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Quaternary Liquid/Liquid Equilibria of Sodium Sulfate, Sodium Sulfite and Water with Two Solvents: Acetone and 2-Propanol

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A.L. Schiozer
(M.S. Thesis)

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Adriana Lopes Schiozer

Abstract

Quaternary Liquid/Liquid Equilibria of Sodium Sulfate, Sodium Sulfite, and Water with Two Solvents: Acetone and 2-Propanol

by

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Aqueous solutions of sodium sulfate and sodium sulfite are produced from sodium carbonate in flue-gas scrubbers. Recovery of these salts often requires multi-effect evaporators; however, a new energy-efficient unit operation called extractive crystallization has been shown to have reduced energy costs. In this process, an organic solvent is added to the aqueous salt solution to precipitate salt. Acetone is a suitable solvent for this process, better than 2-propanol.

Liquid/liquid/solid equilibria for ternary systems containing a salt, water, and an organic solvent were experimentally determined. The systems investigated were sodium sulfite/water/acetone and sodium sulfite/water/2-propanol. Experiments were conducted at salt saturation covering a temperature range between the lower consolute temperature and 48.6°C.

In the attempt to improve the extractive crystallization process for recovery of sodium sulfate from flue-gas scrubbers, attention was given to a feed containing a mixture of sodium sulfite and sodium sulfate.

Liquid-liquid equilibria for quaternary systems containing two salts, water, and an organic solvent were experimentally determined at 35°C. The systems investigated were sodium sulfate/sodium sulfite/water/acetone and sodium sulfate/sodium sulfite/water/2-propanol. The systems were studied at three salt ratios. For each salt ratio, experiments were conducted starting at saturation, water was then added until the one-phase region was reached.

Mixtures of the two salts proved to have a small disadvantage relative to the 100 % sulfate feed process. Therefore, a sulfate-based extractive crystallization process is recommended.

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CHAPTER 1: INTRODUCTION

Several chemical industries produce aqueous salt solutions as wastewater streams. In most cases, it is of interest to treat such streams either before discharge, or for reuse somewhere else in the plant. Salts can be recovered from aqueous solutions by crystallization, and if their solubility in water varies sufficiently with temperature, crystallization can be obtained by a simple temperature change. On the other hand, if the solubility of a salt is relatively insensitive to temperature, precipitation can result only from water evaporation.

Evaporation is a basic separation technique that can easily be achieved by boiling an aqueous solution. However, the high heat of vaporization of water makes such a process very energy-intensive and, therefore, unattractive. For this reason, it is common practice in industry to use multi-effect evaporators which reduce energy consumption.

Energy costs can be reduced further by addition of a hydrophilic solvent. Such a process is called extractive crystallization, a process based on liquid-liquid equilibrium. In extractive crystallization a dry solvent is utilized to extract water from a saturated aqueous salt solution, causing the salt to crystallize. The wet solvent, in turn, can be regenerated by a temperature swing to a temperature where the water and the organic solvent are not miscible, splitting into two relatively pure phases.

When the organic solvent and water are completely miscible at ambient temperature and atmospheric pressure, one component can be stripped out using distillation (Brenner, 1992). Distillation, though, is a very energy-intensive process which makes the overall process unattractive when compared to a process using triple-effect evaporators.

Instead of distillation, an alternative option, which was proven to be very attractive, is the use of a drying agent to treat the organic phase by extracting the water into an aqueous salt solution.

In industry, flue gas that contains sulfur dioxide and an excess of oxygen is often treated with sodium carbonate solution in a gas scrubber producing sodium sulfite. Sodium sulfite, though, oxidizes to sodium sulfate in the presence of oxygen, resulting in a mixture of both salts in an aqueous wastewater stream.

Jaecksch (1993) assumed that the oxidation of the sulfite leaving the gas scrubber was complete, yielding only sodium sulfate as the main product. However, if the oxidation is considered incomplete, the waste stream will contain both salts.

This work develops a process to treat such aqueous wastewater stream containing the two salts. Sodium carbonate will be used as the drying agent since it is a very hydrophilic salt. The process will result in an aqueous sodium carbonate solution that will be used in the scrubber to treat the flue gas. The process will also recover the salts initially in the wastewater stream.

CHAPTER 2: LITERATURE REVIEW

Due to conversion of sodium carbonate to sodium sulfite and sodium sulfate in flue-gas scrubbing processes, industrial wastewater commonly contains considerable amounts of these salts.

The solubility characteristics of sodium sulfate and sodium sulfite in water are shown in Fig. 2.1. Sodium sulfate and sulfite form particular crystal structures at lower temperatures. Sodium sulfate forms decahydrate crystals below 32.4°C, whereas sodium sulfite forms heptahydrate crystals below 33.0°C (Seidell, 1965). Above those transition temperatures, the solubilities of both salts in water are approximately constant and anhydrous crystal structures are formed.

