersaturation and antisolvent concentration profiles in the crystalliser.

III. Increasing the crystalliser solids concentration, to increase the total amount of crystal surface area available for growth and thus to reduce the bulk supersaturation.

IV. Raising the crystallisation temperature to a value in the double liquid phase area. This changes the crystallisation drastically, because in the two liquid phase area three phases coexist in the crystalliser, i.e. a solid NaCl phase, an organic liquid phase and an aqueous liquid phase.

In this work the influence of method I and method IV on the size, shape and purity of NaCl crystals formed by continuous antisolvent crystallisation with 2-isopropoxyethanol is discussed. The improvement of the mixing was not considered to be relevant, since the power input was already very high in the experiments carried out previously (Zijlema, 1995). The effect of an increased solids concentration on agglomeration and average particle size is the subject of current investigations.

2. Experimental

2.1 Chemicals

The chemicals were 2-isopropoxyethanol \(((CH_3)_2CHOCH_2CH_2OH\), Fluka Chemie AG \(\geq 99.7\%\)), pharmaceutical grade sodium chloride (Akzo Nobel) and demineralised water with a conductivity of less than 4 mS·cm\(^{-1}\). Furthermore, technical grade ethanol was used to wash the NaCl crystals.
2.2 Setup

The continuous crystallisation experiments were carried out in a 1.8 l glass draft tube baffled jacketed crystalliser. A schematic representation of the experimental setup can be found in Figure 4. A marine type propeller (down pumping) was used to keep the solids in suspension and the stirrer rate was 400 rpm. The suspension is withdrawn from the crystalliser intermittently. For this three conductivity electrodes were installed: a reference electrode (long), a low level electrode (middle) and a high level electrode (short). If all three electrodes make contact with the solution, a high level is detected and suspension will be withdrawn until both the high and the low level electrodes are above the liquid level. The difference in height between the high and the low level electrodes was approximately 0.5 cm, corresponding to a volume $4.8 \times 10^3$ liter (2.6% of total crystalliser volume). The suspension leaves the crystalliser via a bottom outlet (see Figure 4). This is a glass tube which is slightly curved to prevent the build up of solids in the tube during the time no suspension is removed from the crystalliser. The crystalliser temperature was measured with a PT100 element. The PT100 was connected to a circulation thermostat, which was used to maintain a constant temperature in the crystalliser. The antisolvent and the brine were stored in two 15 l

![Diagram](image)

Figure 4. Schematic representation of the continuous crystallisation setup.
thermostated vessels. Both vessels were positioned on a balance, each of which was connected to a Midilab dosage controller. The Midilabs controlled the frequencies of the Watson Marlow peristaltic pumps that were used to transport both feed streams to the crystalliser. The peristaltic pumps were provided with special pump heads to minimise feed flow rate fluctuations.

2.3 Analyses

Solid samples were taken from the suspension that leaves the crystalliser. The crystals were washed with ethanol and dried in an oven at 100 °C for 24 hours. Pictures of the NaCl crystals were made with a Scanning Electron Microscope. The last solid sample was also used for the determination of the crystal size distribution with a Coulter Multisizer II and for the measurement of the NaCl antisolvent uptake by gas chromatography (Carlo Erba 5300 Mega, column: Pora Plot 27.5 m, incl. 2.5 m particle trap, $\varnothing_{i} \sim 0.32$ mm). Furthermore, during the experiments suspension samples were taken from the crystalliser outlet to determine the suspension solids concentration. The suspension samples were first weighed and then filtered. Subsequently the mass of the washed and dried crystals was determined and the solids concentration was calculated.

3. Results and Discussion

3.1 Crystallisation in the Single Liquid Phase Area

A simplified representation of the mixing of the brine and the antisolvent with the crystalliser contents is presented in Figure 5. Due to an imperfect mixing the antisolvent concentration and the supersaturation are not uniform throughout the crystalliser. In the area of the antisolvent inlet the antisolvent concentration is higher, and in the area of the brine inlet it is lower.
Figure 5. Simplified representation of the mixing of the antisolvent and the brine with the reactor contents.

At the antisolvent inlet the antisolvent is mixed with the crystalliser contents. In Figure 6 (left) the effects of dilution and water binding on the equilibrium salt concentration as a result of adding pure antisolvent to a bulk solution with an antisolvent concentration of 50 wt% at NaCl saturation are displayed. To get some insight in the magnitude of the supersaturations that can be encountered in the area of the antisolvent inlet, the maximum relative supersaturations obtained by mixing of pure antisolvent with the bulk solution were calculated from the concentration differences between the mixing and solubility lines. The calculated maximum relative supersaturations are displayed in the right hand picture of Figure 6. It can be seen that the mixing of pure antisolvent and bulk solution at various ratios can result in very high relative supersaturations.
Figure 6. The mixing of pure antisolvent with a bulk solution at NaCl saturation with an IPE concentration of 50 wt% and the maximum relative supersaturations at the antisolvent inlet.

Similar plots were made for the mixing of the brine with the same bulk solution at various mixing ratios and the maximum relative supersaturations were calculated similarly. In Figure 7 (left) the effects of dilution and water binding on the equilibrium salt concentration are displayed. The NaCl concentration difference between the mixing and the solubility lines is smaller and the NaCl solubility is much higher. Therefore, as is indicated in Figure 7 (right), the maximum relative supersaturations are much lower if brine is mixed with the bulk solution. Consequently the mixing of the antisolvent with the (super-) saturated crystalliser contents during continuous crystallisation will be the most critical.
Figure 7. The mixing of a saturated brine with bulk solution at NaCl saturation with an IPE concentration of 50 wt% and the maximum supersaturations at the brine inlet.

The supersaturation at the inlets can be reduced by diluting the feed streams with water. Dilution will however reduce the yield and thus the solids concentration in the crystalliser. If the antisolvent is diluted with 20 wt% of water, the equilibrium solids concentration will decrease from 4.3 to 0.8 wt%. The right hand picture of Figure 8 shows that adding 20 wt% water to the antisolvent eliminates any supersaturation at the antisolvent inlet. The supersaturation in the brine inlet can be reduced similarly. If the salt concentration in the brine is reduced from 35.9 to 26.4 wt% \( (m_{NaCl}/m_{H2O} \times 100) \), the equilibrium solids concentration is also reduced from 4.3 to 0.8 wt%. The effect of this action is displayed in the left hand picture of Figure 8. In this case the mixture is undersaturated with respect to NaCl at any brine to bulk solution mixing ratio.
Figure 8. The mixing of an unsaturated brine (left) or IPE containing 20 wt% water (right) with a bulk solution at NaCl saturation with an IPE concentration of 50 wt%.

The influence of diluting the antisolvent or the brine on the size, shape and purity of NaCl crystals formed by antisolvent crystallisation with 2-isopropanol has been investigated in continuous crystallisation experiments. The experiments were carried out at 15 °C, which is well below the liquid-liquid equilibrium line of the 2-isopropanol-water-NaCl system (see Figure 2). The mean residence time was 30 minutes in all experiments and the 2-isopropanol concentration in the crystalliser was 50 wt% \( \left( \frac{m_{\text{IPE}}}{m_{\text{H}_2\text{O}} + m_{\text{IPE}}} \times 100 \right) \). In the ‘standard’ experiment NaCl was crystallised by feeding a saturated brine and pure antisolvent to the crystalliser. In the other experiments either the antisolvent was diluted with 20 wt% of water or the NaCl concentration in the brine was decreased from 35.9 to 26.4 wt% \( \left( \frac{m_{\text{NaCl}}}{m_{\text{H}_2\text{O}}} \times 100 \right) \). The most important results of these experiments are summarised in Table 1.
Table I. Mean sizes and antisolvent uptakes of the NaCl crystals separated from the suspension after the tenth residence time for the experiments carried out in the single liquid phase area.

<table>
<thead>
<tr>
<th></th>
<th>undiluted feeds</th>
<th>diluted antisolvent feed</th>
<th>diluted brine feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass weighted mean size (µm)</td>
<td>160</td>
<td>260</td>
<td>120</td>
</tr>
<tr>
<td>antisolvent uptake (ppm)</td>
<td>30</td>
<td>100</td>
<td>90</td>
</tr>
</tbody>
</table>

In the experiment with the undiluted feeds the mass weighted mean size of the formed particles was approximately 160 µm and the 2-isopropanol uptake was 30 ppm. As can be seen from Figure 9 (left) the NaCl crystals were strongly agglomerated. This is attributed to extensive primary nucleation at the antisolvent inlet in the crystalliser. The primary nucleation leads to the formation of small crystals that easily agglomerate if the supersaturation is high.

If the antisolvent is diluted with 20 wt% water, the mass weighted mean particle size strongly increases (see Table I) and the degree of agglomeration decreases significantly as can be seen from Figure 9 (middle). This is consistent with the hypothesis that due to the high supersaturations near the antisolvent inlet small particles are formed that tend to agglomerate. As can be seen from Figure 10 the solids concentration in the crystalliser outlet was not constant throughout the experiment with the diluted antisolvent. The equilibrium solids concentration depicted in Figure 10 corresponds with the solids concentration in the crystalliser at 100% NaCl conversion (chemical equilibrium). Until after the first residence time no crystals were observed visually. Then the solids concentration in the outlet increased from 0.1 wt% after two residence times to 1.9 wt% after ten residence times. This also confirms that the nucleation rate is much lower under these circumstances than in the experiment with the undiluted feeds. The final solids concentration in the outlet of 1.9 wt% is 1.1 wt% above the crystalliser equilibrium solids concentration. This accumulation of solids in the crystalliser is attributed to classification in the curved crystalliser outlet tube. Despite of the increasing solids concentration, the samples that were taken after each residence time consisted of similarly shaped and sized particles.
Figure 9. Scanning electron microscope images of the NaCl crystals formed by continuous crystallisation in the single liquid phase area after ten mean residence times (magnification: 75x).
Figure 10. Solids concentration in the crystalliser outlet for the experiments carried out in the single liquid phase area.

The impurity uptake of the formed NaCl crystals increased from 30 ppm in the experiment with undiluted feeds to 100 ppm with a diluted antisolvent feed. This can be attributed to the fact that the NaCl particles formed with a diluted antisolvent feed show faces with pyramidal shaped depressions. Such crystals, also known as hopper crystals, are formed if the supersaturation is high and the transport of growth units to the crystal surface is rate limiting (Sekerka, 1993). Under these circumstances step sources are generated by surface nucleation on the better accessible edges of the crystal. Due to blocking the steps bunch to form macrosteps under which mother liquor inclusions are likely to be formed due to overgrowth. A certain minimum crystal size is required before instable growth forms, such as hopper crystals, can be recognised. This is probably why hopper crystals were not encountered in the solid samples of the other experiments in the single liquid phase area.

The reduction of the NaCl concentration in the brine feed from 35.9 to 26.4 wt% resulted in the formation of smaller agglomerates than in the experiment with undiluted feeds ($L_{43} = 120 \ \mu m$), consisting of smaller primary particles (Figure 9, right). During the entire experiment the NaCl solids concentration in the outlet remained approximately constant and was close to its calculated equilibrium value. Diluting the brine apparently does not influence the primary nucleation rate significantly. Also here the impurity uptake of the product is
higher than in the experiment with undiluted feeds. No clear explanation was found for this, other than that the degree of agglomeration is higher (more primary particles per agglomerate).

3.2 Crystallisation in the Double Liquid Phase Area

Since the 2-isopropoxyethanol-water-salt system is partially miscible, the NaCl can also be crystallised in the two liquid phase area (Figure 2). In the two liquid phase area there is a water rich and a 2-isopropoxyethanol rich liquid phase. The driving force for crystallisation is obtained by two different mechanisms. One is the extraction of water from the aqueous phase to the organic phase and the other is the dissolution of 2-isopropoxyethanol in the aqueous phase. This changes the crystallisation process drastically. In the two liquid phase area the crystallisation predominantly takes place in the aqueous phase where the NaCl is well soluble, which results in lower relative supersaturations. Furthermore, the mixing of the brine and the antisolvent with the crystalliser contents are very different. The brine and the antisolvent distribute over the aqueous and the antisolvent phases instead of being fully mixed with the crystalliser bulk solution. Furthermore, as a result of the partial miscibility of the antisolvent and the water in the crystalliser, the overall solubility of the salt is higher and thus the NaCl yield lower.

The crystallisation experiments in the double liquid phase area were carried out at a temperature of 35 °C with undiluted feeds at mean residence times of 30 and 60 minutes. At this temperature and an overall 2-isopropoxyethanol concentration of 50 wt%, the 2-isopropoxyethanol-water-NaCl(sat) system splits up into an organic phase containing 31 wt% of water and an aqueous phase in which 15 wt% of 2-isopropoxyethanol dissolves (the antisolvent concentrations are expressed as \( m_{\text{wef}}/(m_{\text{wef}}+m_{\text{pe}}) \times 100 \) wt%). The mixture

<table>
<thead>
<tr>
<th>( \tau = 30 \text{ min} )</th>
<th>( \tau = 60 \text{ min} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass weighted mean size (( \mu \text{m} ))</td>
<td>260</td>
</tr>
<tr>
<td>antisolvent uptake (ppm)</td>
<td>70</td>
</tr>
</tbody>
</table>

Table II. Mean sizes and antisolvent uptakes of the NaCl crystals separated from the suspension after 10 residence times of 30 minutes or after 7 residence times of 60 minutes for the experiments carried out at 35 °C in the double liquid phase area.
consists of approximately 60 wt% of the organic phase and the remaining 40 wt% is the aqueous phase. It is not known which is the continuous phase. Under these circumstances the equilibrium solids concentration at 100% NaCl conversion is approximately 3.4 wt%.

As can be seen from Table II and Figure 12 the crystals formed at a residence time of 30 minutes have a mass weighted mean size of 260 μm, an antisolvent uptake of 70 ppm and are slightly agglomerated. The mean size of these particles equals the mean size of those formed by crystallisation in the single liquid phase area with an antisolvent feed containing 20 wt% of water. Apparently, the partial miscibility of the antisolvent and the bulk solution reduces the supersaturation in the area of the antisolvent inlet and with that the nucleation rate.

![Graph](image)

**Figure 11.** Solids concentration in the crystalliser outlet for the experiments carried out in the double liquid phase area.

Furthermore, the solids concentration in the crystalliser as well as the shapes and sizes of the NaCl crystals encountered in the solid samples were not the same throughout the experiment at a residence time of 30 minutes. After one residence time the NaCl crystals were slightly agglomerated and quite uniform in size. Up to the fifth residence time, after each residence time, the primary particles that constituted the agglomerates grew to larger sizes and the number of primary particles per agglomerate reduced. After the fifth residence time the solids concentration in the crystalliser outlet reached a maximum of 3.9 wt% (Figure 11). This is 0.5 wt% above the equilibrium solids concentration, i.e. the solids concentration in the crystalliser at a NaCl conversion of 100%. This accumulation of solids in the crystalliser is
attributed to classification in the crystalliser outlet, i.e. the larger particles have difficulty to leave the crystalliser via the curved outlet tube. After the sixth residence time the size and shape of the crystals encountered in the solid sample changed drastically (Figure 12) and the solids concentration in the crystalliser outlet dropped to 3.3 wt%. Many agglomerates consisting of primary particles with diameters smaller than 100 μm were encountered along with larger particles, similar to the ones observed in the previous sample (visually estimated characteristic size: 400 μm). Apparently the supersaturation builds up until the fifth residence time, after which it decays as a result of an increased (secondary) nucleation rate. The reduction in the crystalliser solids concentration after the sixth residence time is attributed to the fact that, in contrast to the large particles after the fifth residence time, the smaller particles after the sixth residence time leave the crystalliser more easily via the curved crystalliser outlet tube. After the seventh residence time until the end of the experiment the degree of agglomeration decreased and the average particle size increased. This was accompanied by an increasing solids concentration in the crystalliser.

The second experiment in the double liquid phase area was carried out at a mean residence time of 60 minutes. This experiment showed similar behaviour to the experiment described previously, with the exception that the average particle sizes were larger. Here also the shape and size of the NaCl crystals encountered in the solid samples changed drastically after the

Figure 12. Scanning electron microscope images of the NaCl crystals formed by continuous crystallisation in the double liquid phase area at a mean residence time of 30 minutes (magnification: 75x).
fifth residence time. The crystal product changed from large single crystals (estimated characteristic size: 500 µm) to a combination of similar large single crystals and many agglomerates consisting of primary particles with sizes less than 100 µm. This change in size and shape of the crystals was however, not reflected in a significant reduction in the crystalliser solids concentration as was the case in the previous experiment. Furthermore, the large crystals formed in this experiment generally contained disordered surface structures with irregularities such as holes.

The fact that the mass weighted mean size increases approximately by a factor of 2.4 upon doubling the mean residence time is surprising (see Table II). An explanation for this strong increase in average particle size is that the experiments in the double liquid phase area showed oscillatory behaviour. Because stationary conditions were not obtained in neither of the two experiments, it is impossible to compare the measured average crystal sizes.

Finally, in the experiments in the double liquid phase area fewer hopper crystals were formed. This is attributed to the increased solubility of the NaCl in the aqueous phase from which the crystals grow, resulting in a lower level of the relative supersaturation.

4. Conclusions

Two tools have been identified which enable to some extent the control of particle size and agglomeration in the continuous antisolvent crystallisation of NaCl. One option is to add water to the antisolvent that is fed to the crystalliser. By doing this the supersaturation at the antisolvent inlet and with that the primary nucleation rate are reduced, resulting in the formation of larger less agglomerated primary crystals. A disadvantage of this method is that the yield decreases. An alternative is to crystallise the salt from the two liquid phase area. Continuous crystallisation from the two liquid phase area can provide large single crystals. Due to the limited miscibility of the antisolvent and the crystalliser contents in the double liquid phase area, the supersaturation is lower near the antisolvent inlet resulting in a reduced nucleation rate. Whereas the antisolvent crystallisation in the single liquid phase area shows much similarity with precipitation, i.e. high (local) supersaturations and the formation of small particles, the antisolvent or extractive crystallisation in the double liquid phase area more resembles crystallisation, i.e. low supersaturations and the formation of large single
crystals. However, due to an increased solubility the yield in the double is lower than in the single liquid phase area.

5. Acknowledgements

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6. Literature Cited


Chapter 5b

submitted to Powder Technology

In-line Particle Counter for Counting Fast Moving Small Particles at Low Concentrations

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An in-line particle counter has been developed for counting fast moving small particles at low concentrations. Its intended use is for measuring nucleation rates and induction times in rapid crystallisation processes. The particles are counted by means of obscuration measurements of a focused He-Ne laser beam in an optical flow cell. The counter was calibrated with monodisperse spherical PolyDiVinylBenzene particles with sizes of 1.18 up to 87.50 μm. The maximum used particle concentration during the calibrations was approximately $2 \times 10^{11}$ (#/m$^3$) and up to that concentration coincidence in the measurement volume was insignificant. The counter is still accurate at particle velocities of up to 16 m s$^{-1}$ and can be used at pressures of up to 10 bar. The volume fraction of particles needed for counting one particle per second was $10^9$-$10^{10}$ for particles in the size range of 1.18-10.00 μm and about $10^{-4}$ for particles of 87.50 μm.

Keywords: particle counting, obscuration, in-line, nucleation, crystallisation.

1. Introduction

Rapid crystallisation processes such as precipitation and antisolvent crystallisation exhibit fast reaction kinetics. Therefore the mixing of the reactants is very important to the particle size distribution of the formed crystalline material, since mixing strongly influences the supersaturation around the inlets of the feed streams in a crystalliser. High local supersaturations lead to high primary nucleation rates and, to a lesser extent, to higher crystal growth rates. To be able to predict the influence of the mixing on the particle size distribution of the formed crystals, it is essential to know the primary nucleation and crystal growth rates at the supersaturation levels around the reactor inlets.
A tool was developed for the determination of the nucleation and growth kinetics at well-defined supersaturations. With this tool it is possible to measure induction times for nucleation, i.e. the time needed for the newly formed nuclei to grow to a detectable macroscopic volume, as well as primary nucleation rates. From the experimentally determined induction times and primary nucleation rates, and from the sensitivity of the technique to detect a macroscopic volume, the crystal growth rates can be calculated (Kashchiev, 1991).

In the experimental setup two reactant streams are mixed rapidly in a tee mixer. As a result, a well known supersaturation is created that acts as a driving force for crystallisation or precipitation. The exit of the tee mixer is connected to an optical flow cell (length of 10 cm). In this cell, particles can be counted at various distances from the tee mixer by means of obscuration measurements of a focused He-Ne laser beam. At steady state, the induction time can be measured by determining the distance, i.e. reaction time, between the place where the first particles are counted in the flow cell and the point at which the reactants are mixed (the tee mixer). Beyond this position the number of newly formed particles per unit time can be counted, from which the nucleation rate can be deduced.

In this work the experimental setup, the design of the in-line particle counter and its calibration with monodisperse PDVB particles are discussed.

2. Experimental Setup

The experimental setup contains of two pressurised 15 liter storage vessels (SS-316) from which the reactants are fed to the tee mixer. The pressure in the storage vessels is kept at 10 bar and at the outlet of the flow cell the pressure is atmospheric. This pressure difference is used to transport the feed streams to the tee mixer. Particles with sizes larger than 1 μm are removed from the feed streams with filters. The flow rates are controlled by two needle valves and measured with standard variable area flow meters (Figure 1).
In the tee mixer, the two feed streams are mixed under turbulent conditions. An opposite tee mixer (internal diameter 4.8 mm) was selected here since it promotes fast micromixing. The outlet of the tee mixer is connected to an optical flow cell via PFA tubing. The mean residence time of the mixed flows up to the point where the particles are counted can be controlled by varying the length of the tube that interconnects the optical flow cell and the T-mixer and by changing the position of the particle counter along the optical flow cell.

3. In-line Particle Counter

The particles are counted in the flow cell, which consists of a 2 x 2 mm square tube of 100 mm in length. The focused laser beam passes through two parallel suprasil-1 quartz windows, which are mounted between two stainless steel strips (AISI-316-SS; see Figure 2). The flow cell has been operated at pressures of up to 10 bar and at superficial liquid velocities inside the cell of up to 16 m s⁻¹.
As a light source a 2 mW cylindrical He-Ne laser head is used (λ = 632.8 nm) with a beam diameter of 0.59 mm (1/e² value). A part of the non-linear components of the laser beam are removed by an iris diaphragm (see Figure 2 and Figure 3). The laser beam is then focused in the centre of the flow cell with an achromat lens with a focal length of 16 mm. To eliminate the disturbing influence of laser light reflections on the quartz windows, the laser beam enters the flow cell at an angle of approximately 12°. To be able to position the focal point in the centre of the flow cell, a focus adjustment screw was installed (see Figure 2). With this screw it is possible to move the lens perpendicular to the optical flow cell accurately. The diverging He-Ne laser beam that leaves the flow cell is collected on a high-speed silicon photodiode with an active area of 0.04 mm². A laser interference filter with a bandwidth of 628 to 638 nm was placed in front of the detector to block unwanted background radiation.
The current signal from the photodiode is transformed into an amplified DC potential signal with a wide bandwidth amplifier operated at a transimpedance gain of $10^3$ (see Figure 1). The sensitivity of the particle counter can be improved by working with a silicon photodiode with an active area of 100 mm$^2$ and with increased transimpedance gains. This however, significantly reduces the bandwidth, and with that the sensitivity towards small particles that cross the beam with high superficial velocities. Signals below 1 kHz (mechanical vibrations, laser light intensity fluctuations) and above 2 MHz are filtered from the amplified DC potential signal with a high-low pass filter. The AC signal from the high-low pass filter is monitored on an analogue oscilloscope. Peaks in the filtered AC potential

![Schematic amplified filtered detector signal sampled by the counter. In this particular case 4 out of 6 particles are counted. Particles that cross the beam simultaneously are counted as one (coincidence).]
signal that exceed a certain pre-set trigger level are counted by a digital counter (see Figure 4). The peaks correspond to sufficiently large particles that cross the He-Ne laser beam. During the experiments the number of counted peaks per unit time is stored in a computer which is connected to the counter.

4. Gaussian Beam Optics

According to Gaussian beam optics the diameter of the focal point (or spot size) of a focused He-Ne laser beam has a finite size as is indicated in Figure 5 (Self, 1983). The spot size of the He-Ne laser beam determines the minimum detectable particle size, because in the spot the intensity of the laser light is maximal. The minimum spot size of a focused Gaussian beam can be calculated as follows:

$$D_{\text{spot}} = \frac{4\lambda f}{\pi D_{\text{beam}}}$$

In this equation $D_{\text{spot}}$ is the diameter of the focal point ($1/e^2$ value), $\lambda$ the wavelength of the light, $f$ the focal length of the lens and $D_{\text{beam}}$ the diameter of the incident parallel laser beam ($1/e^2$ value). For the He-Ne laser beam ($D_{\text{beam}} = 0.59$ mm) and lens ($f = 16$ mm) used, the minimum spot diameter is $11$ $\mu$m. However, due to spherical aberration the spot size will in practice be larger than this calculated minimum value. Therefore with the counter trigger level set at $3.8\%$ of the amplified potential signal corresponding to zero obscuration, the smallest particle that can be detected is a particle blocking $3.8\%$ of the laser light in the focal point. If the irradiance were the same at any position in the laser beam at the focal point, this

![Diagram of laser beam focusing](image)

Figure 5. Focusing of a laser beam. The size of the focal waist is greatly exaggerated for illustrative purposes.
would correspond to a particle with a diameter of approximately 1.1 μm.

However, this is not the case since a He-Ne laser beam emitted in the TEM\textsubscript{00} mode obtains a Gaussian transverse irradiance profile (see Figure 6). The irradiance distribution of a Gaussian TEM\textsubscript{00} beam is the same at all cross sections and can be described as follows:

$$I(r) = I_0 e^{-2r^2/w(z)^2} = \frac{2P}{\pi w(z)^2} e^{-2r^2/w(z)^2}$$

where $P$ is the total power of the beam and $w(z)$ the radius of the 1/e$^2$ irradiance contour after the wave has propagated a distance $z$, and $r$ is the contour radius (Born, 1965). So the most distant contour radius ($R_{\text{max}}$) of the laser beam at which a particle of a given size $d_p$ can still be counted, can be calculated by integrating the irradiance $I(r)$ over $r$ from $R_{\text{max}}$ to ($R_{\text{max}}+d_p$). This integral should yield 3.8% of the total power divided by the particle diameter:

$$\int_{R_{\text{max}}}^{R_{\text{max}}+d_p} I(r)dr = \frac{0.038P}{d_p}$$

Therefore if the 1/e$^2$ irradiance contour of the focused He-Ne laser beam inside the flow cell is known as a function of the distance from the focal point $z$, the minimum detectable particle size and the $R_{\text{max}}$ values for particles of different sizes as a function of $z$ can be calculated. The $R_{\text{max}}$ values for a given particle size can be used to determine the cross section of the detection volume, i.e. the volume in which a particle of a given size should be present to be counted. The division of the cross section of the detection volume by the cross section of the flow cell will then provide a measure for the counted fraction of the total number of particles of a given size present in the flow cell.

5. Calibration Experiments

5.1 The 1/e$^2$ Irradiance Contour of the Focused He-Ne laser Beam Inside the Flow Cell

To determine the volume of the focused laser beam inside the flow cell and the minimum beam waist, the course of the diameter of the 1/e$^2$ irradiance contour of the focused He-Ne laser beam was measured. This was carried out by moving a razor blade perpendicularly in
the laser beam with an XY-translation table (partially adjustable to 1 μm) at the focal point and at several positions in the vicinity of the focal point. The amount of laser light that was blocked by the razor blade as a function of its position in the beam was measured with a silicon photodiode with an active area of 100 mm². Also the influence of the presence of a suprasil-1 quartz window, identical to the ones used in the flow cell, on the diameter of the focal point was determined. The measurements were carried out in air under atmospheric conditions.

5.2 Particle Counting

The in-line particle counter was calibrated with uniformly sized spherical PolyDiVinylBenzene particles with sizes of 1.18, 2.07, 3.10, 5.06, 10.00 and 87.50 μm (Coulter Electronics). These experiments were carried out by recirculating ultrapure water over the flow cell and a buffer vessel with a centrifugal pump. The PDVB particles were added to the system via the buffer vessel and the flow rate was measured with a standard variable area flow meter. The experiments were carried out at a temperature of 15 °C in a climate room. The room was provided with dried air in order to prevent condensation of water on the quartz windows of the flow cell.

![Graphs showing diameter and irradiance profile](image)

Figure 6. Left: diameter of the 1/e² irradiance contour of the focused He-Ne laser beam. Right: irradiance profile at the focal point.
6. Results and Discussion

6.1 The 1/e² Irradiance Contour of the Focused He-Ne laser Beam Inside the Flow Cell

The 1/e² irradiance contour of the focused He-Ne laser beam inside the flow cell is displayed in Figure 6 (left). The diameter of the focal point was 20 μm (Figure 6 - right) and the volume of the He-Ne laser beam inside the flow cell was calculated to be 1.7·10⁻³ μl. Due to spherical aberration of the lens this is approximately twice the minimum spot size as predicted by the Gaussian beam theory (equation 1). The presence of a suprasil-1 quartz window did not influence the shape of the focused laser beam significantly.

6.2 Particle Counting

In Figure 7 the results of the calibration experiment with particles of 5.16 μm are displayed. The number of counted particles per unit time increased linearly with the particle concentration. This was the case in the calibration experiments for all tested particle sizes. The maximum applied particle concentration was 2·10¹¹ (#/m³) and up to that concentration coincidence of particles in the detection volume was insignificant. Furthermore the experiments showed that the particle counter can detect very low concentrations of relatively small particles. The sensitivity or α-factor of the detection technique is expressed as the volume concentration of particles needed for counting one particle per second. The α-factor is determined for each particle size from the calibration curves. The α-factor was in the order of 10⁻²-10⁻¹⁰ (m³ m⁻³) for the particles in the size range of 1.18-10.00 μm. For the particles of 87.50 μm the α-factor was in the order of 10⁻⁴ (see Table I). Thus for the particles of 87.50 μm a much larger volume concentration is needed for counting one particle per second. This is attributed to the fact, that at the same volume concentration the number concentration of the particles with a size of 87.50 μm is much smaller than for the particles in the size range of 1.18-10.00 μm.
Figure 7. Calibration experiment with particles of 5.16 μm.

From the results of the calibration experiments, the fraction of the total number of particles present in the system that was counted, was calculated for each particle size with equation 4:

\[
\frac{\Phi_{p,\text{counted}}}{\Phi_p} = \text{counted number fraction} \quad \text{equation 4}
\]

In equation 4, \( \Phi_{p,\text{counted}} \) is the number of particles or voltage peaks that are counted (\#/s), and \( \Phi_p \) is the total number of particles that pass a cross section of the flow cell per unit time. As can be seen in Table I and Figure 8, the counted number fraction strongly increases with particle size. The counted number fraction was \(1.6 \times 10^{-5}\) for particles of 1.18 μm and increased

Figure 8. The counted fraction of particles as a function of particle size.
to a value of $1.6 \times 10^{-1}$ for particles of 87.5 μm. This is due to the fact that the smaller particles can only be counted at or near the focal point, whereas the particles of 87.50 μm can be counted in a much larger volume. In Table 1 counted number fractions predicted from equation 3 for the PDVB particles used are also presented. The predicted values are in rather good agreement with the experimental values. The minimum detectable particle size was calculated to be 2.45 μm, whereas in the calibration experiments particles with a diameter of 2.07 μm could be counted without difficulty. The particles of 1.18 μm could hardly be counted, indicating that the detection limit with respect to particle size is close to 1.18 μm.

In Figure 9 the predicted cross sections of the detection volumes for particles with sizes ranging from 2.45 to 87.50 μm are displayed. According to the calculations, the particles of

Figure 9. Cross section of the laser beam inside the flow cell and the calculated detection volume cross sections for particles with diameters ranging from 3.10 to 87.5 μm. The predicted minimum detectable particle size was determined to be 2.45 μm.
Table I. Results of the calibration experiments of the particle counter with PDVB particles.

<table>
<thead>
<tr>
<th>Size (μm)</th>
<th>( \alpha )-factor (-)</th>
<th>Counted Fraction - experimental (-)</th>
<th>Counted Fraction - predicted (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.18</td>
<td>3.3 \times 10^{-9}</td>
<td>1.6 \times 10^{-5}</td>
<td>0</td>
</tr>
<tr>
<td>2.07</td>
<td>4.5 \times 10^{-10}</td>
<td>6.6 \times 10^{-4}</td>
<td>0</td>
</tr>
<tr>
<td>3.10</td>
<td>6.0 \times 10^{-10}</td>
<td>1.6 \times 10^{-3}</td>
<td>1.7 \times 10^{-3}</td>
</tr>
<tr>
<td>5.16</td>
<td>5.2 \times 10^{-10}</td>
<td>8.7 \times 10^{-3}</td>
<td>7.4 \times 10^{-3}</td>
</tr>
<tr>
<td>10.00</td>
<td>1.9 \times 10^{-9}</td>
<td>1.8 \times 10^{-2}</td>
<td>2.2 \times 10^{-2}</td>
</tr>
<tr>
<td>87.50</td>
<td>1.4 \times 10^{-4}</td>
<td>1.6 \times 10^{-1}</td>
<td>1.1 \times 10^{-1}</td>
</tr>
</tbody>
</table>

2.45 μm can only be counted if they are positioned exactly in the focal point. The particles of 3.10 μm can only be counted inside the \( 1/e^2 \) irradiance contour of the laser beam in the vicinity of the focal point. The particles of 5.16 μm can be counted further away from the focal point. The particles with sizes of 10.0 and 87.5 μm can also be counted at the walls of the flow cell (at a distance of 1 \times 10^{-3} and -1 \times 10^{-3} m from the focal point). Due to their large size only a relatively small fraction of the particles of 87.5 μm needs to be in the laser beam in order to block sufficient light. Therefore the cross section of the detection volume of these particles well extends beyond the cross section of the \( 1/e^2 \) contour of the He-Ne laser beam.

Other experiments (not shown here) demonstrated that the number of counts increases linearly with the superficial velocity of the suspension in the optical flow cell at constant PDVB particle concentrations. These tests were performed at superficial velocities of up to 16 m s\(^{-1}\).

7. Conclusions and Recommendations

An in-line particle counter has been developed for counting fast moving small particles at low concentrations. It is integrated in an experimental setup which is intended for the measurement of nucleation rates and induction times in rapid crystallisation processes. Particles are counted by means of obscuration measurements of a focused He-Ne laser beam.

The counter has been calibrated with spherical monodisperse PDVB particles. The maximum particle concentration used during the calibration experiments was approximately \( 2 \times 10^{11} \) (# m\(^{-3}\)), and up to that concentration coincidence in the measurement volume was
insignificant. Experiments demonstrated that the counter is still accurate at particle velocities of up to 16 m s\(^{-1}\) and that it can be used at pressures of up to 10 bar. The sensitivity or \(\alpha\)-factor of the detection technique, expressed as the volume concentration of particles needed for counting one particle per second, was in the order of \(10^9-10^{10}\) (m\(^3\) m\(^{-3}\)) for the particles in the size range of 1.18-10.00 \(\mu\)m. For the particles of 87.50 \(\mu\)m the \(\alpha\)-factor was in the order of \(10^{-4}\). Thus for the particles of 87.50 \(\mu\)m a much larger volume concentration is needed for counting one particle per second. This is attributed to the fact that at the same volume concentration, the number concentration of particles with a size of 87.50 \(\mu\)m is much smaller than for particles in the size range of 1.18-10.00 \(\mu\)m. The fraction of the total number of particles present in the suspension that is counted was \(1.6\cdot10^{-5}\) for particles of 1.18 \(\mu\)m, and increased to a value of \(1.6\cdot10^{-4}\) for particles of 87.50 \(\mu\)m. This is due to the fact that the smaller particles can only be counted at or near the focal point, whereas the particles of 87.50 \(\mu\)m can be counted in the entire laser beam inside the flow cell. These counted fractions can be predicted rather well by using the Gaussian beam theory.

The sensitivity of the particle counter can be improved by working with a silicon photodiode with an active area of 100 mm\(^2\) and with increased amplifier transimpedance gains. This however, significantly reduces the bandwidth and with that the sensitivity towards small particles that cross the beam with high superficial velocities.

8. Acknowledgements

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9. Literature Cited


Chapter 5c

Primary Nucleation in the Antisolvent Crystallisation of NaCl with 2-Isopropoxyethanol

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Nucleation rate measurements of NaCl crystallised with the antisolvent 2-isopropoxyethanol have been carried out. The antisolvent and the brine were mixed very rapidly in a tee mixer. The mixed flows were fed to an in-line particle counter, which was used to determine the particle concentration in the suspension from which the nucleation rates were calculated. The reproducibility of the measurements was generally poor. This can be attributed to scaling. The three most successful nucleation rate measurements at antisolvent concentrations of 40, 50 and 60 wt% and supersaturation ratios of 1.12, 1.20 and 1.32 have been analysed. Despite of the differences in antisolvent concentration and supersaturation the measured nucleation rates were almost identical and were in the order of $10^8 \text{ m}^{-3}\text{s}^{-1}$. The calculated induction times varied between 0.33 to 0.58 s.

Keywords: nucleation, crystallisation, induction time, antisolvent, sodium chloride.

1. Introduction

Well soluble inorganic salts with a weak solubility temperature dependence like sodium chloride are usually separated from their solutions by evaporative crystallisation. The energy consumption in the production of these salts can be reduced by applying antisolvent crystallisation with organic substances that can be recovered from the spent mother liquor at low energy costs (Weingaertner, 1991). With respect to this 2-isopropoxyethanol is a suitable antisolvent for the crystallisation of sodium chloride, because it is partially miscible with aqueous sodium chloride solutions. Above temperatures of 28 °C 2-isopropoxyethanol can be recovered from the mother liquor by a temperature induced liquid-liquid phase split (see chapter 2).
In anisotropic crystallisation the size distribution of the formed particles is strongly affected by local effects. At the anisotropic inlet in the crystalliser, locally the salt solubility approaches zero and the relative supersaturation infinity. The high supersaturations in the area of the anisotropic inlet will lead to high primary nucleation rates resulting in the formation of small crystals that easily agglomerate if the supersaturation in the bulk solution is also high.

To get a better basic understanding of how the size distribution of the formed particles is influenced by these local effects a tool has been developed. It enables the measurement of primary nucleation rates and induction times for nucleation, i.e. the time needed for the newly formed nuclei to grow to a detectable macroscopic volume, at various anisotropic concentrations. To exclude the influence of mixing on the measured kinetic data, the aqueous NaCl solution and the anisotropic are mixed rapidly in an opposite tee mixer. The mixed flows that leave the tee mixer are fed to an optical flow cell. In this cell the particle concentrations in the anisotropic-water-salt mixture can be determined with an optical particle counter at various distances, or mean residence times, from the point where the anisotropic and the salt solution are mixed. From the particle concentrations nucleation rates and induction times can be calculated and in combination with the sensitivity of the used detection technique, they provide the crystal growth rates calculated from the poly-nuclear model proposed by Kashchiev et al. (1991).

In this work attempts are made to measure the primary nucleation rate for the anisotropic crystallisation of NaCl with 2-isopropoxyethanol.

2. Theory

Crystals are created when nuclei are formed, that subsequently grow. If a solution contains neither foreign particles nor parent seed crystals, nuclei can only be formed by primary homogeneous nucleation. In homogeneous nucleation nuclei are born due to the collision of solute entities that result in the formation of clusters. If foreign substrates such as dust particles or traces of impurities are present in the solution, nuclei can also be formed by heterogeneous nucleation. Depending on the surface and the lattice structure of the substrate, the nucleation work can be reduced substantially if the nucleation step takes place on the foreign surface. In the presence of parent crystals nucleation can occur at much lower supersaturations and the nuclei are born as attrition fragments. This type of nucleation is
referred to as secondary nucleation. At high supersaturations however, like in antisolvent crystallisation, primary nucleation generally prevails.

If a supersaturation is imposed on a solution a certain time will elapse before the first crystals are detected. This period of time is also known as the induction time and is a measure of the systems ability to remain in a metastable equilibrium. If more nuclei have time to come into being while the first nucleus grows to a certain macroscopic size then the induction time \( t_i \) can be calculated according to the poly-nuclear mechanism proposed by Kashchiev et al. (1991):

\[
t_{i,PN} = \left( \frac{1}{BV} \frac{V_{\text{macro}}}{a_4 G^4} \right)^{\frac{1}{4}}
\]

in which \( a_4 \) is a numerical shape factor, \( G \) the growth rate and \( V_{\text{macro}}/V \) the macroscopic volume fraction \( \alpha \) needed for detection. So if the poly-nuclear mechanism applies and both the induction time and the nucleation rate can be measured experimentally with a detection technique with a known \( \alpha \)-factor, also the growth rate can be deduced from the experimental results by equation 1.