In this work, anhydrous salt crystals are chosen to be the final product, and since the salt solubilities are not strong functions of the temperature, extractive crystallization can be considered.

Extractive crystallization has been suggested in previous works for several water/solvent/salt ternary systems. Weingaertner (1988) studied the extractive crystallization of sodium carbonate with 1-butanol and with 1-propanol and that of sodium chloride with di-isopropyl amine (DIPA), where he obtained lower energy costs with respect to a triple-effect evaporation process. Ting (1991) proved that extractive crystallization of sodium chloride and that of sodium sulfate with N,N-diethyl-methyl-amine (DEMA) is a feasible alternative process for salt production and offers considerable energy savings when compared to triple-effect evaporation plants.

In the process developed by Ting (1991) to produce sodium sulfate, DEMA could extract water from the salt solution near ambient temperature, causing decahydrate crystals to precipitate. In this case, DEMA was regenerated simply by heating the organic phase to a temperature where DEMA and water are no longer miscible with each other.

Because amines are toxic and unpleasant to work with, Brenner (1992) investigated some low-molecular weight alcohols as solvents to extract sodium sulfate from wastewater streams. The alcohols studied, 2-propanol, 1-propanol, and t-butanol, are totally miscible with water at any temperature above 0°C, and for this reason, it was found upon using those solvents that the process could not operate with solvent regeneration by phase-splitting at a different temperature, as shown in previous studies. Therefore, distillation was used to regenerate the solvents. However, because distillation is very energy-intensive, this process showed no advantage over triple-effect evaporation.

In both Ting and Brenner's works, sodium sulfate was crystallized as decahydrate crystals as the first step. Since the anhydrous form was the desired one, the salt was melted before entering the filter, which was the last stage of the process.

In a precursor to the present study, Jaecksch (1993) showed that acetone, 2-propanol, and t-butanol can extract water and precipitate anhydrous sodium sulfate at temperatures in excess of 32.4°C. Her process was isothermal and the solvent was regenerated by bringing the organic phase into contact with a drying agent to separate water from the organic solvent. Her results showed that in terms of energy consumption alone, extractive crystallization of sodium sulfate with any one of the three solvents can compete with triple-effect evaporation. Even for the solvent with the highest energy requirement, there was a 50% savings over triple-effect evaporation.

The choice of a solvent in extractive crystallization is very important. It is desirable for the solvent to have a high capacity for water. Moreover, the solubility of the salt in the solvent should be small, so that little salt is extracted with water. Salt is preferably recovered through the bottom of the crystallizer, and for that, the solvent ought to have a density lower than that of water. The solvent cannot react with the components in the process. The toxicity and the stability of the solvent are also characteristics of interest as it will be part of a continuous process.