The dependence of the induction time on the supersaturation ratio and the mother liquor composition is determined by the way these parameters influence the nucleation rate \( B \) and the growth rate \( G \). The classical theory by Volmer (1933) for homogeneous nucleation can be used to demonstrate these dependencies for primary nucleation:

\[
B_{\text{hom}} = N_c A_c \beta Z
\]

in which \( N_c \) is the number of critical nuclei per unit volume, \( A_c \) the surface of one critical nucleus, \( \beta \) the impingement rate of solute entities per unit surface and \( Z \) the nonequilibrium factor (Becker, 1935). Basically the nucleation rate is expressed as the impingement rate of solute entities per unit surface of critical clusters present in the reaction volume. The number of critical nuclei per unit volume can be expressed as a Boltzmann distribution:

\[
N_c = CN_c'' \exp \left( -\frac{\Delta G_c}{kT} \right)
\]
with \( C \) as the molar concentration of solute entities in the bulk and \( \Delta G_c \) as the “critical” Gibbs free energy of a nucleus of the minimum stable size. This “critical” Gibbs free energy can be expressed as follows:

\[
\Delta G_c = \frac{16\pi}{3} \gamma_{cl} \left( \frac{V_m}{kT \ln S} \right)^2
\]

in which \( S \) is the supersaturation ratio, \( \gamma_{cl} \), the mother liquor - crystal interfacial tension. The surface area of one critical nucleus can be expressed in terms of the critical Gibbs free energy and the interfacial tension:

\[
A_c = \frac{3\Delta G_c}{\gamma_{cl}}
\]

Finally, the impingement rate of solute entities per unit surface \( \beta \) can be estimated according to Kind et al. (1983):

\[
\beta = \frac{3}{4} D_{ab} \left( CN_{A'} \right)^{\frac{4}{3}}
\]

with \( D_{ab} \) as the diffusion coefficient. Since the solubility of the salt and thus \( S \) is influenced by the antisolvent to water mixing ratio, the primary homogeneous nucleation kinetic equation will be sensitive to changes in the concentration of the antisolvent. Furthermore, according to Nielsen et al. (1971) the crystal - mother liquor interfacial tension bears some relation with the solubility of the salt in water. Since the concentration of the antisolvent determines the solubility of the salt in the water volume in the mixture, it may also affect \( \gamma_{cl} \) and with that the kinetics of primary homogeneous nucleation. According to Schubert (1996) an equation similar to equation 2 can be formulated for heterogeneous nucleation, which is also sensitivity to fluctuations in antisolvent concentration.

The relationship between the growth rate \( G \) and the supersaturation ratio and the mother liquor antisolvent to water ratio is determined by the prevailing mechanism of crystal growth. In solution crystal growth various mechanisms can be distinguished, e.g. volume diffusion controlled growth, spiral growth or poly-nuclear growth. The following relation can be used to calculate the volume diffusion controlled growth rate:
\[ G_d = k_d \frac{k_e}{3k_r} (S - 1) = \frac{D_{ab}^* Sh}{L} \left( \frac{k_a}{3k_r} \right) (S - 1) \]  

\text{equation 7}

with \( k_d \) as the mass transfer coefficient, \( L \) as the characteristic length of the crystal, \( Sh \) as the Sherwood number for flow around particles (\( Sh = 2 + 0.66 \Re\rho^{\frac{1}{2}} Sc^{\frac{1}{2}} \)) and \( k_a \) and \( k_r \) as shape factors. Changes in the mother liquor antisolvent to water ratio will affect the mass transfer coefficient \( k_d \) and therefore the crystal growth rate at a given supersaturation. According to Nielsen (1984) the spiral and poly-nuclear growth rates can be calculated from equation 8 and equation 9 respectively:

\[ G_{ap} = k_{ap} (S - 1)^2 \]  

\text{equation 8}

\[ G_{pn} = k_{pn} S^{\frac{1}{4}} (S - 1)^{\frac{3}{2}} (\ln S)^{\frac{1}{2}} \exp \left[ - \frac{K_{pn}}{(\ln S)} \right] \]  

\text{equation 9}

with \( k_{ap} \) and \( k_{pn} \) as the rate constants which depend upon the solubility of the salt and the crystal - mother liquor interfacial tension. Hence these rate constants change if the solvent composition varies.

From the above it follows that the nucleation and growth kinetic equations and thus the induction time depend upon the mother liquor antisolvent to water ratio. These dependencies can be determined by measuring the induction time and the nucleation rate at several antisolvent to water ratios and supersaturations. With equation 1 the crystal growth rates can then be calculated.

3. Experimental

3.1 Setup

A schematic representation of the experimental setup is displayed in Figure 1. It consists of two pressurised 15 l storage vessels (AISI-316SS) from which the antisolvent and the NaCl solution are fed to a tee mixer. The pressure in the storage vessels is kept at 10 bar and at the outlet of the setup the pressure is atmospheric. This pressure difference is used to transport the feed streams to the tee mixer. Particles with sizes larger than 1 \( \mu \text{m} \) are removed from the
feed streams with filters. The flow rate is controlled by two needle valves and measured with standard variable area flow meters. In the tee mixer the two feed streams are mixed very rapidly. An opposed tee mixer was selected for this purpose since it promotes a fast micromixing. The outlet of the tee mixer is connected to an optical flow cell via 4 m of PFA tubing. The mean residence time of the mixed flows until the point where the particles are counted can be controlled by varying the length of the tube that interconnects the optical flow cell and the tee mixer or by changing the position of the particle counter along the optical flow cell. In the experiments the mean residence time can be varied in order to determine the induction time for primary nucleation.

Figure 1. Schematic representation of the experimental setup.

3.2 Experiments

The chemicals used in the experiments were sodium chloride (pharmaceutical quality, Akzo Nobel), ultra pure water (from an Elga Maxima ultra pure water device) and 2-isopropoxyethanol ((CH₃)₂CHOCH₂CH₂OH, Fluka Chemie AG ≥ 99.7%).

The experiments presented in this work concentrated on the measurement of the primary nucleation rate at three different antisolvent concentrations (and supersaturations). The
residence time of the mixed flows until the point where the particles are counted was not varied to determine the induction time for primary nucleation experimentally. The crystallisation experiments were carried out at 2-isopropropoxyethanol concentrations of 40, 50 and 60 wt% \((m_{\text{IPPE}}/(m_{\text{IPPE}}+m_{\text{H2O}})) \times 100\) at supersaturation ratios of 1.12, 1.20 and 1.32 respectively. In each experiment 5 wt% of water was added to the antisolvent in order to prevent scaling in the tee mixer and the salt concentration in the brine was 24.6 wt%. Both the sodium chloride solution and the antisolvent were stored in the pressurized vessels at 10 bar and at a temperature of 10 °C. During the experiments the temperature in the flow cell was approximately 15 °C. This temperature increase is the result of the enthalpy of mixing, which is released when the two reactants meet in the tee mixer. To prevent the condensation of water on the quartz windows of the optical flow cell during the experiments, the experimental setup was built up in a climate room. The room was provided with dried air and was maintained at a constant temperature of 15 °C during all the experiments. The experiments were started by opening the needle valves. When the two feed streams are mixed the crystallisation process begins, and particles are counted in the flow cell. Generally after approximately 10 seconds constant feed flow rates were obtained. After this time the number of particles (or voltage peaks) counted per unit time were stored in the computer and used for the calculation of the nucleation rate. The experiments usually lasted approximately 2 minutes. In many occasions however, the experiments had to be terminated earlier because of scaling problems. At the end of the experiment a small suspension sample was taken, which was filtered immediately on a millipore filter with pore size of 3.0 μm. The crystals on the filter were dried and stored. Since generally very small amounts of solids were collected, the particles were not removed from the filter but Scanning Electron Microscopic images were made of parts of the filters.

4. Particle Counting

In this section only a short description of the developed in-line particle counter is given. An extensive description of the in-line particle counter and its calibration with monodisperse PolyDiVinylBenzene particles can be found in the second part of this chapter.
4.1 In-line Particle Counter

The particles are counted by means of obscuration measurements of a focused HeNe laser beam in a flow cell, consisting of a 2 x 2 mm square tube of 100 mm in length. The cell is provided with two suprasil-1 quartz windows through which the focused HeNe laser beam passes. Before being focused a part of the non linear components of the HeNe laser beam is removed with an iris diaphragm. A laser interference filter with a bandwidth of 628 to 638 nm was placed in front of the detector to block unwanted background radiation. The detector signal is first amplified and filtered and then fed to a digital counter and an analogue oscilloscope. In the counter peaks in the filtered potential signal exceeding the preset trigger level are counted. The trigger level is set at a level of approximately two times the (electrical) noise bandwidth with the help of the analogue oscilloscope. The peaks correspond to sufficiently large particles that cross the HeNe laser beam. During the experiments the number of counted voltage peaks per unit time is stored in a computer which is connected to the counter.

4.2 Monodisperse Particles

The counter was calibrated with monodisperse spherical PolyDivinylBenzene particles with sizes of 1.18 up to 87.50 μm. The α-factor of the detection technique, i.e. the volume concentration of the solid phase needed for counting one particle per second, was $10^{-9}$-$10^{-10}$ (m$^3$ m$^{-3}$) for the particles in the size range of 1.18-10.00 μm and about $10^4$ for the particles of 87.50 μm. Thus for the particles of 87.50 μm a much larger volume concentration is needed for counting one particle per second. This can be attributed to the fact that at the same volume concentration the number concentration of the particles with a size of 87.50 μm is much smaller than for the particles in the size range of 1.18-10.00 μm. The number fraction of the present particles that is counted was $1.6 \times 10^5$ for the particles of 1.18 μm and increased strongly with particle size to a value of $1.6 \times 10^7$ for the particles of 87.5 μm (see Figure 2). This is due to the fact that larger particles can be detected further away from the focal point and therefore obtain a larger detection volume.
Figure 2. The fraction of the particles present in the flow cell that is counted versus particle size.

4.3 Polydisperse Particles

Since during a crystallisation experiment the particles that cross the laser beam are not uniform in size, the number of counted particles per unit time cannot directly be translated into a number concentration of particles and a nucleation rate. To do this information on the particle size distribution is required as will be explained in the following.

The particle flow rate $\Phi_p$ in the flow cell, i.e. the number of particles that pass a cross section of the flow cell per unit time, can be written in terms of the volumetric flow rate and the cumulative number concentration of particles:

$$\Phi_p = \Phi_v N$$

*equation 10*

The cumulative number concentration of particles in this equation can also be written as the integral of the population density over the particle size from zero to infinity:

$$N = \int_0^\infty n dl$$

*equation 11*
For obvious reasons the number of particles that are counted per unit time is less than the actual particle flow rate and can be written as follows:

\[ \Phi_{p,\text{counted}} = \Phi_r N_{\text{counted}} \]  

equation 12

The cumulative number concentration of particles from equation 12 can be calculated from the population density function by taking into account that only a limited number of the particles of each size class is counted:

\[ N_{\text{counted}} = \int_{l_{\text{min}}}^{l_{\text{max}}} X_p(l)ndl \]  

equation 13

A relationship for \( X_p \) as a function of particle size can be obtained from Figure 2. Since it is not (yet) possible to measure the crystal size distribution and count the particles in the flow cell simultaneously, a population density function has to be assumed in order to calculate the counted cumulative number concentration of particles from equation 13. Under the assumptions of plug flow, a constant supersaturation and the absence of agglomeration the number concentration of particles in each size class is the nucleation rate divided by the

![Figure 3](image)

Figure 3. The crystal size distribution under the assumptions of plug flow, a constant supersaturation and the absence of agglomeration, size dependent growth and growth rate dispersion.

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growth rate and the maximum particle size equals the growth rate times the residence time (see Figure 3). Now equation 13 can be written as follows:

\[ N_{\text{counted}} = \frac{B}{G} \int_{l_{\text{m}}}^{G_t} X_p \, dl \]  

\text{equation 14}

In this equation \(N_{\text{counted}}\) can be substituted by the experimental accessible parameters \(\Phi_{p,\text{counted}}\) and \(\Phi_r\) from equation 12:

\[ \frac{\Phi_{p,\text{counted}}}{\Phi_r} = \frac{B}{G} \int_{l_{\text{m}}}^{G_t} X_p \, dl \]  

\text{equation 15}

Therefore the nucleation rate can be calculated from the experimentally measured number of counts per unit time as follows, provided that the crystal growth rate is known at the given level of supersaturation:

\[ B = \frac{G \Phi_{p,\text{counted}}}{\Phi_r \int_{l_{\text{m}}}^{G_t} X_p \, dl} \]  

\text{equation 16}

If the growth rate is unknown, it can be estimated from SEM pictures of the solid samples. Also, if the induction time for nucleation is known at the given set of experimental conditions the growth rate can be determined by substituting equation 16 in equation 1:

\[ t_{i,PN} = \left( \frac{\Phi_r \int_{l_{\text{m}}}^{G_t} X_p \, dl}{G \Phi_{p,\text{counted}} a_4 G^3} \right)^{\frac{1}{4}} \]  

\text{equation 17}

In this equation the crystal growth rate \(G\) is the only unknown.

5. Results and Discussion

Nucleation rate measurements of NaCl crystallised with the antisolvent 2-isopropanol have been carried out. Generally the reproducibility of the measurements was poor. Because
of scaling in the tee mixer and in the flow cell, many of the experiments had to be stopped before stationary conditions were obtained. Scaling increased the pressure drop over the system, so the flow rates dropped in the course of the experiment. The three most successful experiments are analysed here. The experiments were carried out at antisolvent concentrations of 40, 50 and 60 wt% at supersaturation ratios of 1.12, 1.20 and 1.32 respectively. For all three experiments the same brine and antisolvent stock solutions were used. The antisolvent concentration was varied by changing the brine and antisolvent feed flow rates.

![Graph showing counts versus time for different antisolvent concentrations](image)

**Figure 4.** Number of counts versus time for the crystallisation experiments carried out at antisolvent concentrations of 40, 50 and 60 wt% ($\frac{m_{\text{IPE}}}{m_{\text{IPE}} + m_{\text{H2O}}} \times 100$).

During the experiments the mixing of the brine and the antisolvent was observed visually through variations in the refractive index of the liquid inside the PFA tube connected to the tee mixer. In all three experiments the antisolvent and the brine were visually fully mixed after approximately 5 cm of PFA tubing corresponding to a mixing time of ca. 20 ms.

In Figure 4 the number of counted particles per unit time for all three experiments are displayed. In the experiments at antisolvent concentration of 40 and 50 wt%, a constant average number of counts was obtained almost directly after the experiments were started. In these experiments the volumetric flow rates remained constant. In the experiment at an
antisolvent concentration of 60 wt% and a supersaturation ratio of 1.32 scaling played an important role. Approximately 20 seconds after stationary flows were obtained, the feed flow rates started to drop. At this point in time the number of counted particles started to rise (see Figure 4). This could be a consequence of the fact that relatively large scaling fragments passed the laser beam together with the newly formed crystalline material. By gradually opening the feed stream needle valves further the flow rates were kept at their set point values. However, after approximately 60 seconds it was no longer possible to correct for the decaying flow rates manually and the experiment was terminated. Salt deposits as a result of scaling were observed visually in the corners of the flow cell.

In Figure 5 SEM pictures of the formed NaCl crystals are displayed. In the experiment at an antisolvent concentration of 40 wt% only a very few crystals were collected on the filter. The maximum primary particle size was approximately 15 μm, corresponding to a growth rate of approximately 3 μm·s⁻¹ if a total growth time of 6 seconds is assumed (residence time until sampling point and filtration time). In Table 1 the maximum sizes of the NaCl crystals encountered in the solid samples and the crystal growth rates determined from these maximum particle sizes are given. Also the estimated diffusion limited growth rates from equation 7 with \( Sh = 2 \) and \( L = 10 \mu m \) are displayed in this table. These estimated crystal growth rates are in good agreement with the experimental growth rates for the experiments carried out at 40 and 50 wt% antisolvent. At an antisolvent concentration of 60 wt% the experimentally determined growth rate is larger than the diffusion limited growth rate. This might be caused by the presence of scaling fragments in the sample, which have had a growth time of more than 6 seconds.

**Table I. Experimentally determined and calculated crystal growth rates.**

<table>
<thead>
<tr>
<th>[IPE] ([m_{IPE}/(m_{IPE}+m_{H2O}) \times 100])</th>
<th>(S) [-]</th>
<th>(d_{p,max}) [μm]</th>
<th>(G_{exp}) [μm·s⁻¹]</th>
<th>(G_d) [μm·s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.12</td>
<td>15</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>50</td>
<td>1.20</td>
<td>25</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>60</td>
<td>1.32</td>
<td>40</td>
<td>7</td>
<td>5</td>
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Figure 5. SEM pictures of the formed NaCl crystals. The total growth time of the crystals, i.e. the residence time until the sampling point (~1.5 s) and the time needed for filtration (~4.5 s), is approximately 6 seconds in all cases.
In Table II the average number of counted particles per unit time and the estimated primary nucleation rates and induction times are displayed. The nucleation rates were calculated from equation 16 in which the diffusion limited growth rates from Table I were used. Despite of the differences in antisolvent concentration and supersaturation the estimated primary nucleation rates were almost identical in all three experiments. A possible explanation for this is, that increased interfacial tensions cancel out the influence of the increased levels of supersaturation on the value of \( \Delta G \) in equation 3, which equation mainly determines the dependency of the primary homogeneous nucleation rate on the antisolvent concentration and supersaturation. Another explanation could be that especially at the higher antisolvent concentrations scaling and agglomeration reduce the number concentration of the particles in the suspension.

The induction times for nucleation were estimated from equation 16. This was done by substituting the diffusion limited growth rates and the nucleation rates from Table I and Table II in equation 16, and by subsequently calculating the residence time \( \tau \) at which one particle per second is counted (\( \Phi_{p,\text{counted}} = 1 \text{ s}^{-1} \)). Also the induction times according to the poly-nuclear model by Kashchiev et al. (equation 1) were calculated with an \( \alpha \)-factor of \( 2\times10^9 \) and a numerical shape factor of 2 (\( a_0 \)). The used \( \alpha \)-factor is an average value of the PDVB particles, that were used for calibrating the particle counter, of sizes ranging between 2 and 10 \( \mu \)m. This is the estimated particle size range at the detection point, when taking into account the (mean) residence time of the suspension until the detection point of ca. 1.4 s. The induction times decreased at increasing supersaturation and antisolvent concentration and were in the range of 0.33 to 0.58 s. The poly-nuclear induction time calculated from equation 1 and the induction time calculated from equation 16 did not differ strongly. The induction time calculated from

<table>
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<tr>
<th>Table II. Results crystallisation experiments.</th>
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<tbody>
<tr>
<td>[IPE]</td>
</tr>
<tr>
<td>( \frac{m_{\text{IPE}}}{(m_{\text{IPE}}+m_{\text{H_2O}}) \times 100} )</td>
</tr>
<tr>
<td>40</td>
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<tr>
<td>50</td>
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</table>

\( a \) calculated from equation 16
equation 16 probably gives the most accurate estimate, since this method accounts for the sensitivity of the detection technique by using the relationship for the counted fraction $X_p$ as a function of particle size (see Figure 3), whereas the poly-nuclear model uses an averaged $\alpha$-factor of particles of sizes from 2 to 10 $\mu$m.

6. Conclusions and Recommendations

Nucleation rate measurements of NaCl crystallised with the antisolvent 2-isopropanol have been carried out. The reproducibility of the measurements was generally poor. This lack of reproducibility can be mainly attributed to scaling. Nucleation rates were measured at antisolvent concentrations of 40, 50 and 60 wt% and supersaturation ratios of 1.12, 1.20 and 1.32 respectively. Despite of the differences in antisolvent concentration and supersaturation the measured nucleation rates were almost identical and were in the order of $10^8$ (m$^3$.s$^{-1}$). Increased interfacial tensions may cancel out the influence of the increased levels of supersaturation on the nucleation rate at higher antisolvent concentrations. Another explanation may be that scaling and agglomeration play a more important role in the experiments at higher supersaturations and antisolvent concentrations. Finally, the calculated induction times varied between 0.33 to 0.58 s and decreased at an increasing antisolvent concentration and supersaturation.

To improve the reproducibility of the nucleation rate measurements the problems of scaling should be resolved. Scaling can probably be reduced by avoiding abrupt changes in the hydraulic diameter in the parts of the experimental setup in which the crystallisation takes place. Abrupt changes in the hydraulic diameter result in the creation of dead zones where the flow rate is reduced or where the direction of the flow is even reversed. In such zones scaling is likely to occur if the supersaturation is high.

7. Acknowledgments

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8. Literature Cited


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9. Nomenclature

\[a_4\] numerical shape factor (-)

\[A_c\] the surface of one critical nucleus (m²)

\[B\] nucleation rate (m³·s⁻¹)

\[B_{homo}\] primary homogeneous nucleation rate (m³·s⁻¹)

\[C\] the molar concentration of solute entities in the bulk (mol·m⁻³)

\[l\] diameter (m)

\[l_{min}\] minimum detectable particle size (m)

\[l_{p,max}\] observed maximum particle size (m)

\[D_{AB}\] the diffusion coefficient (m²·s⁻¹)

\[G\] growth rate (m·s⁻¹)

\[G_d\] volume diffusion limited growth rate (m·s⁻¹)

\[G_{exp}\] experimentally determined growth rate (m·s⁻¹)

\[G_{pn}\] poly-nuclear growth rate (m·s⁻¹)

\[G_{sl}\] surface integration limited growth rate (m·s⁻¹)

\[\Delta G_c\] the "critical" Gibbs free energy of a nucleus of the minimum stable size (J)
$k$  Boltzmann constant (J·K$^{-1}$)

$k_a$  surface shape factor (-)

$k_d$  volume diffusion limited growth rate constant (m·s$^{-1}$)

$k_v$  volumetric shape factor (-)

$k_{pm}$  poly-nuclear growth rate constant (m·s$^{-1}$)

$K_{pm}$  constant poly-nuclear growth mechanism (-)

$k_{si}$  surface integration limited growth rate constant (m·s$^{-1}$)

$L$  characteristic length of the crystal (m)

$n$  population density (m$^{-1}$·m$^3$)

$N$  cumulative number concentration of particles (m$^{-3}$)

$N_{counted}$  cumulative number concentration of particles from counted particles per unit time (m$^{-3}$)

$N_{AV}$  Avogadro number (mol$^{-1}$)

$N_C$  the number of critical nuclei per unit volume (m$^{-3}$)

$S$  the supersaturation ratio (-)

$T$  temperature (K)

$t_i$  induction time (s)

$t_{i,PN}$  poly-nuclear induction time (s)

$V$  parent phase volume (m$^3$)

$V_m$  molecular volume (m$^3$)

$V_{macr}$  detectable macroscopic volume (m$^3$)

$X_p$  counted fraction (-)

$Z$  the Zeldovich nonequilibrium factor (-)

$\alpha$  volume fraction needed for detection (-)

$\beta$  the impingement rate of solute entities per unit surface (m$^2$·s$^{-1}$)

$\gamma_{CL}$  the mother liquor - crystal interfacial tension (N·m$^{-1}$)

$\Phi_p$  particle flow rate (s$^{-1}$)

$\Phi_{p,counted}$  particles counted with digital counter (s$^{-1}$)

$\Phi_v$  volumetric flow rate (m$^3$·s$^{-1}$)

$\nu$  number of ions per molecule (-)

$\tau$  mean residence time (s)

$\tau_{detection}$  mean residence time until the position where the particles are counted (s)

Re  Reynolds number (-)

Sc  Schmidt number (-)

Sh  Sherwood number (-)
CHAPTER 6

6a Guidelines for the Design of an Antisolvent Crystallisation Process

6b Antisolvent Crystallisation as an Alternative to Evaporative Crystallisation for the Production of Sodium Chloride
Chapter 6a

Guidelines for the Design of an Antisolvent Crystallisation Process

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Guidelines have been provided for the selection of the optimal process conditions and antisolvent for the antisolvent crystallisation of inorganic salts that are usually produced by evaporative crystallisation. Suitable antisolvents are organic substances that have a double liquid phase area with water, because they can (partly) be separated from the water at a low energy consumption by a temperature induced liquid-liquid phase split. Because of the (limited) mutual solubilities of the antisolvent and the water in the double liquid phase area, this liquid-liquid phase split must generally be carried out in combination with other separation techniques. Important tools in the control of particle size are the water concentration in the antisolvent feed and the crystallisation temperature, which can be chosen either in the single or in the double liquid phase area. Furthermore, the purity of the salt can be improved strongly by introducing a recrystallisation step.

Keywords: crystallisation, antisolvent, salt, process, design, costs.

1. Introduction

Antisolvent crystallisation can be an energy saving crystallisation technique for the production of inorganic salts that are produced by evaporative crystallisation (Weingaertner, 1991). In antisolvent crystallisation the salt is precipitated by the addition of an organic substance. After the crystallisation the antisolvent has to be recovered at low energy costs. With respect to this, antisolvents that are partially miscible with water are suitable. These antisolvents can be (partly) recovered from a spent mother liquor by increasing or decreasing its temperature to a value in the double liquid phase area, where the mutual solubilities of the
antisolvent and the water are low. A simplified block diagram of the antisolvent crystallisation process is displayed in Figure 1.

The crystallisation can either be carried out in the single or in the double liquid phase area. In the single liquid phase area the salt crystallises because of the presence of the antisolvent, that reduces the solubility of the salt by binding of the water. In the double liquid phase area three phases coexist in the crystalliser, i.e. a solid NaCl phase, an antisolvent rich and a water rich liquid phase. Here the driving force for crystallisation is created by the extraction of water from the aqueous phase into the organic phase, and by the dissolution of the antisolvent in the aqueous phase.

A common phenomenon in the crystallisation of salts is the formation of hydrates. NaCl, Na₂SO₄ and Na₂CO₃ are all examples of salts which form hydrates when crystallised at low temperatures. If the specific salt has hydrated crystal modifications, then the antisolvent crystallisation can also be carried out in two steps. In a first step the hydrate is formed by antisolvent crystallisation, which in a second step is recrystallised into the anhydrate in a purer brine. This additional recrystallisation step strongly reduces the antisolvent uptake of the salt.

The objective of the work presented here is to provide guidelines for selecting the best antisolvent and the best process conditions for the crystallisation of inorganic salts, that are usually produced by evaporative crystallisation. First the ideal antisolvent crystallisation process with partially miscible antisolvents needs further elucidation. Then based upon
thermodynamic and kinetic consideration the limitations and the conflicting demands will be discussed. Finally a list of important questions has been put together, that should be paid attention to in the course of developing an antisolvent crystallisation process.

2. The Ideal Antisolvent Crystallisation Process

In a viable antisolvent crystallisation process a salt is produced at costs that are low compared to the evaporative crystallisation process and with a quality equivalent to the quality of the salt produced by evaporative crystallisation. To make an antisolvent crystallisation process feasible it must satisfy a number of requirements related to the following subjects:

- The physical properties of the antisolvent-water-salt system. Important physical properties are the solubility of the salt in mixtures of water and the antisolvent, the recoverability of the antisolvent from the water in the double liquid phase area and the heat of mixing of water and the antisolvent.

- The crystallisation of the salt in the presence of the antisolvent. The antisolvent crystallisation of the salt should yield a product of the required quality. The quality of the product is determined by its purity, particle size distribution, morphology and degree of agglomeration.

- The operability of the process with the selected antisolvent. The operability relates to the temperature and pressure at which the process can be carried out and the extra precautions that have to be taken in a process in which large volumes of an organic substance are used. The desired properties with respect to these three topics needed for a hypothetical ideal antisolvent crystallisation process are presented in the following.

2.1 Physical Properties

Most favourable is an antisolvent that:

- Reduces the solubility of the salt strongly so that little antisolvent suffices to obtain a 100% yield.

- Has no heat of mixing with water.

- Can be fully recovered from the spent mother liquor by a slight temperature variation.
2.1.1 Salt Solubility in Water-Antisolvent Mixtures

In Figure 2 salt solubilities in mixtures of two different antisolvents and water are displayed. The solid lines are the equilibrium lines and the dotted line represents the salt concentrations that arise from the mixing of the antisolvents with a saturated brine in an arbitrary mixing ratio. The concentration difference between this mixing line and the solubility line is representative for the amount of salt that crystallises when the brine and the antisolvent are mixed. Therefore compound B is more effective as an antisolvent than A.

![Salt concentration diagram](image)

**Figure 2.** Solubility diagrams for two different antisolvents (a & b).

2.1.2 Heat of Mixing of the Antisolvent and Water

Another important physical property is the heat of mixing of the antisolvent and the water. This heat of mixing has to be removed from or added to the system in the crystalliser, depending on whether the mixing is exo- or endothermic, and vice versa in the antisolvent recovery where the demixing takes place. This transport of heat between the crystallisation and the antisolvent recovery sections is unfavourable, because it increases the total heat exchanger surface area required as well as the steam (heaters) and electricity and/or cooling water (coolers) consumptions within the process. Therefore the heat of mixing should be zero in the ideal antisolvent crystallisation process.
2.1.3 Recoverability of the Antisolvent in the Double Liquid Phase Area

In Figure 3 two ideally shaped two phase envelopes of antisolvent-water-salt systems are displayed. One has a lower and the other an upper critical solution temperature. Both the lower critical solution temperature (LCST) and the upper critical solution temperature (UCST) lie at approximately 45 °C so that in both cases the lowest temperature level in the process is ca. 40 °C, enabling the use of water as the cooling medium. At temperatures above the LCST and below the UCST the antisolvent separates from the water phase completely. Consequently the aqueous and the organic phases that leave the recovery section do not need further purification. Most ideally the presence of the salt does not alter the shape and the position of the phase diagrams, so that the demixing lines for supersaturated and desupersaturated mother liquors lie at exactly the same positions. This enables a very small temperature difference between the crystallisation and the antisolvent recovery sections and therefore minimises the heat streams between these two sections and the total amount of heat exchanger surface area required.

There are also other types of separation techniques, such as pervaporation or nanofiltration, that can be used to separate an antisolvent from the spent mother liquor at low costs. These alternatives are not discussed here, since this work is primarily aimed at the antisolvent crystallisation with organic substances that can be (partly) recovered by a temperature induced liquid-liquid phase split.

Figure 3. Ideal phase diagrams of antisolvent-water-NaCl systems with a lower critical solution temperature (left) and with an upper critical solution temperature (right).
2.2 Crystallisation

Besides the described physical properties, that determine to a large extent the investment and energy costs of the antisolvent crystallisation process, the quality of the salt crystals produced is of paramount importance. If salt crystals with the required purity, size and shape cannot be produced by antisolvent crystallisation, antisolvent crystallisation will not be an option regardless how low the production costs are. Generally, the crystallisation is carried out ideally if:

- The particles have the required size distribution. In most cases this means large single crystals with a narrow size distribution.
- The particles have the required purity. The ideal situation is particles of 100% purity. This is never the case if agglomerates are formed with antisolvent containing mother liquor volumes entrapped in the voids between the primary crystals of the agglomerates. The crystals should also contain no mother liquor inclusions and the antisolvent molecules should not be built into the crystal lattice.
- The particles have the required shape, i.e. the product consists of single crystals that do not contain morphological instabilities.

2.3 Operability of the Process

The operation of an antisolvent crystallisation process distinguishes itself from the conventional multi-effect evaporative crystallisation process in a number of ways. An important difference in favour of the antisolvent crystallisation process is, that it can generally be carried out at atmospheric pressure and at temperatures close to ambient temperature, whereas the pressure and temperature in for instance the multi-effect evaporative crystallisation of NaCl vary between 0.1 - 1.5 bar and 40 - 120 °C.

A disadvantage of the antisolvent crystallisation process is that large volumes of a possibly environmentally polluting, explosive, flammable, toxic, malodorous, volatile, corrosive, chemically instable and expensive substance have to be used. In the ideal antisolvent crystallisation process the antisolvent obviously should have none of these properties.
3. The Real Antisolvent Crystallisation Process

In reality there is no such thing as an ideal antisolvent crystallisation process. Compromises have to be made. The type of concessions will depend on whether the production costs or the quality of the product has the highest priority.

3.1 Physical Properties

It is impossible to find an antisolvent that complies with all the requirements with respect to the physical properties of an antisolvent-water-salt system. When the antisolvent and the water mix, bonds will be broken and formed again, which will either produce or consume heat. Furthermore, the antisolvents distinguish themselves from each other in the way they reduce the solubility of the salt and in the extent to which they can be separated from a spent mother liquor by a temperature induced liquid-liquid phase split.

3.1.1 Thermodynamics of Partially Miscible Antisolvent-Water Systems

Obviously a number of the demands mentioned in section 2.1 are related through a common set of thermodynamic properties of the antisolvent-water-salt system. To reduce the number of demands a thermodynamic description of partial miscibility in antisolvent-water-salt systems is required.

3.1.1.1 Water-Antisolvent Systems with a Lower Critical Solution Temperature

If complete mixing is to occur irrespective of the mixing ratio of the antisolvent and the water, the Gibbs free energy of the mixture must always be smaller than the sum of the Gibbs free energies of the pure components. For partially miscible systems with an LCST this condition is met only below the lower critical temperature. Consider a partially miscible mixture of an antisolvent and water below its lower critical temperature (see Figure 4). At temperature $T_0$ slightly below the phase line in the single liquid phase area, the Gibbs free energy of mixing is negative (equation 1). Therefore at $T_0$ the amine and the water will mix spontaneously. At temperature $T_1$ slightly above phase line in the double liquid phase area, the Gibbs free energy of mixing is positive (equation 2), i.e. the mixing of the amine and the water will result in the formation of two separate liquid phases.
single liquid phase area:  \[ \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T_0 \Delta S_{\text{mix}} < 0 \]  

double liquid phase area:  \[ \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T_1 \Delta S_{\text{mix}} > 0 \]

The small positive change in temperature \( \Delta T = T_1 - T_0 \) changes the sign of the Gibbs free energy of mixing from negative to positive. This can only happen if the entropy of mixing is negative and is balanced by a negative or exothermic enthalpy of mixing.

Figure 4. Simplified representation of partial miscibility of antisolvent-water systems obtaining an LCST.

This leads to the conclusion that there must be a strong coordination of water and antisolvent molecules in the mixture, and that this coordination is absent in at least one of the pure phases. Water in the liquid state has an extensive hydrogen bond structure. Any disruption of this structure must lead to an entropy gain of the water. An entropy loss upon mixing can therefore only occur if the antisolvent loses entropy. Therefore the antisolvent must be weakly coordinated in the pure state and strongly coordinated in the mixture with water. The entropy loss upon mixing is also reflected by the fact that the excess heat capacities for these antisolvent-water systems are generally positive (see chapter 2 or Davison, 1960). A strongly coordinated network in the solution needs a larger energy input to generate the same amount of thermal motion (read temperature increase) than a weakly coordinated system.
3.1.1.2 Water-Antisolvent Systems with an Upper Critical Solution Temperature

Analogous to LCST systems the phase diagram of an UCST system has a two phase region (Figure 5). A system having two distinct liquid phases at a temperature $T_0$ will mix when heated to temperature $T_1$ above the critical temperature of the system. At $T_0$ the Gibbs free energy of mixing is therefore positive, whereas it is negative at temperature $T_1$. The small positive change in temperature $\Delta T = T_1 - T_0$ changes the sign of the Gibbs free energy of mixing from positive to negative. This is can only happen if the entropy of mixing is positive and is balanced by a positive or endothermic enthalpy of mixing. This leads to the conclusion that the water and the antisolvent molecules are less coordinated in the mixture than in the corresponding pure phases.

![Phase diagram of UCST system](image)

Figure 5. Simplified representation of partial miscibility of antisolvent-water systems obtaining an UCST.

3.1.1.3 The Influence of Salt on the Liquid-Liquid Equilibria of H$_2$O-Antisolvent Systems

If an antisolvent-water mixture is saturated with a salt, this will alter the shape and the position of the liquid-liquid equilibrium line. Generally it will decrease a lower critical solution temperature, increase an upper critical solution temperature and decrease the mutual solubilities of the antisolvent and the water in the two liquid phase area. If salt is added to a system with a lower critical solution temperature, this leads to an even stronger coordination of all the species present in the mixture. Thus the entropy of mixing will become more
negative and as a result of that the LCST will decrease. If the salt is added to a system with an upper critical solution temperature the UCST will increase, because now not only water-water hydrogen bonds but also the water-ion bonds have to be broken in order to accommodate the antisolvent.

3.1.2 Salt Solubility in Water-Antisolvent Mixtures

The ideal antisolvent reduces the solubility of the salt strongly so that little antisolvent suffices to obtain a 100% yield. In practice unfortunately, considerable amounts of antisolvent are needed in order to obtain high yields. Most antisolvents reduce the solubility of a salt similarly. The solubility of the salt in a pure antisolvent generally approaches zero and the same antisolvent will have a stronger effect on the solubility of a bivalent salt than on the solubility of a monovalent salt. Organic substances such as ethylene glycol behave differently, because they show a limited salt solubility. With such antisolvents a 100% yield can thus not be obtained.

3.1.3 Heat of Mixing of the Antisolvent and Water

Most ideally the heat of mixing of the antisolvent and the water is zero. This, however, cannot be the case. Thermodynamics dictate that systems with an LCST must have a negative heat of mixing and systems with an UCST must show endothermic mixing. Therefore in the case of an LCST heat has to be removed at the lower crystalliser temperature level which has to be added at the higher recovery temperature level. For an UCST system the opposite holds.

3.1.4 Recoverability of the Antisolvent in the Double Liquid Phase Area

In the ideal antisolvent crystallisation process the antisolvent can be fully recovered from the spent mother liquor by a slight temperature variation. The critical solution temperature is approximately 45 °C regardless of the NaCl concentration in the mixture. Unfortunately, this is impossible. First of all, the antisolvent can never be fully recovered by a temperature induced liquid-liquid phase split, since in the two liquid phase area there will always be limited mutual solubilities of the antisolvent and the water. Secondly, the presence of the salt generally strongly influences the position and the shape of the phase diagram. In the case of the NaCl-water-dimethylisopropylamine system the LCST shifts from 65 to 7 °C upon NaCl
saturation (see chapter 2 or Zijlema, 1995). This means that during the crystallisation the LCST of the amine-water-salt system is approximately 7 °C, and that in the most extreme situation the LCST in the recovery section can be as high as 65 °C. A similar argumentation can be set up for antisolvents that obtain an UCST with water.

Examples of LCST obtaining organic substances and therefore potential antisolvents, are nitrogen containing compounds such as alkylamines. These substances show lower critical solution temperatures because of nitrogen to water hydrogen bonds, which are broken by heating (see appendix - I for a list of these amines). Ethers also show lower critical solution temperatures with water (appendix - I). At lower temperatures the oxygen linkage of the ether can participate in hydrogen bonding with water, which bonds are broken by thermal motion at elevated temperatures.

Examples of UCST obtaining organic substances are oxygenated compounds such as alcohols, ketones, aldehydes, carboxilic acids or ethers (appendix - I). These substances generally form hydrogen bonds with themselves and with water. However, since they also contain substantial aliphatic parts, several water-water hydrogen bonds must be broken to accommodate the antisolvent molecules. This limits the solubilities of these antisolvents at lower temperatures. At higher temperatures however, the molecules possess enough kinetic energy to break the water-water hydrogen bonds and with that the mutual solubilities of the water and the antisolvent increase.

After the liquid-liquid phase separation both the water and the antisolvent phases may need further purification. In the case of the antisolvent crystallisation of NaCl the water stream is recycled to the mine or discarded into the environment. Therefore the antisolvent content in this stream must be very low. The traces of the antisolvent that remain in the aqueous phase can be removed by several techniques. A fairly simple one is a combination of extraction and distillation. In a first step the antisolvent is extracted with an organic compound that does not dissolve in water. Subsequently the antisolvent is separated from the extractant by distillation. Therefore the extractant should not form an azeotrope with the antisolvent, and to keep the distillation column reboiler duty low the extractant should have a higher boiling point than the antisolvent. Other options to recover traces of the antisolvent from the water phase are steam stripping, in case of volatile antisolvents, direct distillation of the antisolvent from the water stream or (organophylic) pervaporation. The antisolvent stream
leaving the recovery section can be dried further by distillation or by using a zeolite bed if necessary.

3.2 Crystallisation

The product characteristics that are most important to the quality of the product are the size distribution of the formed particles, the purity of the product and the shape of the particles. In antisolvent crystallisation these product characteristics can be influenced in a number of ways:

- Dilution of the antisolvent. This reduces the supersaturation in the area of the antisolvent inlet.
- The reactor configuration or stirring. This determines the supersaturation and antisolvent concentration profiles in the crystalliser.
- The crystallisation temperature. This determines whether the salt is crystallised from one or from two liquid phases.
- The introduction of a recrystallisation step. If the salt of interest forms hydrate modifications, then a recrystallisation step can be introduced to reduce the antisolvent uptake in the product.

In the following the influence of these parameters on the three product characteristics is discussed in detail.

3.2.1 Particle Size Distribution

The particle size distribution of the formed crystals will be strongly affected by local effects. At the antisolvent inlet in the crystalliser, locally the salt solubility will approach zero and the relative supersaturation infinity. The high supersaturations in the area of the antisolvent inlet will lead to high primary nucleation rates resulting in the formation of small particles. Any measures taken to reduce the supersaturation in the antisolvent inlet flame will lead to a larger mean crystal size.

Dilution of the antisolvent feed stream with water strongly reduces the supersaturation in the area of the antisolvent inlet and with that the primary nucleation rate. Diluting the antisolvent feed will however reduce the yield. Another measure to influence the primary
nucleation rate at the inlet flame is to improve the mixing in the reactor by changing its configuration or stirring.

The crystallisation can also be performed in the two liquid phase area. In the two liquid phase area the driving force is created by the extraction of water from the aqueous phase to the antisolvent phase and by the dissolution of antisolvent in the aqueous phase. The crystallisation predominantly takes place in the aqueous phase in which the NaCl is well soluble, resulting in lower relative supersaturations. Furthermore, due to the limited miscibility of the antisolvent and the crystalliser contents the supersaturation is lower near the inlet of the antisolvent, resulting in a reduced (primary) nucleation rate. As a result of the reduced local and bulk supersaturations, the crystals formed in the double liquid phase area are significantly larger than the crystals formed in the single liquid phase area.

If the specific salt obtains a hydrate modification, than a recrystallisation step can be introduced. The hydrate is precipitated by addition of the antisolvent in a first step and in a second step it can be recrystallised by changing the temperature to a value at which the anhydrate is stable. The hydrate will then dissolve and the anhydrate will crystallise. In such a recrystallisation process the driving force is limited by the recrystallisation temperature, because it determines the difference in solubility between the stable anhydrate and the metastable hydrate. Since this temperature is easier to control than the mixing of an organic antisolvent with a brine, larger less agglomerated particles can be produced.

3.2.2 Product Purity

A drawback of antisolvent crystallisation is the introduction of a new impurity, i.e. the antisolvent itself. Regardless of the nature of the antisolvent, the primary aim is always to reduce the antisolvent content in the product as much as possible. Due to the high supersaturations involved in antisolvent crystallisation, also other impurities which pose no problem when using evaporative crystallisation can become a problem. The occurrence of agglomerates or morphological instabilities form a good indicator of the product purity, since these growth forms are sensitive to mother liquor entrapment. Inside the agglomerates, the voids will be filled with mother liquor and in hopper growth mother liquor inclusions are likely to be formed due overgrowth of macrosteps.
The most effective tool to strongly reduce the uptake of impurities is the introduction of a recrystallisation step. If carried out in a purer brine the recrystallisation will bring about a strong purification of the solid phase. The impurities enclosed in the hydrate will redistribute over the mother liquor and the anhydrate, since the recrystallisation is solution mediated.

3.2.3 Particle Shape

The shape or morphology of a crystal is the result of growth over a longer period of time. A certain minimum crystal size is required before instable growth forms such as hopper crystals can be recognised. The morphology of the product is therefore determined by the bulk supersaturation. Measures which alter the bulk supersaturation will hence have a strong influence on the formation of hopper crystals and other morphological instabilities.

Agglomeration however, is influenced strongly by the level of supersaturation in the reactor antisolvent inlet flame as well as by the supersaturation in the bulk. A high supersaturation the antisolvent inlet flame will lead to extensive primary nucleation due to which many small particles are formed. These particles agglomerate easily if also the supersaturation in the bulk is high. Measures that reduce local and bulk supersaturation levels, will suppress agglomeration.

3.3 Operability of the Process

In a process in which large volumes of an organic substance are used, special precautions need to be taken. Depending on the characteristics of the used antisolvent, the presence of the antisolvent will give rise to additional expenses related to the materials of construction of the plant, industrial safety and protection of the environment. These aspects should, together with the energy consumption and the quality of the product formed by antisolvent crystallisation, be taken into account in the process of taking the decision whether to produce a salt by antisolvent crystallisation or by evaporative crystallisation.

4. The Design of an Antisolvent Crystallisation Process

In the following questions are treated, that are important in the course of developing an antisolvent crystallisation process. The questions concerning the crystallisation presented in section 4.1, are very important to the quality of the formed. The questions in section 4.2
focus on the antisolvent recovery and are therefore crucial to the economy of the process. In section 4.3 a number of questions concerning the process in general are treated, which are important to mainly the production costs of the salt of interest.

4.1 Crystallisation - Product Quality

- Does the salt form hydrates?
  If so, a choice can be made between the direct formation of the anhydrate by antisolvent crystallisation or the crystallisation of the hydrate with the antisolvent and a subsequent recrystallisation step. At the expense of increased production costs a higher product quality can be obtained if the option that includes recrystallisation is applied.

- What is the required purity level of the salt product?
  If a very low impurity uptake is essential, then, if possible, a recrystallisation step should be applied.

- What is the required particle size distribution?
  If it is important to make large single crystals, the crystallisation should either be carried out in the double liquid phase area or a recrystallisation step should be applied. In both cases the supersaturation is generally low. If particle size is unimportant and the formation of agglomerates does not create any problem, it is best to crystallise in the single liquid phase area, because in the single liquid phase area the overall solubility reduction and with that the yield are the highest.

- What is the required morphology?
  If morphological instabilities are undesirable, the supersaturation should be kept low. This can be done by crystallising from the double liquid phase area or by applying a recrystallisation step. If not, the crystallisation can also be carried out in the single liquid phase area.

- What is the required crystallisation temperature range?
  If the stability of the product is temperature sensitive, the temperature range in which the crystallisation can take place is confined. This will limit the choice of the antisolvent, since the antisolvent should have a critical point with water and salt in the temperature range where the product is stable.

- What is the required yield?
If a high yield is essential the crystallisation is preferably carried out in the single liquid phase area at a high antisolvent concentration. A disadvantage of crystallising under these conditions is the formation of impure agglomerates and the low solids concentrations in the crystalliser. Furthermore if the yield is high, a considerable temperature variation is required to separate the antisolvent from the water phase after the crystallisation. This is because the mutual solubilities of the antisolvent and the water in the double liquid phase area rise if the salt concentration in the mixture decreases.

4.2 Antisolvent Recovery - Production Costs

- Is an UCST or an LCST antisolvent favourable?
  Most important is that the upper or lower critical point is close to the required crystallisation temperature, which is set by the temperature of the brine feed or the temperature sensitivity of the required product.

- Does the water stream from the recovery need treatment?
  If so, several promising techniques can be used to separate the antisolvent from the water. The antisolvent can be extracted with an organic substance that does not dissolve in water, and that can be separated from the antisolvent by distillation. Other options are steam stripping, organophylic pervaporation or the direct distillation of the antisolvent from the aqueous phase.

- Does the antisolvent stream from the recovery need treatment?
  Additional drying of the antisolvent will reduce the antisolvent recycle to the crystalliser. A technique that one can think of is distillation or the use of a zeolite bed to remove the water.

- Can the liquid-liquid phase split be substituted by a different separation technique?
  An interesting option is the use of antisolvents that can be separated from the spent mother liquor by techniques other than a liquid-liquid separation. Promising techniques are, in case of volatile substances, distillation or pervaporation. If the antisolvent has a molecular weight exceeding 200 Dalton the use of nanofiltration to separate the antisolvent from the spent mother liquor should also be considered.
4.3 The Process - General Questions

- Is the temperature in the crystalliser or in the recovery section above the atmospheric boiling point of the antisolvent-water mixtures present in those process parts? If so, the process must (partly) be operated at elevated pressures. This will increase the investment costs.

- Are mixtures of the antisolvent and the brine corrosive?
  Some antisolvent-water-salt mixtures can be highly corrosive, especially if the process is carried out at elevated temperatures. This will determine largely the choice of the used materials in most process parts.

- Is the antisolvent toxic, malodorous, explosive or flammable?
  If the antisolvent has one or more of the above described properties special precautions need to be taken in order to minimise the risks involved the production of the salt.

- Is the antisolvent environmentally polluting or expensive?
  If so, the maximum allowable antisolvent concentration in waste streams will be very low.

- Is the antisolvent chemically stable in a closed loop process?
  If the antisolvent is chemically unstable, the amount of antisolvent in the process will decrease in time and organic substances other than the antisolvent will be present in the process. It is of course impossible to say how these substances influence the process, where they will leave the process and if not, in which process section they will accumulate.

5. Conclusions

Suitable antisolvents for the crystallisation of inorganic salts that are usually produced by evaporative crystallisation, are organic substances that have a double liquid phase area with water. These antisolvents can be partly separated from the water at a low energy consumption by a temperature induced liquid-liquid phase split. Because of the (limited) mutual solubilities of the antisolvent and the water in the double liquid phase area, this liquid-liquid phase split must generally be carried out in combination with other separation techniques.

Important tools in the control of particle size are the water concentration in the antisolvent feed and the crystallisation temperature, which can be chosen either in the single or in the double liquid
phase area. Dilution of the antisolvent with water or crystallisation in the double instead of in the single liquid phase area increases particle size and suppresses agglomeration, but reduces the yield. Finally, the purity of the salt can be improved strongly by introducing a recrystallisation step.

6. Literature Cited


Appendix - I

List of lower and upper critical solution temperatures of oxygen and nitrogen containing hydrocarbons with water from the Dechema Data Series (Arlt, 1979).

<table>
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Chapter 6b
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Antisolvent Crystallisation as an Alternative to Evaporative
Crystallisation for the production of Sodium Chloride

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A comparison has been made between the antisolvent crystallisation of NaCl with
diisopropylamine and the traditional four effect evaporative crystallisation of NaCl.
Calculations demonstrated that for a 1 Mton/y salt production plant with an on-site
integrated steam power plant the reduction in energy costs can be 29 % if antisolvent
crystallisation is applied. The estimated fixed capital costs however, are 4 to 50 % higher
for the antisolvent crystallisation of NaCl, depending on the used process configuration.
A disadvantage of the antisolvent crystallisation of NaCl is, that the crystals are generally
small, tend to agglomerate and are contaminated with the antisolvent. The quality of the
product can be strongly improved in a two step process. In a first step NaCl.2H₂O is
formed by antisolvent crystallisation, which can be recrystallised in a purer brine in a
second step. In this two step process large and pure NaCl crystals can be produced at the
expense of increased major operating costs.
Keywords: crystallisation, antisolvent, amines, sodium chloride, design, costs, energy.

1. Introduction

In industry sodium chloride is produced in three different ways: by solar evaporation from
saline water and by shaft mining or solution mining from rock salt deposits. The use of solar
evaporation however, is limited by geographic considerations and the use for solid sodium
chloride recovered directly by shaft mining is limited by the presence of impurities. In
solution mining a saturated sodium chloride solution is obtained by pumping water into a
rock salt deposit. The raw brine is purified and a high purity solid sodium chloride product
can be obtained by evaporative crystallisation.
The minimum amount of work needed to separate NaCl from its saturated solution is the ‘ideal’ work that results when the process is carried out completely reversible. The ‘ideal’ work can be calculated from the Gibbs free energies of formation of the crystalline and the dissolved sodium chloride (Jongema, 1983):

\[ \Delta G_{\text{NaCl(aq)}} = -392.96 \text{ kJ/mole (at 25 °C)} \]
\[ \Delta G_{\text{NaCl(s)}} = -384.48 \text{ kJ/mole (at 25 °C)} \]
\[ W_{\text{ideal}} = 8.477 \text{ kJ/mole} = 0.145 \text{ MJ/kg NaCl} \]

If the salt is produced in a four effect evaporative crystallisation plant, 1.82 MJ is needed for the production of one kilogram of solid sodium chloride. So the energy efficiency of the four effect evaporative crystallisation process is only \( \frac{0.145}{1.82} \cdot 100 \% = 8 \% \).

To reduce the energy consumption within the production of NaCl the water evaporation step can be substituted by the addition of an antisolvent that reduces the solubility of the salt. Weingaertner et al. (1991) showed that the reduction in energy costs by applying antisolvent (or extractive) crystallisation can be as high as 63 % compared to a three-effect evaporation plant. Weingaertner used DiisoPropylAmine (DiPA) as the antisolvent, which is partially miscible with water (Davison, 1960). The crystallisation was carried out at -5 °C in the single liquid phase area and the DiPA was recovered from the spent mother liquor by increasing its temperature to a value in the two liquid phase area. However, in his calculations Weingaertner did not acknowledge the fact that the mixing of DiPA and water is strongly exothermic and that at a crystallisation temperature of -5 °C not the NaCl but the NaCl.2H₂O crystal modification is formed (see Figure 1). This modification is not a suitable end product because it is unstable at room temperature. Furthermore the estimated heat of crystallisation of -17 kJ/mole for NaCl.2H₂O (-1.6 kJ/mole for NaCl) significantly contributes to the energy consumption within the process.
Besides the reduction in the energy consumption, the purity and size of the NaCl crystals formed by antisolvent crystallisation is of paramount importance, since the salt is used in electrolysis plants and for consumption. Continuous crystallisation experiments of NaCl with DiMethylisoPropylAmine (DMiPA) demonstrated that the quality of the formed crystalline material is generally poor. The DMiPA uptake of the sodium chloride crystals varied between 40 and 630 ppm (Zijlema, 1995). Furthermore, the crystals formed by antisolvent crystallisation are generally small and agglomerated (see Figure 2, left). This can be attributed to excessive primary nucleation at the antisolvent inlet in the crystalliser, since in the inlet flame the antisolvent concentration is increased which reduces the solubility of the salt and consequently increases the level of supersaturation. The formation of more primary nuclei leads to smaller crystals that easily agglomerate if the supersaturation is high. However, a high quality product can be obtained in a two step process. In the first step NaCl.2H₂O is formed by antisolvent crystallisation, which can be recrystallised in a purer brine in a second step. Experiments showed that such a recrystallisation can give a 100 to 900 fold purity increase of the solid phase, resulting in a NaCl product with an antisolvent uptake of 6 ppm or less (Zijlema, 1999). Furthermore the supersaturation during the recrystallisation of NaCl.2H₂O into NaCl is limited by the solubility difference between the stable NaCl and the metastable NaCl.2H₂O crystal modifications, which is set by the recrystallisation temperature (Figure 1). Therefore the supersaturation and with that the average particle size
of the formed NaCl crystals is much easier to control in the recrystallisation of NaCl·2H₂O into NaCl than in the antisolvent crystallisation of NaCl. In Figure 2 (right) an example of NaCl crystals formed by recrystallisation is displayed.

![Figure 2](image)

**Figure 2.** NaCl crystals formed by antisolvent crystallisation (left, magnification: 350x) and by antisolvent crystallisation of NaCl·2H₂O and a consecutive recrystallisation step (right, magnification: 35x).

In this work estimates of the energy consumption and the fixed capital costs of the production of NaCl either via the antisolvent crystallisation of NaCl or via the antisolvent crystallisation of NaCl·2H₂O with a consecutive recrystallisation step are compared with the energy consumption and the fixed capital costs in the production of NaCl in a four effect evaporative crystallisation plant. Furthermore solid-liquid and liquid-liquid equilibrium data, enthalpies of mixing and specific heats of amine-H₂O-NaCl systems are presented.

### 2. The Amine-H₂O-NaCl Systems

Liquid-liquid and solid-liquid equilibria experiments demonstrated that the amines diisopropylamine and dimethylisopropylamine are suitable antisolvents for the crystallisation of NaCl. Both amines reduce the sodium chloride solubility significantly and have a two liquid phase area with brine close to room temperature.
The NaCl solubility in mixtures of DMiPA and water (Zijlma, 1995) and the NaCl•2H₂O solubility in mixtures of DiPA and water are plotted in Figure 3. In the solubility plot of NaCl•2H₂O in DiPA water mixtures, also solubilities measured by Weingaertner et al. (1988) are displayed. These values, that were determined in the temperature range of -12.5 to -3.9 °C fall approximately on the same line as the solubilities measured at a constant temperature of -12 °C. This demonstrates the fact that the solubility of the salt in DiPA-water mixtures is only a weak function of temperature and is mainly determined by the DiPA concentration. At amine weight fractions above 0.75 the NaCl solubility approaches zero.

![Figure 3. Solubility of NaCl in DMiPA-H₂O at 5 °C (left) and of NaCl•2H₂O in DiPA-H₂O (right).](image)

In Figure 4 the two phase envelopes of the binary amine-H₂O mixtures (Davison, 1960) and the ternary amine-H₂O mixtures saturated with NaCl (Zijlma, 1995; Weingaertner, 1988) are displayed. The lower critical solution temperatures (LCST) of the DiPA-H₂O and the DMiPA-H₂O systems were estimated at 27 and 65 °C respectively. Below these temperatures there is one single liquid phase present regardless of the concentration of the amine. The LCST's of both systems, as well as the mutual solubilities of the amines and the water in the two liquid phase area, decrease in the presence of sodium chloride. This is due to the fact that the sodium and the chloride ions surround themselves with water molecules and reject the amine molecules. At lower temperatures however, the amines are sufficiently
hydrophilic to be fully miscible with water at NaCl saturation. The LCST's of the DiPA-H₂O and the DMiPA-H₂O systems saturated with NaCl were estimated to be -11.7 and 6.6 °C. The LCST of the DiPA-H₂O system saturated with NaCl deviates from the value presented by Weingaertner et al. who estimated it at -7.5 °C.

Figure 4. Liquid-liquid equilibria of the binary amine-H₂O systems (Davison, 1960) and the amine-H₂O systems saturated with NaCl (Weingaertner, 1991; Zijlema, 1995).

The experimentally determined enthalpies of mixing of amine-H₂O mixtures as well as the specific heats of the amine-H₂O and the DMiPA-H₂O system saturated with NaCl are presented in Figure 5. All measurements were carried out in the single liquid phase area at temperatures varying between 272-298 K (see chapter 2). The results demonstrate that the mixing process is strongly exothermic, indicating that the amine-water interactions are strong compared to the water-water and amine-amine interactions. The highest measured enthalpies of mixing were 105 J/g mixture for the DMiPA-H₂O system at w_{DMiPA} = 0.49 and 81 J/g mixture for the DiPA-H₂O system at w_{DiPA} = 0.60.
Figure 5.  Enthalpies of mixing and specific heats of the amine-H₂O systems and specific heats of the DMiPA-H₂O system saturated with NaCl as a function of the amine weight fraction.

The fact that the mixing of the amines and water is exothermic is not surprising. At a temperature $T_1$ slightly below the liquid-liquid equilibrium line in the single liquid phase area the Gibbs free energy of mixing is negative (equation 1), i.e. the amine and the water will mix spontaneously. At a temperature $T_2$ slightly above the equilibrium line in the double liquid phase area the Gibbs free energy of mixing is positive (equation 2), i.e. the mixing of the amine and the water will result in the formation of two separate liquid phases.

\[
\text{single liquid phase area: } \Delta G_\text{mix} = \Delta H_\text{mix} - T_1 \Delta S_\text{mix} < 0 \quad \text{equation 1}
\]

\[
\text{double liquid phase area: } \Delta G_\text{mix} = \Delta H_\text{mix} - T_2 \Delta S_\text{mix} > 0 \quad \text{equation 2}
\]

The small positive change in temperature $\Delta T = T_2 - T_1$ changes the sign of the Gibbs free energy of mixing from negative to positive. This is can only happen if the entropy of mixing is negative and is balanced by a negative or exothermic enthalpy of mixing. The entropy loss upon mixing is also reflected by the positive excess heat capacities of the amine-water mixtures (see Figure 5). A strongly coordinated network in the solution requires a larger energy input to generate the same amount of thermal motion (read temperature increase) than a weakly coordinated system.
3. Process Configurations

Two different process configurations for the production of sodium chloride by antisolvent crystallisation have been investigated. One option is to crystallise NaCl directly by adding the antisolvent to the brine at a temperature above the NaCl-NaCl\(2\)H\(_2\)O transition temperature. A block scheme for this option is displayed in Figure 6. The saturated brine from the raw material deposit is mixed with the amine in the crystalliser. The NaCl crystals are removed from the crystalliser and the amine is recovered from the spent mother liquor by a temperature induced liquid-liquid phase separation. Traces of the amine that remain in the aqueous phase after the liquid-liquid phase separation are removed by extraction with octane (not indicated in Figure 6). The recovered antisolvent is reused in the crystalliser and the amine free water stream can be reused for another dissolution step.

![Figure 6](image)

Figure 6. A block scheme for the antisolvent crystallisation of NaCl.

The second option is to crystallise NaCl\(2\)H\(_2\)O by the addition of the amine to the brine and a consecutive recrystallisation step. A block scheme for this option is displayed in Figure 7. In this case the feed brine is distributed over the NaCl\(2\)H\(_2\)O crystalliser and the recrystalliser. The NaCl\(2\)H\(_2\)O crystals formed by antisolvent crystallisation at a temperature below the NaCl-NaCl\(2\)H\(_2\)O transition temperature are removed from the NaCl\(2\)H\(_2\)O crystalliser and are resuspended in a fresh feed brine in the recrystalliser. At the recrystalliser temperature, which is above the NaCl-NaCl\(2\)H\(_2\)O transition temperature, the NaCl\(2\)H\(_2\)O
crystals dissolve and the NaCl crystals nucleate and grow. The NaCl crystals are removed from the recrystalliser and the clear mother liquor is fed to the NaCl.2H₂O crystalliser.

![Diagram showing the process of antisolvent crystallisation of NaCl.2H₂O](image)

Figure 7. A block scheme for the antisolvent crystallisation of NaCl.2H₂O and a consecutive recrystallisation step.

The crystallisation will preferably be carried out at amine concentrations exceeding 75 wt%. Under these conditions the NaCl solubility is very low and consequently high yields can be obtained. A disadvantage of crystallising at high antisolvent concentrations is however, that the NaCl concentration in the spent mother liquor will be very low resulting in increased mutual solubilities of the amine and the water in the two liquid phase area. Therefore the liquid-liquid phase separation temperature needs to be high in order to get a good separation between the amine and the water, resulting in a large temperature difference between the crystallisation and the antisolvent recovery sections within the process. This is unfavourable, because an extensive heat exchanger network will be required to heat the spent mother liquor to the antisolvent recovery temperature and to cool the recovered antisolvent to the crystallisation temperature. This temperature difference is smallest when DiPA is used, because the mutual solubilities of DiPA and water increase less with a decreasing NaCl concentration in the mixture than the mutual solubilities of DMiPA and water. This can be seen in Figure 4. The reduction in lower critical solution temperature upon NaCl saturation is
38.7 °C for DiPA-H₂O and 58.4 °C for DMiPA-H₂O. This together with the fact that the mixing of DiPA and water is less exothermic, makes DiPA the more suitable antisolvent for the crystallisation of either NaCl or NaCl₂H₂O.

4. Flow Sheet Design and Costs Estimations

Flow sheets have been designed for 1 Mton/year (8000 h) salt production plants based on the crystallisation of either NaCl or NaCl₂H₂O with diisopropylamine. The incoming brine feed stream is first treated in a conventional brine purification section, in which impurities will be removed. Since this purification step will be essentially the same as in the evaporative crystallisation process, it is not incorporated in the flow sheets. The required electricity and steam in the processes can be obtained from an on-site integrated steam power plant. For both process routes the energy and the fixed capital costs have been estimated.

4.1 Antisolver Crystallisation of NaCl with Diisopropylamine

4.1.1 Process Conditions

The NaCl is crystallised at a temperature of 0.3 °C, which is slightly above the NaCl-NaCl₂H₂O transition temperature in pure water. The antisolvent concentration was set at 81 wt%, at which 81 wt% of the dissolved NaCl in the brine feed is converted into solid NaCl. Under these circumstances 566 ton/h of saturated feed brine is needed to produce 1.0 Mton NaCl per year and the NaCl concentration in the water stream that is transported back to the mine is 6.4 wt%. At this temperature and antisolvent concentration there are two liquid phases and a solid phase present in the crystalliser. With a crystalliser antisolvent concentration of 81 wt% and NaCl₀H₂O as the desired crystal modification, the crystallisation temperature must be selected in the double liquid phase area, because NaCl₂H₂O is the stable crystal modification at temperatures in the single liquid phase area. Other than, that the NaCl solubility reduction in the double liquid phase area is slightly less than in the single liquid phase area, there are no important disadvantages of crystallising in the double liquid phase area. At equilibrium the mother liquor consists for 98.4 wt% of an organic phase with a NaCl free DiPA concentration of 82.6 wt%. The remaining 1.6 wt% is the aqueous phase, that contains 2.0 wt% of DiPA (NaCl free wt%). The amine recovery
temperature is set at 74 °C. At this temperature the spent mother liquor splits up into a salt free organic phase with a DiPA concentration of 94.2 wt% and an aqueous phase consisting of 92.5 wt% water, 6.4 wt% NaCl and 1.1 wt% amine (Weingaertner, 1988). The DiPA remaining in the aqueous phase is removed by extraction with octane, leaving a waste water stream containing 1 ppm DiPA. This stream can be used for another dissolution step (see Figure 6).

The crystallisation and antisolvent recovery conditions mentioned in the above were optimised roughly with respect to energy and fixed capital costs. A reduced antisolvent concentration leads to a lower yield due to the higher NaCl solubility in the crystalliser. The NaCl concentration in the waste water stream will rise and a larger brine feed stream is necessary in order to produce 1.0 Mton NaCl yearly. An increased antisolvent concentration gives a higher yield but complicates the antisolvent recovery, since the amine-water miscibility increases with a decreasing NaCl concentration.

4.1.2 Flow Sheet

In Figure 8 a simplified flow sheet for the direct crystallisation of NaCl with DiPA is depicted. The corresponding process stream summary can be found in Appendix I. The brine feed (stream nr. 4) is precooled to 5.3 °C in heat exchanger E03 and cooled to the crystalliser temperature in refrigerator E04. Stream 1 is make-up DiPA for the DiPA that leaves the process in the adhering mother liquor in stream 14. In this flow sheet as much as 4 ton/h make-up DiPA is needed. In practice this stream will be much smaller, because the crystals will be washed in the centrifuge with fresh feed brine. For the sake of simplicity the washing of the NaCl crystals in the centrifuge has been omitted in this flow sheet. The make-up DiPA is also precooled to 5.3 °C in E01 and cooled further to the crystalliser temperature in refrigerator E02. The rest of the DiPA is fed to the crystalliser via streams 20 and 32. Stream 30, the DiPA distillate (4.8 ton/h), is precooled from 84.4 °C (atmospheric bp. DiPA) to 5.3 °C in E08 and cooled further to the crystalliser temperature in refrigerator E05. The main DiPA feed, stream number 18, is precooled to 5.3 °C in E09 and cooled to 5 degrees below the crystalliser temperature, i.e. to -5 °C, in E07. This is done to partly compensate for the enthalpies of mixing and crystallisation that are released in the crystalliser. The remaining part of the enthalpies of mixing and crystallisation are removed in circulation cooler E06. A
part of the mother liquor is removed from the crystalliser via a hydrocyclone in which the suspension from the crystalliser is separated in a clear liquid and a thickened suspension, which is sent back to the crystalliser. This clear liquor advance increases the crystalliser solids concentration from 4 to 20 wt% and reduces the total crystalliser volume required. The suspension that leaves the crystalliser via stream 9, is fed to a centrifuge. The NaCl product stream with a solids concentration of 96 wt% can be used for electrolysis or dried and stored. The clear liquid stream from the centrifuge (stream nr. 13) is combined with stream nr. 12. This stream of spent mother liquor (nr. 15) has to be heated to a temperature of 74 °C at which the amine will be separated from the water phase. This is mainly carried out by exchanging heat with the antisolvent stream from the settler to the crystalliser (stream nr. 18) in E09. The rest of stream 15 is heated in EX, symbolising heat exchange with other process streams in E01, E03, E08, E15 and E16. The streams leaving EX and E09 are combined and heated to the desired temperature of 74 °C in E10. In E10 also the heat of demixing is added to the system. The organic and aqueous phases are separated in the settler. The aqueous phase that leaves the settler (stream 21) is fed to a rotating disc contactor in which DiPA is extracted from the aqueous phase with octane. The water stream that leaves the RDC contains 1 ppm DiPA and 6 wt% of NaCl and it can be reused for another dissolution step. The octane is separated from the DiPA in the distillation column and both the DiPA and the octane are reused.
Figure 8. Simplified flow sheet for the direct crystallisation of NaCl with DiPA.
4.1.3 Major Equipment Items

To be able to determine the total fixed capital cost and the energy consumption within the process, the dimensions of the major equipment items were estimated. Most of them are operated at atmospheric pressure. Carbon steel and stainless steel have been selected as the main materials of construction. For the process parts that come into contact with NaCl stainless steel was used (AISI 316SS or 316L).

Experiments demonstrated that a residence time of the crystals of 100 minutes is sufficient to form a crystal product with a mass weighted mean size of $L_{4,3} = 250 \mu m$. From this the total required crystalliser volume was calculated at 967 m$^3$. This is divided over four identical parallel crystallisers of 242 m$^3$ each. The antisolvent and brine feeds are divided over the four crystallisers equally and each crystalliser is operated at the same conditions. To remove the enthalpies of mixing and crystallisation the content of each crystalliser is circulated over a refrigerator (E06). Therefore each crystalliser is provided with a centrifugal pump with a capacity of 0.4 m$^3$ s$^{-1}$. A combination of 11 hydrocyclones with a $d_{50}$ of 40 $\mu$m, a diameter of 0.72 m and an inlet velocity of 18 m s$^{-1}$ (Sinnott, 1991; pp 327-330) is used to remove 2602 ton/h of clear mother liquor from the crystallisers (~651 ton/h per crystalliser). To separate the suspension outlets from the four crystallisers into clear mother liquor and 96 wt% dry NaCl crystals two continuous pusher type centrifuges are needed with a diameter of 1.2 m and a capacity of 60 ton/h solids each.

For the separation of the organic phase from the aqueous phase in the antisolvent recovery a settler is used with a total surface area of 356 m$^2$ and a vessel height of 12 m (Sinnott, 1991; p 344-346). The DiPA remaining in the aqueous phase that leaves the settler is extracted with octane. Since the distribution coefficient for DiPA over octane and water was not known, the distribution coefficient of DMiPA over heptane and water, which is 4.5 (based on concentrations in weight percentages), was used. The required number of equilibrium stages and the amount of octane needed were calculated with the Kremser equation (Perry, 1984). With a mass fraction of DiPA that is not extracted of $9.3 \cdot 10^{-5}$, the required number of equilibrium stages was estimated at 20, and 150 ton/h octane is needed to perform the extraction. The extraction can be carried out in a Rotating Disc Contactor in which the aqueous phase is the continuous phase. With an octane droplet diameter of 1.6 mm, a specific
power input of 0.018 m$^2$ s$^{-3}$ and a rotator frequency of 0.5 Hz, a total length of 55 m of RDC is needed with a column diameter of 4.0 m, a stator ring diameter of 2.8 m, a rotor diameter of 2.0 m and a compartment height of 0.4 m (Lo, 1991; pp 391-405). This length can be divided over five columns in series with a length of 11 m each. After the extraction the DiPA is separated from the octane by distillation. The calculations for the design of the distillation column were carried out in Aspen Plus™ with the Redlich-Kwong-Soave property set and a column pressure of 1 bar. According to these calculations a total of 35 equilibrium stages (minimum 15) and a reflux ratio of 14.1 (minimum 13.0) are sufficient to separate the octane-DiPA feed into an octane stream containing 318 ppm DiPA and a DiPA stream with 63 ppm of octane. These low concentrations were neglected in the overall mass balance over the process. The corresponding reboiler and condensor duties are 6.6 and 6.5 MW respectively. With an assumed plate efficiency of 65% a total number of 54 real stages are required. With a plate spacing of 0.5 m, a maximum superficial vapour velocity of 0.65 m s$^{-1}$ and a maximum vapour rate of 20 kg s$^{-1}$ the column length and diameter are approximately 27 and 3.4 m (Sinnott, 1991; p 449).

Within the process an extensive heat exchanger network is required. This is mainly due to the considerable temperature difference between the crystallisation and antisolvent recovery sections within the process and the magnitude of the streams between the two sections. As much as 28557 m$^2$ divided over 29 heat exchangers of 985 m$^2$ each, is required to transfer 143 MW in E09 with a minimum temperature difference at both ends of $\Delta T = 5.0$ °C. This is by far the largest contribution to the total amount of heat exchanger surface area needed in the design. This area can be reduced to 19794 m$^2$ by increasing the mean temperature difference between the two streams to $\Delta T_m = 7.2$ °C (logarithmic mean). This will however, increase the energy consumption within the process. Heat is removed in refrigerators E2, E4 and E5 by evaporating NH$_3$ at -5 °C and condensing it at 30 °C, resulting in a coefficient of performance (COP) of 5.34, if a centrifugal compressor with an efficiency of 0.80 is used (Smith, 1987; pp 274-287). Refrigerators E06 and E07 evaporate NH$_3$ at -10 °C and condense at 30 °C and have a COP of 4.43. The heat produced in the condensors can partly be used to evaporate NH$_3$ (or another medium) at a temperature of 25 °C. The formed NH$_3$ vapour is compressed with a centrifugal compressor and condensed at a temperature of 79 °C (COP 2.95). The heat produced in the condensor of this ‘heat pump’ can be used in E10 to heat the settler feed to 74
°C and to provide the enthalpy of demixing. The rest of the heat produced in the condensers of the refrigerators can be removed with cooling water. An alternative is to fully remove the heat produced in the condenser with cooling water. In this case steam is needed in E10. In most cases shell and tube type heat exchangers were used, but also some plate heat exchangers were applied. Furthermore, in all calculations of the heat transfer areas the overall heat transfer coefficient was set at 1 kW/m² °C.

4.1.4 Fixed Capital Costs

According to Lang the fixed capital costs are given as a function of the total equipment cost by the equation: \( C_f = f_I C_e \); where \( C_f \) are the fixed capital costs, \( f_I \), the ‘Lang factor’ and \( C_e \) the total delivered costs (or FOB costs) of all process items. The delivered costs were estimated with the help of various cost databases. The ‘Lang factor’ is usually 3.1 for predominantly solids processing plants, 3.6 for mixed fluids-solids processing plants and 4.7 for predominantly fluids processing plants. In the investment costs estimations presented here a ‘Lang factor’ of 4.0 is used.

<table>
<thead>
<tr>
<th>Heat Exchange</th>
<th>Antisolvent recovery: ( \Delta T_{aw} ) in E09 (°C):</th>
<th>Heat pump</th>
<th>Heat exchangers</th>
<th>Heat pump / heater</th>
<th>Steam</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5.0</td>
<td>7.2</td>
<td>5.0</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13273</td>
<td>8400</td>
<td>13258</td>
<td>8400</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10395</td>
<td>10596</td>
<td>10067</td>
<td>10422</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8270</td>
<td>10960</td>
<td>496</td>
<td>589</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31937</td>
<td>29956</td>
<td>23821</td>
<td>19411</td>
</tr>
</tbody>
</table>

In Table 1 the FOB equipment costs involved in the exchange of heat within the plant are displayed. These costs form the most important contribution to the total fixed capital costs. One option is to use a heat pump to provide for the heat of demixing in E10. This reduces the energy consumption within the process. The alternative is to use steam in E10, which strongly reduces the total FOB equipment costs but increases the energy consumption. For both options the FOB equipment costs can be reduced by increasing the temperature difference in E09 from 5.0 °C to a logarithmic mean temperature difference of 7.2 °C by reducing the temperature of stream 16 from 69 to 64 °C. In Table 2 the FOB costs of the other major equipment items are displayed.
Table 2. FOB costs (\(\cdot 10^3\) USD) of the major equipment items.

<table>
<thead>
<tr>
<th>Process Equipment</th>
<th>Cost ((\cdot 10^3) USD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>crystallisers</td>
<td>1754</td>
</tr>
<tr>
<td>centrifuges</td>
<td>211</td>
</tr>
<tr>
<td>hydrocyclones</td>
<td>365</td>
</tr>
<tr>
<td>settler</td>
<td>837</td>
</tr>
<tr>
<td>distillation column</td>
<td>478</td>
</tr>
<tr>
<td>extraction columns</td>
<td>3686</td>
</tr>
<tr>
<td>total</td>
<td>7331</td>
</tr>
</tbody>
</table>

With an estimated brine purification section fixed capital costs of \(5 \cdot 10^6\) USD the total fixed capital costs are \(162 \cdot 10^6\) or \(155 \cdot 10^6\) USD for the option that includes the heat pump and \(130 \cdot 10^6\) or \(112 \cdot 10^6\) USD if steam is used in E10. The investment required for the project is recovered as a charge on the project, which is taken as 20% of the fixed capital yearly (typically 10-20% (Sinnott, 1991; p 198). The capital charges are then \(32.5 \cdot 10^6\) or \(30.9 \cdot 10^6\) USD/year for option I and \(26.0 \cdot 10^6\) or \(22.5 \cdot 10^6\) USD/year for option II (Table 3).

Table 3. Fixed capital costs.

<table>
<thead>
<tr>
<th>Fixed Capital</th>
<th>heat pump ((\cdot 10^6) USD)</th>
<th>steam ((\cdot 10^6) USD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>antisolvent recovery:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\Delta T_m) in E09 ((^\circ C)):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>heat exchange - FOB</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>process equipment - FOB</td>
<td>7.3</td>
<td>7.3</td>
</tr>
<tr>
<td>major equipment - fixed capital</td>
<td>157</td>
<td>125</td>
</tr>
<tr>
<td>brine purification - fixed capital</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>total fixed capital</td>
<td>162</td>
<td>130</td>
</tr>
<tr>
<td>capital charges</td>
<td>32.5</td>
<td>26.0</td>
</tr>
<tr>
<td>((\cdot 10^6) USD/year)</td>
<td>32.5</td>
<td>26.0</td>
</tr>
<tr>
<td>(USD/ton NaCl)</td>
<td>32.5</td>
<td>26.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.1.5 Energy Consumption

Large heat streams are present in the process. Depending on the temperature difference in E09, the total amount of cooling required is 218 or 227 MW (Table 4) from which 46 or 48 MW has to be removed in the refrigerators. The refrigerators are used to cool down the crystalliser feeds from 5.3 to 0.3 °C and to remove the enthalpies of mixing and crystallisation of 30 and 0.9 MW respectively. To drive the compressors of the refrigerators 10 or 11 MW electricity is needed. Furthermore in E11 the RDC octane feed is cooled to 74
°C with water. The rest of the cooling is carried out by exchanging heat with other process streams.

The total heating required is 223 MW in all cases. At a temperature level of approximately 125 °C, 7 MW is needed to heat the distillation column feed to its atmospheric boiling point and for the distillation column reboiler. For this saturated steam of 350 kPa and 139 °C ($\Delta H_{\text{evap}} = 2.15 \text{ MJ/kg}$) obtained from an on-site steam power plant can be used (Smith, 1987; pp 254-260). A heat pump can be utilised to heat the settler feed to 74 °C (6 or 17 MW) and to add the heat of demixing (29 MW) in E10. To drive the centrifugal compressors of this heat pump 9 or 12 MW of electricity is needed (Table 4). An alternative is to use 100 kPa saturated steam (100 °C, $\Delta H_{\text{evap}} = 2.26 \text{ MJ/kg}$) from the steam power plant in E10. The rest of the heating is carried out by exchanging heat with other process streams.

Table 4. Overview of energy household for the direct antisolvent crystallisation of NaCl with DiPA.

<table>
<thead>
<tr>
<th>antisolvent recovery</th>
<th>$\Delta T_{\text{m}}$ E09 (°C)</th>
<th>cooling (MW)</th>
<th>electricity (MW)</th>
<th>heating (MW)</th>
<th>electricity E10 (MW)</th>
<th>steam E10 (MW)</th>
<th>100 kPa (kg/s)</th>
<th>steam E13/14 350 kPa (kg/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>heat pump</td>
<td>5.0</td>
<td>227</td>
<td>10</td>
<td>223</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>218</td>
<td>11</td>
<td>223</td>
<td>12</td>
<td>-</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>steam</td>
<td>5.0</td>
<td>227</td>
<td>10</td>
<td>223</td>
<td>-</td>
<td>35</td>
<td>15.6</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>218</td>
<td>11</td>
<td>223</td>
<td>-</td>
<td>47</td>
<td>20.6</td>
<td>7</td>
</tr>
</tbody>
</table>

The price of 350 kPa steam is 13.5 USD/ton. The same price was used for the 100 kPa steam. A correction for the overrating of the 100 kPa steam was made by taking into account that in the steam power plant 113 kJ electricity can be produced if 1 kg of 375 kPa steam (25 kPa for pressure drop in transport to heater) is expanded to 150 kPa (50 kPa for pressure drop) in a turbine with an efficiency of 75 % (Smith, 1987; pp 254-260). With an electricity price of 4·10⁻² USD/kWh this leads to the steam and net electricity costs as listed in Table 5.

Table 5. Energy costs.

<table>
<thead>
<tr>
<th>antisolvent recovery</th>
<th>$\Delta T_{\text{m}}$ E09 (°C)</th>
<th>electricity (USD/ton NaCl)</th>
<th>steam (USD/ton NaCl)</th>
<th>energy (USD/ton NaCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>heat pump</td>
<td>5.0</td>
<td>6.9</td>
<td>1.4</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>8.1</td>
<td>1.4</td>
<td>9.4</td>
</tr>
<tr>
<td>steam</td>
<td>5.0</td>
<td>3.0</td>
<td>7.7</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>3.0</td>
<td>9.7</td>
<td>12.7</td>
</tr>
</tbody>
</table>
4.1.6 Major Operating Costs

Based on the estimated capital charges and the energy costs, the major operating costs were calculated (Table 6). The energy costs comprise the steam and electricity costs involved in the exchange of heat, but do not include other contributions such as pump work. The capital charges are calculated from the fixed capital costs, which were estimated with an approximate accuracy of -30 to +50%. The calculated operating costs vary between 35.2 and 40.7 USD/ton NaCl. From Table 6 it can be seen that a reduction in the energy costs by using a heat pump instead of steam or by decreasing the temperature difference in E09 is accompanied with a stronger increase in the fixed capital costs. The operating costs are minimal if steam is applied in E10 and if the logarithmic mean temperature difference over E09 is 7.2 °C. At the expense of an increased energy costs, the operating costs can probably be reduced further if this temperature difference is increased.

Table 6. Major operating costs.

<table>
<thead>
<tr>
<th>Antisolvent Recovery</th>
<th>ΔT_m E09 (°C)</th>
<th>Fixed Capital Costs (-10^6 USD; -30% to +50%)</th>
<th>Capital Charge (USD/ton NaCl)</th>
<th>Energy Costs (USD/ton NaCl)</th>
<th>Major Operating Costs (USD/ton NaCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat pump</td>
<td>5.0</td>
<td>162</td>
<td>32.5</td>
<td>8.2</td>
<td>40.7</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>155</td>
<td>30.9</td>
<td>9.4</td>
<td>40.3</td>
</tr>
<tr>
<td>Steam</td>
<td>5.0</td>
<td>130</td>
<td>26.0</td>
<td>10.7</td>
<td>36.7</td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td>112</td>
<td>22.5</td>
<td>12.7</td>
<td>35.2</td>
</tr>
</tbody>
</table>

4.2 Antisolvent Crystallisation NaCl.2H₂O with Diisopropylamine and a Recrystallisation Step

4.2.1 Process Conditions

For this process route the selected crystallisation conditions are a temperature of -5 °C, which is well below the NaCl-NaCl.2H₂O transition temperature in pure water, and a crystalliser DiPA concentration of 79 wt%. Under these circumstances there is one liquid phases and a solid phase present in the crystalliser. The NaCl dissolved in the brine feed is, after recrystallisation, converted into solid NaCl for 81 % and 566 ton/h of saturated feed brine is needed to produce 1.0 Mton/NaCl per year. The NaCl.2H₂O crystals are recrystallised in a fresh feed brine in a recrystalliser at 0.5 °C. At the recovery temperature of 74 °C the spent mother liquor splits up into a salt free organic phase with a DiPA concentration of 94.2 wt%
and an aqueous phase consisting of 92.8 wt% water, 6.2 wt% NaCl and 1.1 wt% amine (Weingaertner, 1988). The DiPA remaining in the aqueous phase is removed by extraction with octane, leaving a water stream containing 6.2 wt% NaCl and 1 ppm DiPA. This stream can be used for another dissolution step.

4.2.2 Flow Sheet

In Figure 9 a simplified flow sheet for the crystallisation of NaCl.2H₂O with DiPA and a consecutive recrystallisation step is displayed. The corresponding process stream summary can be found in Appendix II. The brine feed (stream nr. 4) is divided over the NaCl.2H₂O crystalliser (Cr1) and the NaCl crystalliser (Cr2). The brine feed to the NaCl.2H₂O crystalliser is precooled to 0.5 °C in E03 and cooled to the crystalliser temperature in E04 (-5 °C). The make-up DiPA and the DiPA condensate from the distillation column are also precooled to 0.5 °C in E01 and E08 and cooled to the crystalliser temperature in E02 and E07. The main DiPA feed, stream 24, is precooled to 0.5 °C in E10 and cooled to a temperature of 5 degrees below the crystalliser temperature in E09. This is done to partly compensate for the enthalpies of mixing and crystallisation that are released in the crystalliser. The remaining part is removed in circulation cooler E06. A hydrocyclone is used to remove clear mother liquor and with that the antisolvent crystalliser solids concentration is increased to 20 wt%. The suspension that leaves the crystalliser via stream 13 is fed to a centrifuge (Cf1) in which no washing takes place. The NaCl.2H₂O crystals leave the centrifuge in a stream that consists for 91 wt% out of solids (stream nr. 15). The crystals together with uncooled fresh brine are fed to the NaCl crystalliser (Cr2), in which the recrystallisation takes place at a temperature of 0.5 °C. After complete conversion of the NaCl.2H₂O, the NaCl solids concentration in this crystalliser is 20 wt% and the mother liquor DiPA concentration is 3.5 wt%. To compensate for the enthalpy of dissolution of the NaCl.2H₂O, the recrystalliser content is heated in E18. The suspension product stream (stream nr. 16) is fed to a centrifuge (Cf2) in which the washing of the NaCl crystals has been omitted as in the direct antisolvent crystallisation of NaCl. The NaCl crystals leave the process in a stream with a solids concentration of 96 wt%. The clear mother liquor from the centrifuge is recycled to the NaCl.2H₂O crystalliser (Cr1) and cooled to the crystalliser temperature in E05. The clear mother liquor from centrifuge Cf1 is combined with the clear
mother liquor from the hydrocyclone and heated in E10, EY and E11 to a temperature of 74 °C. The part of stream 21 that does not exchange heat with stream 24 in E10 exchanges heat with other process streams in E01, E02, E08, E12, E16 and E17, depicted as EX in Figure 9. The organic and the aqueous phases are separated in the settler. The organic phase is recycled and the aqueous phase is further purified by extraction and leaves the flow sheet as a stream with 1 ppm DiPA and 6.2 wt% NaCl.

4.2.3 Major Equipment Items

The required volume of the NaCl.2H₂O crystalliser can be estimated roughly with \( L_{4,3} = 4Gr \) from the MSMPR theory (Randolph, 1988). With an estimated linear growth rate of \( 2.5 \times 10^{-8} \) m s⁻¹ and a desired mass weighted mean size of 250 μm, the required crystal mean residence time and crystalliser volume are 42 minutes and 817 m³. From the recrystallisation experiments it was estimated that a suspension mean residence time of 21 minutes in the recrystalliser is sufficient to get NaCl crystals with a mass weighted mean size of 250 μm. This results in a total required recrystalliser volume of 149 m³.

The total NaCl.2H₂O crystalliser volume can be divided over four identical parallel crystallisers of 204 m³ each. The antisolvent and brine feeds are divided over the four crystallisers equally and each crystalliser is operated at the same conditions. To remove the enthalpies of mixing and crystallisation from the NaCl.2H₂O crystallisers, the content of each crystalliser is circulated over a refrigerator with a centrifugal pump with a capacity of 0.7 m³ s⁻¹. In this case a combination of 6 hydrocyclones, equivalent to the ones described previously in the section on the direct crystallisation of NaCl, are used to remove 1913 ton/h of clear mother liquor from the crystallisers (~478 ton/h per crystalliser). To separate the product NaCl.2H₂O crystals from the mother liquor four continuous pusher type centrifuges are needed with a diameter of 1.2 m and a capacity of 60 ton/h solids each. For the separation of the NaCl crystals from their mother liquor only two of these centrifuges are needed.
Figure 9. Simplified flow sheet for the crystallisation of NaCl.2H₂O with DiPA and a consecutive recrystallisation step.
A settler with a surface area of 320 m² and a height of 12 m is used to separate the organic phase from the aqueous phase in the antisolvent recovery (Sinnot, 1991; p 344-346). The DiPA concentration in the aqueous phase is reduced to 1 ppm by extraction with octane. Subsequently the DiPA is recovered from the octane by distillation. For the extraction 20 equilibrium stages are needed, with a DiPA fraction that is not extracted of 9.3 $10^5$ and an octane flow rate of 149 ton/h. This can be carried out in an RDC with a total length of 53 m with dimensions identical to the dimensions of the RDC used for the extraction of DiPA in the direct antisolvent crystallisation of NaCl. This length is divided over five columns in series with a length of 10.6 m each. The distillation is carried out in a column identical to the one described previously. With reboiler and condenser duties of 6.5 and 6.4 MW the octane-DiPA feed is separated into an octane stream containing 319 ppm DiPA and a DiPA stream with 63 ppm of octane.

Also here an extensive heat exchanger network is required. As much as 25719 m² divided over 26 heat exchangers of 989 m² each, is required to transfer 135 MW in E10 with a logarithmic mean temperature difference of $\Delta T_m = 5.2$ °C. This area can be reduced to 17925 m² by increasing the logarithmic mean temperature difference between the two streams to $\Delta T_m = 7.5$ °C. This will however, increase the energy consumption within the process. In refrigerators E02, E04, E05 and E07 NH₃ is evaporated at -10 °C and condensed at 30 °C with a COP of 4.43 ($\eta_{\text{comp}} = 0.80$). Refrigerators E06 and E09 evaporate NH₃ at -15 °C and condense at 30 °C and have a COP of 3.80. The heat of condensation of the NH₃ produced in the refrigerators can, also in this case, partly be used in a heat pump to heat the settler feed to 74 °C and to provide the enthalpy of demixing in E11. The alternative is to use steam in E11.

4.2.4 Fixed Capital Costs

In Table 7 the FOB equipment costs involved in the exchange of heat within the flow sheet are displayed. A heat pump or steam can be used to raise the settler feed temperature to 74 °C and to add the enthalpy of demixing to the system. The FOB equipment costs for both options can be reduced to $32897 \times 10^3$ and $21547 \times 10^3$ USD respectively by increasing the temperature difference in E10 from 5.2 to 7.5 °C. This can be done by reducing the temperature of stream 22 from 69 to 64 °C. In Table 8 the FOB costs of the other major equipment items are displayed. With a 'Lang factor' of 4 the fixed capital costs are $180 \times 10^6$ or $167 \times 10^6$ USD if a
Table 7. FOB costs ($10^3$ USD) involved in the exchange of heat.

<table>
<thead>
<tr>
<th>Heat Exchange</th>
<th>heat pump</th>
<th>steam</th>
</tr>
</thead>
<tbody>
<tr>
<td>antisolvent recovery:</td>
<td>5.2</td>
<td>7.5</td>
</tr>
<tr>
<td>$\Delta T_m$ in E10:</td>
<td>11328</td>
<td>8277</td>
</tr>
<tr>
<td>heat exchangers</td>
<td>13855</td>
<td>12922</td>
</tr>
<tr>
<td>refrigerators</td>
<td></td>
<td></td>
</tr>
<tr>
<td>heat pump / heater</td>
<td>10976</td>
<td>11697</td>
</tr>
<tr>
<td>total</td>
<td>36158</td>
<td>32897</td>
</tr>
</tbody>
</table>

heat pump is used and $135\cdot10^6$ or $121\cdot10^6$ USD if steam is used in E11. From this the capital charges, i.e. 20% of the fixed capital per year, are calculated (Table 9).

Table 8. FOB costs ($10^3$ USD) of major equipment items.

<table>
<thead>
<tr>
<th>Process Equipment</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>crystallisers</td>
<td>1772</td>
</tr>
<tr>
<td>centrifuges</td>
<td>635</td>
</tr>
<tr>
<td>hydrocyclones</td>
<td>187</td>
</tr>
<tr>
<td>settler</td>
<td>753</td>
</tr>
<tr>
<td>distillation column</td>
<td>469</td>
</tr>
<tr>
<td>extraction columns</td>
<td>3585</td>
</tr>
<tr>
<td>total</td>
<td>7401</td>
</tr>
</tbody>
</table>

4.2.5 Energy Consumption

In this alternative process route the total amount of cooling required is 225 MW (see Table 10) from which 55 MW has to be removed with refrigerators. The refrigerators are used to cool the crystalliser feeds from 0.3 °C to the crystalliser temperature of -5 °C and to remove the enthalpy of mixing and crystallisation of 31 MW and 11 MW. Since the enthalpy of crystallisation of NaCl.2H$_2$O could not be found in the literature, it was estimated with the molecular modelling package Cerius$^2$. Its estimated value of -16.8 kJ mol$^{-1}$ (exothermic) is

Table 9. Fixed capital costs.

<table>
<thead>
<tr>
<th>Fixed Capital</th>
<th>heat pump</th>
<th>steam</th>
</tr>
</thead>
<tbody>
<tr>
<td>antisolvent recovery:</td>
<td>5.2</td>
<td>7.5</td>
</tr>
<tr>
<td>$\Delta T_m$ in E10 (°C):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>heat exchange - FOB ($10^6$ USD)</td>
<td>36.2</td>
<td>32.9</td>
</tr>
<tr>
<td>process equipment - FOB ($10^6$ USD)</td>
<td>7.4</td>
<td>7.4</td>
</tr>
<tr>
<td>major equipment - fixed capital ($10^6$ USD)</td>
<td>174</td>
<td>161</td>
</tr>
<tr>
<td>brine purification - fixed capital ($10^6$ USD)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>total fixed capital ($10^6$ USD)</td>
<td>180</td>
<td>167</td>
</tr>
<tr>
<td>capital charges ($10^6$ USD/year)</td>
<td>36.0</td>
<td>33.3</td>
</tr>
<tr>
<td>(USD/ton NaCl)</td>
<td>36.0</td>
<td>33.3</td>
</tr>
</tbody>
</table>

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close to the enthalpies of dissolution of similar hydrates such as NaBr.2H₂O and NaI.2H₂O, whose enthalpies of dissolution are 16.3 and 19.3 kJ mol⁻¹ respectively at infinite dilution (Mullin, 1993; p 477).

Table 10. Overview of energy household for the antisolvent crystallisation of NaCl.2H₂O with DiPA and a consecutive recrystallisation step.

<table>
<thead>
<tr>
<th>antisolvent recovery</th>
<th>ΔTₑ₁₀ (°C)</th>
<th>cooling (MW)</th>
<th>electricity (MW)</th>
<th>heating (MW)</th>
<th>electricity E₁₁ (MW)</th>
<th>steam E₁₁ (MW)</th>
<th>100 kPa steam (MW)</th>
<th>350 kPa steam E₁₄/₁₅ (MW)</th>
<th>350 kPa (kg/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>heat pump</td>
<td>5.2</td>
<td>225</td>
<td>14</td>
<td>233</td>
<td>11</td>
<td>-</td>
<td>7</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>225</td>
<td>14</td>
<td>233</td>
<td>12</td>
<td>-</td>
<td>7</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>steam</td>
<td>5.2</td>
<td>225</td>
<td>14</td>
<td>233</td>
<td>-</td>
<td>48</td>
<td>21.5</td>
<td>7</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>225</td>
<td>14</td>
<td>233</td>
<td>-</td>
<td>54</td>
<td>23.8</td>
<td>7</td>
<td>3.3</td>
</tr>
</tbody>
</table>

The total heating required is 233 MW in all cases. At a temperature level of approximately 125 °C 7 MW is needed to heat the distillation column feed to its atmospheric boiling point and for the distillation column reboiler. For this saturated steam of 350 kPa is used. A heat pump, that utilises the heat of condensation produced in the refrigerator condensors, can be used to heat the settler feed to 74 °C and to add the heat of demixing in E₁₁. To drive the centrifugal compressors of such a heat pump 11 or 12 MW of electricity is needed (Table 10). An alternative is to use 100 kPa steam from the steam power plant. The rest of the heating is carried out by exchanging heat with other process streams. From this the total steam and net electricity costs were calculated (Table 11).

Table 11. Energy costs.

<table>
<thead>
<tr>
<th>antisolvent recovery</th>
<th>ΔTₑ₁₀ (°C)</th>
<th>electricity (USD/ton NaCl)</th>
<th>steam (USD/ton NaCl)</th>
<th>costs (USD/ton NaCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>heat pump</td>
<td>5.2</td>
<td>9.2</td>
<td>1.4</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>9.6</td>
<td>1.4</td>
<td>11.0</td>
</tr>
<tr>
<td>steam</td>
<td>5.2</td>
<td>4.3</td>
<td>10.1</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>4.2</td>
<td>11.0</td>
<td>15.2</td>
</tr>
</tbody>
</table>

4.2.6 Major Operating Costs

The calculated major operating costs vary between 39.5 and 46.5 USD/ton (Table 12). The operating costs are minimal if steam is applied in E₁₀ and if the logarithmic mean
temperature difference over E10 is 7.5 °C. At the expense of an increased energy costs, the operating costs may be reduced further if this temperature difference is increased.

Table 12. Major operating costs.

<table>
<thead>
<tr>
<th>Antisolvent recovery</th>
<th>$\Delta T_{m}E10$ (°C)</th>
<th>fixed capital costs (x 10^6 USD; ±20% to +50%)</th>
<th>capital charge (USD/ton NaCl)</th>
<th>energy costs (USD/ton NaCl)</th>
<th>operating costs (USD/ton NaCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>heat pump</td>
<td>5.2</td>
<td>180</td>
<td>36.0</td>
<td>10.5</td>
<td>46.5</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>167</td>
<td>33.3</td>
<td>11.0</td>
<td>44.3</td>
</tr>
<tr>
<td>steam</td>
<td>5.2</td>
<td>135</td>
<td>27.0</td>
<td>14.4</td>
<td>41.4</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>121</td>
<td>24.2</td>
<td>15.2</td>
<td>39.5</td>
</tr>
</tbody>
</table>

5. Discussion

The major operating costs of the two routes of the antisolvent crystallisation of NaCl have been compared with the major operating costs of the four effect evaporative crystallisation of NaCl. Furthermore attention has been paid to the differences in product quality that can be expected, and to practical considerations that may influence the selection of a process route. Finally some guidelines will be given for the selection of more suitable antisolvents for the crystallisation of NaCl.

5.1 Major Operating Costs

From the designed flow sheets and major equipment items, the major operating costs for the antisolvent crystallisation processes have been estimated. From Table 13 it follows that both the fixed capital costs and the energy costs are lower for the direct antisolvent crystallisation of NaCl. This is mainly due to the fact that the crystallisation of NaCl.2H₂O is approximately ten times more exothermic than the crystallisation of NaCl and that the enthalpies of crystallisation and mixing have to be removed at a lower temperature level.
Table 13. Costs involved in the production of NaCl by antisolvent or evaporative crystallisation.

<table>
<thead>
<tr>
<th>process route</th>
<th>antisolvent recovery</th>
<th>$\Delta T_m$ E09/E10 (°C)</th>
<th>fixed capital ($10^6$ USD)</th>
<th>capital charge (USD/ton)</th>
<th>energy costs (USD/ton)</th>
<th>major operating costs (USD/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS crystallisation</td>
<td>heat pump</td>
<td>5.0</td>
<td>162</td>
<td>32.5</td>
<td>8.2</td>
<td>40.7</td>
</tr>
<tr>
<td>NaCl</td>
<td>steam</td>
<td>7.2</td>
<td>155</td>
<td>30.9</td>
<td>9.4</td>
<td>40.3</td>
</tr>
<tr>
<td>5.0</td>
<td>130</td>
<td>26.0</td>
<td>10.7</td>
<td></td>
<td></td>
<td>36.7</td>
</tr>
<tr>
<td>7.2</td>
<td>112</td>
<td>22.5</td>
<td>12.7</td>
<td></td>
<td></td>
<td>35.2</td>
</tr>
<tr>
<td>AS crystallisation</td>
<td>heat pump</td>
<td>5.2</td>
<td>180</td>
<td>36.0</td>
<td>10.5</td>
<td>46.4</td>
</tr>
<tr>
<td>NaCl.2H2O and</td>
<td>steam</td>
<td>7.5</td>
<td>167</td>
<td>33.3</td>
<td>11.0</td>
<td>44.3</td>
</tr>
<tr>
<td>recrystallisation</td>
<td></td>
<td>5.2</td>
<td>135</td>
<td>27.0</td>
<td>14.4</td>
<td>41.4</td>
</tr>
<tr>
<td>7.5</td>
<td>121</td>
<td>24.2</td>
<td>15.2</td>
<td></td>
<td></td>
<td>39.5</td>
</tr>
<tr>
<td>evap. cryst. NaCl</td>
<td>-</td>
<td>-</td>
<td>108</td>
<td>21.6</td>
<td>11.5</td>
<td>33.1</td>
</tr>
</tbody>
</table>

To make a realistic comparison between these two routes for the antisolvent crystallisation of NaCl and the four effect evaporative crystallisation of NaCl, the major operating costs in the evaporative crystallisation process should be calculated similarly. The fixed capital costs for a 1 Mton/y four effect evaporative crystallisation plant were estimated at 108 million USD (Geertman, 1998), resulting in a capital charge of 21.6 USD/ton. Furthermore, for the production of one ton NaCl approximately 0.85 ton of steam (139 °C, 3.5 bar) is required, corresponding to an energy costs of 11.5 USD/ton NaCl. As can be seen from Table 13, the best case scenario is an energy costs reduction of 29 % by applying antisolvent crystallisation instead of evaporative crystallisation and the worst case is an increase in the energy costs of 32 %. In all cases however, the fixed capital costs and consequently the capital charges are higher in the antisolvent crystallisation of NaCl. Because the capital charges are taken as 20% of the fixed capital yearly, they have a very dominant effect on the major operating costs. As a result of this the major operating costs are the lowest for the 4 effect evaporative crystallisation of NaCl.

However, since the current industrial price for one ton of NaCl in the Netherlands is approximately 27.0 USD, salt producing companies apparently take a much smaller percentage of the fixed capital for their capital charges. If also here a smaller percentage would be used, this would work in favour of the antisolvent crystallisation process, because this reduces the relative importance of the capital charges.

If the capital charges in both processes were the same, the maximum reduction in energy costs of 29%, or 3.3 USD/ton, would result in a 12% reduction in the NaCl cost price. So, if the fixed capital costs of the antisolvent crystallisation process could be reduced by for
instance replacing the shell and tube type heat exchangers by more efficient types of heat exchangers, the antisolvent crystallisation process could become economically attractive.

5.2 Product Quality

It is obviously very hard to predict the quality of the product made by bulk antisolvent crystallisation, but some general remarks can be made. First of all, laboratory scale experiments demonstrated that it is possible to make large NaCl crystals with an amine uptake of less than 6 ppm by the antisolvent crystallisation of NaCl₂H₂O and a consecutive recrystallisation step. It is very important that the NaCl crystals contain very little of the amine, since an amine may form the explosive compound NCl₃ in the electrolysis of the NaCl. In the direct antisolvent crystallisation of NaCl the crystals are generally small, tend to agglomerate and contain more of the amine. For these reasons it is not likely that the direct crystallisation of NaCl with amines will replace evaporative crystallisation. However, if an antisolvent can be found that causes less problems in the electrolysis of the NaCl, the direct antisolvent crystallisation of NaCl is a very interesting alternative to evaporative crystallisation. An advantage of the antisolvent crystallisation process could be that it contains a very large bleed stream, i.e. the purified aqueous phase from the antisolvent recovery that is recycled to the raw material deposit. The presence of this bleed limits the build up of the impurities SO₄²⁻, Ca²⁺ and Br⁻ in the system, and probably reduces the uptake of these impurities in the salt product.

5.3 Practical Considerations

An important disadvantage of the antisolvent crystallisation process is that it requires the presence of large quantities of an organic substance, that might be flammable, toxic, chemically instable in a closed loop process and environmentally polluting. An advantage is that the process is carried out at atmospheric pressure, whereas in the evaporative crystallisation of NaCl water is evaporated at pressures below atmospheric pressure in three of the four effects (Jongema, 1983). Furthermore, in the four effect evaporative crystallisation the NaCl yield generally approaches 100 % since practically all the water is evaporated from the feed brine. In the antisolvent crystallisation a NaCl yield of 100 % is not wanted, since the
absence of dissolved NaCl in the spent mother liquor increases the mutual solubilities of the antisolvent and the water at the antisolvent recovery conditions, giving rise to extremely large recycles of relatively wet antisolvent. In the flow sheets discussed here salt yields of 81% are obtained, leaving aqueous streams containing 6 wt% NaCl that is pumped back to the mine.

5.4 Possibilities for Improvement

If an antisolvent can be found with improved characteristics, the major operating costs of the antisolvent crystallisation of NaCl could be reduced further. The most important aspects when considering a different antisolvent are: the shapes and positions of the binary antisolvent-water and the ternary antisolvent-water-NaCl two phase envelopes, the heat of mixing of the antisolvent and the water, and the efficiency of the antisolvent in suppressing the solubility of the NaCl.

The antisolvent crystallisation process involves extensive heat exchanging between the antisolvent recovery and crystallisation sections. If the temperature difference between the crystallisation and the antisolvent recovery could be reduced by using a different antisolvent or by applying a different or additional separation method for the recovery of the antisolvent, this would reduce the fixed capital costs.

In the designed processes mostly shell and tube type heat exchangers have been applied. The use of different more efficient types of heat exchangers could reduce the FOB costs involved in the exchange of heat, which have a dominating effect on the fixed capital costs of the processes.

An antisolvent with a lower heat of mixing would significantly reduce both the fixed capital and the energy costs, since refrigerators are needed to remove the heat of mixing in the crystalliser and a heat pump or steam is used to add the heat of demixing in the antisolvent recovery section.

6. Conclusions

Calculations demonstrated that for a 1 Mton/y salt production plant with an on-site integrated steam power plant the reduction in energy costs can be 29% if antisolvent crystallisation is applied. The estimated fixed capital costs, which are dominated by the costs involved in heat
exchange, are 4 to 50 % higher for the direct antisolvent crystallisation of NaCl depending on
the used process configuration.

A disadvantage of the antisolvent crystallisation of NaCl is, that the crystals are generally
small, tend to agglomerate and are contaminated with the antisolvent. The quality of the
product can be strongly improved in a two step process. In a first step NaCl.2H₂O formed by
antisolvent crystallisation, which can be recrystallised in a purer brine in a second step. In this
two step process large and pure NaCl crystals can be produced at the expense of increased
major operating costs.

7. Acknowledgements

The authors would like to acknowledge Roger J.A.J. Hollman, Frank van der Ham, Gerard
Zijlema, Akzo Nobel and Novem BV.

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Appendix I.

PROCESS STREAM SUMMARY
Project: Antisolvent crystallisation of NaCl with diisopropylamine.

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## PROCESS STREAM SUMMARY

Project: Antisolvent crystallisation of NaCl.2H$_2$O with diisopropylamine and a recrystallisation step.

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Jongema, P. Optimization of the Fuel Consumption of an Evaporation Salt Plant with the Aid of the Exergy Concept. Sixth Int. Symp. on Salt 1983, 2, 463-469.


Summary

The Antisolvent Crystallisation of Sodium Chloride

The aim of this study is to develop an antisolvent crystallisation process based on scientific knowledge and understanding, constituting the antisolvent crystallisation and recovery steps, that provides NaCl crystals with a quality equivalent to the quality of the salt crystals produced by evaporative crystallisation at a reduced energy consumption.

The main criteria for the selection of the antisolvent are the extent to which its presence reduces the sodium chloride solubility in water, and its separability from the aqueous phase after crystallisation. With respect to this diisopropylamine, dimethylisopropylamine and 2-isopropanol are suitable antisolvents for the crystallisation of NaCl. These antisolvents are partially miscible with a brine showing Lower Critical Solution Temperatures close to room temperature. The salt can be crystallised at temperatures below the LCST in the single liquid phase area, and the antisolvent can be recovered at elevated temperatures in the double liquid phase area, where the mutual solubilities of the antisolvents and water are low.

Important to the energy household is the enthalpy of mixing of the antisolvent and water. The highest measured enthalpies of mixing for the amine-water systems were -105 J g⁻¹ (mixture) for dimethylisopropylamine-H₂O and -81 105 J g⁻¹ (mixture) for diisopropylamine-H₂O at amine concentrations of 49 wt% and 60 wt% respectively.

An experimental setup has been built for the investigation of the continuous antisolvent crystallisation. The 1 liter crystalliser can be used at temperatures of -20 to 200 °C and at pressures of up to 20 bar. To prevent corrosion Hastelloy-C has been used as the main material of construction. Solid as well as liquid samples can be taken and the crystalliser is equipped with an in-line image probe for the visualisation of the crystals inside the vessel.

The size, shape, purity and degree of agglomeration of the particles formed by continuous antisolvent crystallisation with diisopropylamine or dimethylisopropylamine has been investigated. The formed sodium chloride crystals did not satisfy the product quality requirements. The product generally consisted of small and agglomerated crystals with amine
uptakes of 40 to 630 ppm, which is too high. An amine uptake of less than 10 ppm is essential, since the amines form the explosive compound NC1, in the electrolysis of the salt.

The antisolvent uptake can be reduced significantly if first NaCl·2H2O is formed by antisolvent crystallisation which is subsequently recrystallised into NaCl in a purer brine. The purification that can be obtained by applying this recrystallisation step has been studied in batch experiments in brines containing either 0 or 5 wt% of dimethylisopropylamine. The recrystallisations carried out at various temperatures, gave 100 to 900 fold purity increases of the solid phase. The average dimethylisopropylamine concentration in the NaCl·2H2O was ca. 1000 ppm, whereas the dimethylisopropylamine concentration in the NaCl product was between 1 and 6 ppm.

The influence of the antisolvent on the kinetics of nucleation and crystal growth and the effect of the high levels of supersaturation, often encountered in antisolvent crystallisation, on mainly particle size, shape and agglomeration has been investigated. Continuous crystallisation experiments demonstrated that NaCl crystals formed by antisolvent crystallisation in the single liquid phase area are generally small and agglomerated. This results from extensive primary nucleation at the antisolvent inlet in the crystalliser. The supersaturation at the antisolvent inlet and with that the primary nucleation rate can be reduced by adding water to the antisolvent, resulting in the formation of larger less agglomerated crystals. This however, reduces the yield. An alternative is to crystallise the salt from the two liquid phase area. Due to the limited miscibility of the antisolvent and the crystalliser contents in the double liquid phase area, the supersaturation at the antisolvent inlet is lower, resulting in the formation of large single crystals. However, the yield in the double is lower than in the single liquid phase area.

To get a better understanding of how the size distribution of the formed particles is influenced by locally high supersaturations a tool has been developed. It enables the measurement of primary nucleation rates and induction times as a function of the antisolvent concentration at supersaturation levels that prevail in the area of the crystalliser antisolvent inlet. To exclude the influence of mixing on the measured kinetic data, the brine and the antisolvent are mixed rapidly in an opposite tee mixer. The mixed flows that leave the tee mixer are fed to an optical flow cell. In this cell the particle concentrations in the antisolvent-
water-salt mixture can be determined with an optical particle counter at various distances, or reaction times, from the point where the antisolvent and the salt solution are mixed.

Nucleation rate measurements were carried out at antisolvent concentrations of 40, 50 and 60 wt% and supersaturation ratios of 1.12, 1.20 and 1.32. Despite of the differences in antisolvent concentration and supersaturation the measured nucleation rates were almost identical and were in the order of $10^8 \, (m^3 \, s^{-1})$. The calculated induction times varied between 0.33 to 0.58 s and decreased at an increasing antisolvent concentration.

Guidelines have been provided for the selection of the optimal process conditions and the antisolvent for the antisolvent crystallisation of inorganic salts, that are produced by evaporative crystallisation. Based on these guidelines processes have been designed for the production of NaCl, either via the antisolvent crystallisation of NaCl or via the antisolvent crystallisation of NaCl.2H$_2$O followed by a recrystallisation step. The estimated costs and energy consumptions of these antisolvent crystallisation processes and of the traditional four effect evaporative crystallisation route have been compared. The calculations demonstrated that the reduction in energy costs can be as much as 30 %, if NaCl is crystallised directly by antisolvent crystallisation. The estimated fixed capital costs however, are 4 to 50 % higher for the direct antisolvent crystallisation of NaCl. In the two step process, including the recrystallisation of NaCl.2H$_2$O, large and pure NaCl crystals can be produced at the expense of increased operating costs.

Tjakko Zijlema
Samenvatting

De Antisolvent Kristallisatie van Natrium Chloride

Het doel van deze studie is het op basis van wetenschappelijke kennis en begrip ontwikkelen van een antisolvent kristallisatieproces voor de productie van NaCl als alternatief voor verdampingskristallisatie, bestaande uit een antisolvent kristallisatiestap en een antisolvent terugwinningstap, waarin bij een gereduceerd energieverbruik NaCl geproduceerd wordt met een kwaliteit equivalent aan die van het door middel van verdampingskristallisatie geproduceerd zout.

De hoofdpunten in de selectie van het antisolvent zijn de mate waarin het antisolvent de oplosbaarheid van het NaCl in water verlaagt en de terugwinbaarheid van het antisolvent uit de uitgeputte moederloog na kristallisatie. Gericht op deze randvoorwaarden zijn diisopropylamine, dimethylisopropylamine en 2-isopropoxyethanol geschikte antisolvents voor de kristallisatie van NaCl. Deze antisolvents zijn gedeeltelijk mengbaar met pekel. De antisolvent pekel mengsels bezitten een lager kritisch punt nabij kamertemperatuur. Het zout kan gekristalliseerd worden bij temperaturen beneden het lager kritisch punt in het één-vloeistoffasegebied, en het antisolvent kan teruggewonnen worden bij verhoogde temperaturen in het twee-vloeistoffasegebied, waar de wederzijdse oplosbaarheden van het antisolvent en water laag zijn.

Belangrijk voor de energiehuishouding is de mengenthalpie van het antisolvent en water. De hoogste gemeten mengenthalpieën voor de amine-water systemen waren -105 J g⁻¹ mengsel voor dimethylisopropylamine-H₂O en -81 J g⁻¹ mengsel voor diisopropylamine-H₂O bij amine concentraties van 49 wt% en 60 wt% respectievelijk.

Een experimentele opstelling is gebouwd voor onderzoek aan continue antisolvent kristallisatie. De 1 liter kristallisator kan bedreven worden bij temperaturen van -20 tot 200 °C en bij drukken tot 20 bar. Om corrosie te voorkomen is gebruik gemaakt van Hastelloy-C als constructiemateriaal. Zowel vaste- als vloeistofmonsters kunnen genomen worden en de kristallisator is uitgerust met een in-line visualisatie probe voor de observatie van de kristallen in het vat.
De grootte, vorm, zuiverheid en agglomeratiegraad van de deeltjes gevormd door continue antisolvent kristallisatie met diisopropylamine en dimethylisopropylamine werd bestudeerd. De gevormde NaCl kristallen voldeden niet aan de gestelde kwaliteitseisen. Het product bestond over het algemeen uit kleine en geagglomereerde kristallen met te hoge amine gehaltes van 40 tot 630 ppm. Een amine opname van minder dan 10 ppm is essentieel, aangezien de amines de explosieve verbinding NCl₁ vormen bij de electrolyse van het zout.

De antisolventopname kan significant verlaagd worden door in een eerste stap NaCl·2H₂O te vormen door antisolvent kristallisatie, hetgeen in een tweede stap in een zuiverdere pekel omgekristalliseerd kan worden in NaCl. De zuivering die door toepassing van deze omkristallisatiestap behaald kan worden werd onderzocht in batch experimenten in pekels, die 0 of 5 wt% dimethylisopropylamine bevatten. De omkristallisaties uitgevoerd bij diverse temperatures leidden tot een honderd tot negenhonderdvoudige zuiverheidstoename van de vaste fase. De gemiddelde dimethylisopropylamine concentratie in het NaCl·2H₂O was ca. 1000 ppm, terwijl de amine concentratie in het NaCl eindproduct zich tussen de 1 en 6 ppm bevond.

De invloed van het antisolvent op de kinetiek van nucleatie en kristalgroei en het effect van hoge niveau’s van oververzadiging op hoofdzakelijk deeltjesgrootte, -vorm en agglomeratie werd onderzocht. Continue kristallisatieexperimenten toonden aan dat NaCl kristallen gevormd door antisolvent kristallisatie in het één-vloeistofasegebied over het algemeen klein en geagglomereerde zijn. Dit is het gevolg van omvangrijke primaire nucleatie in de zone van de antisolvent inlaat in de kristallisator. De oververzadiging en daarmee de primaire nucleatiesnelheid in de buurt van de antisolvent inlaat, kan verlaagd worden door water toe te voegen aan het antisolvent, resulterend in de vorming van grotere en minder geagglomereerde kristallen. Deze maatregel verlaagt echter de opbrengst. Een alternatief is de uitvoering van de kristallisatie in het twee vloeistofasegebied. Als gevolg van de gedeeltelijke mengbaarheid van het antisolvent en de kristallisatorinhoud in het twee-vloeistofasegebied is de oververzadiging in buurt van de antisolvent inlaat lager, hetgeen resulteert in de vorming van grote kristallen. De opbrengst is echter lager dan in het één-vloeistofasegebied.
Ter verkrijging van een beter inzicht in hoe de grootteverdeling van de gevormde deeltjes wordt beïnvloed door locaal hoge oververzadigingen is een meetopstelling gebouwd. Met deze meetopstelling kunnen primaire nucleatiesnelheden en inductietijden gemeten worden bij oververzadigingsniveau's zoals die zich voordoen in het gebied van de kristallisator antisolvent inlaat. Om de invloed van menging op de gemeten kinetische data te minimaliseren worden de pekel en het antisolvent snel gemengd in een T-menger. De gemengde stromen die de T-menger verlaten worden aan een doorstroomde optische cel gevoed. In deze cel kunnen de deeltjesconcentraties in het antisolvent-water-zout mengsel bepaald worden met behulp van een optische deeltjesteller op verschillende afstanden, of reactietijden, vanaf het punt waar het antisolvent en de pekel gemengd worden.

Nucleatiesnelheidsmetingen werden uitgevoerd bij antisolvent concentraties van 40, 50, en 60 wt% en bij oververzadigingen van 1.12, 1.20 en 1.32. Ondanks de verschillen in antisolvent concentratie en oververzadiging waren de gemeten nucleatiesnelheden ongeveer gelijk, en in de orde $10^4 \text{ (m}^3 \text{ s}^{-1})$. De berekende inductietijden varieerden tussen 0.33 en 0.58 s en namen toe met de antisolvent concentratie.

Richtlijnen werden geformuleerd voor de selectie van de optimale procesomstandigheden en het antisolvent voor de antisolvent kristallisatie van anorganische zouten, die geproduceerd worden door verdampingskristallisatie. Op basis van deze richtlijnen zijn processen ontworpen voor de productie van NaCl via de directe antisolvent kristallisatie van NaCl en via de antisolvent kristallisatie van NaCl.2H_2O gevolgd door een omkristallisatiestap. De geschatte kosten en energieconsumpties van dezeantisolvent kristallisatiewapen en van de traditionele vier effect verdampingskristallisatie route zijn met elkaar vergeleken. De berekeningen toonden aan, dat voor de directe antisolvent kristallisatie van NaCl de reductie in energiekosten circa 30% kan bedragen. De geschatte investeringskosten liggen echter 4 tot 50% hoger voor de directe antisolvent kristallisatie van NaCl. In de route met omkristallisatie kunnen grote zuivere kristallen geproduceerd worden tegen verhooghde productiekosten.

Tjacco Zijlema
Dankwoord

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