SOLUBILITY CURVES FOR SODIUM SULFITE

AND SULFATE IN WATER

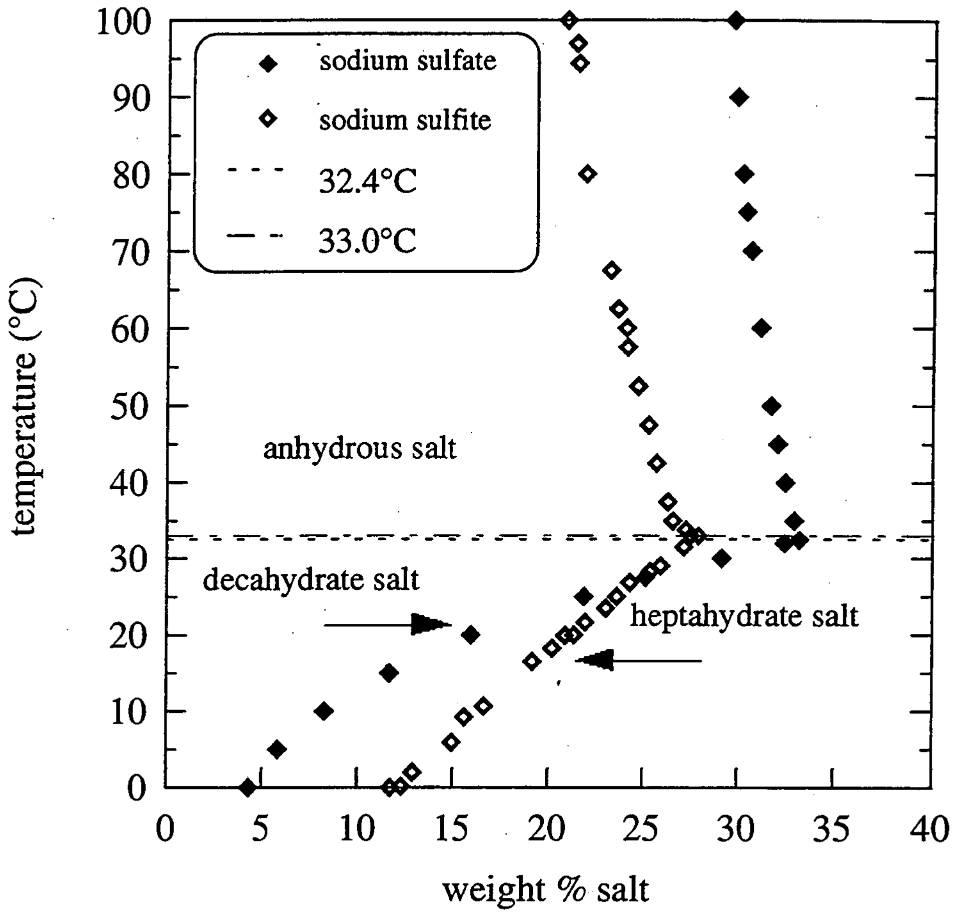


Fig. 2.1 Solubilities of Sodium Sulfate and Sodium Sulfite in Water (Seidell, 1965).

Selection of the solvents from the alcohols and ketones was studied by Brenner (1992) and Jaecksch (1993). Although amines exhibit very desirable characteristics as solvents to extract water and to be regenerated as part of an extractive-crystallization process, they are toxic, unpleasant to work with because of the smell, and environmentally hazardous.

The alcohols and ketones studied have densities as well as boiling points below those of water. Acetone is the most hydrophilic among the solvents tested, followed by 2-propanol, and lastly by t-butanol. Acetone, according to Jaecksch (1993), proved to have the greatest capacity to absorb water at temperatures above 30°C. However, it also proved to be the solvent most difficult to regenerate. Therefore, in terms of the extractive crystallization step only, without any other considerations, acetone was the solvent of choice in an extractive crystallization process to recover sodium sulfate.

In this work it was decided to study acetone and 2-propanol. 2-Propanol, together with t-butanol, had lower overall energy requirements than acetone. On the other hand, equipment size and its relation to cost must also be considered. In the t-butanol process, 16 times more solvent is recycled through the process compared to using acetone. For 2-propanol, the amount of solvent used is only 4 times larger. From the points highlighted here it was decided that 2-propanol and acetone would be the two solvents with the most potential advantage over triple-effect evaporation.

CHAPTER 3 : EXPERIMENTAL WORK

3.1 Liquid/Liquid and Liquid/Liquid/Solid Equilibria

Sodium sulfite and sodium sulfate are found in wastewater streams leaving processes wherein sulfur dioxide is removed from a flue gas. The extractive crystallization of sulfite and sulfate with a solvent can be an attractive alternative to evaporation because it reduces costs. Therefore, measurements were made to determine liquid-liquid equilibria for the systems acetone/water/sodium sulfite/sodium sulfate and 2-propanol/water/sodium sulfite/sodium sulfate at a temperature suitable for an isothermal extractive crystallization process. Experiments were performed under subsaturation conditions relative to the salts for both solvents.

Measurements were also made to determine liquid/liquid/solid equilibria for the salt-saturated system acetone/water/sodium sulfite as a function of temperature.

3.1.1 Experimental Apparatus

The apparatus used in all experiments is shown in Fig. 3.1. The experiments were conducted in a flat-bottomed glass test tube 6 cm in diameter, tightly closed with a neoprene stopper and provided with constant stirring. The tube was immersed in a constant-temperature bath that was appropriately controlled. The temperature of the bath could easily be altered by a controller that regulated both a heater and a cooler.

Samples were withdrawn from the solution inside the test tube using small diameter glass tubes, with the help of a three-way valve connected to an air line that produced a difference in pressure. During experiments, the valve was connected to a nitrogen cylinder as well as to a trap to ensure an over pressure of a few centimeters of water. Nitrogen was used as an inert atmosphere to avoid oxidation of the sodium sulfite.

In Fig. 3.1, the numbers refer to the following:

1. 3-gallon water bath
2. Impeller
3. Cooling bath/circulator (Forma-Scientific 2160)
4. Immersion heater (500-watt)
5. Temperature controller (Hart-Scientific 3002 PID)
6. Quartz thermometer (Hewlett-Packard 2804A)
7. Three-way valve connected to a nitrogen cylinder
8. Sampling tubes (1.6 mm O.D.)
9. Polypropylene cover
10. Sample cylinder (34 cm x 6 cm)
11. Organic phase
12. Aqueous phase
13. Solid salt
14. Magnetic stirrer and stir bar
15. Insulation
16. Water level

3.1.2 Experimental Procedure

3.1.2.1 Ternary System

Experiments were performed using the apparatus described in Section 3.1.1 where each experiment reached thermal and chemical equilibrium.

The first set of experiments conducted was with the quaternary system sodium sulfate/sodium sulfite/water/2-propanol. The experiments were run at saturation

EXPERIMENTAL APPARATUS

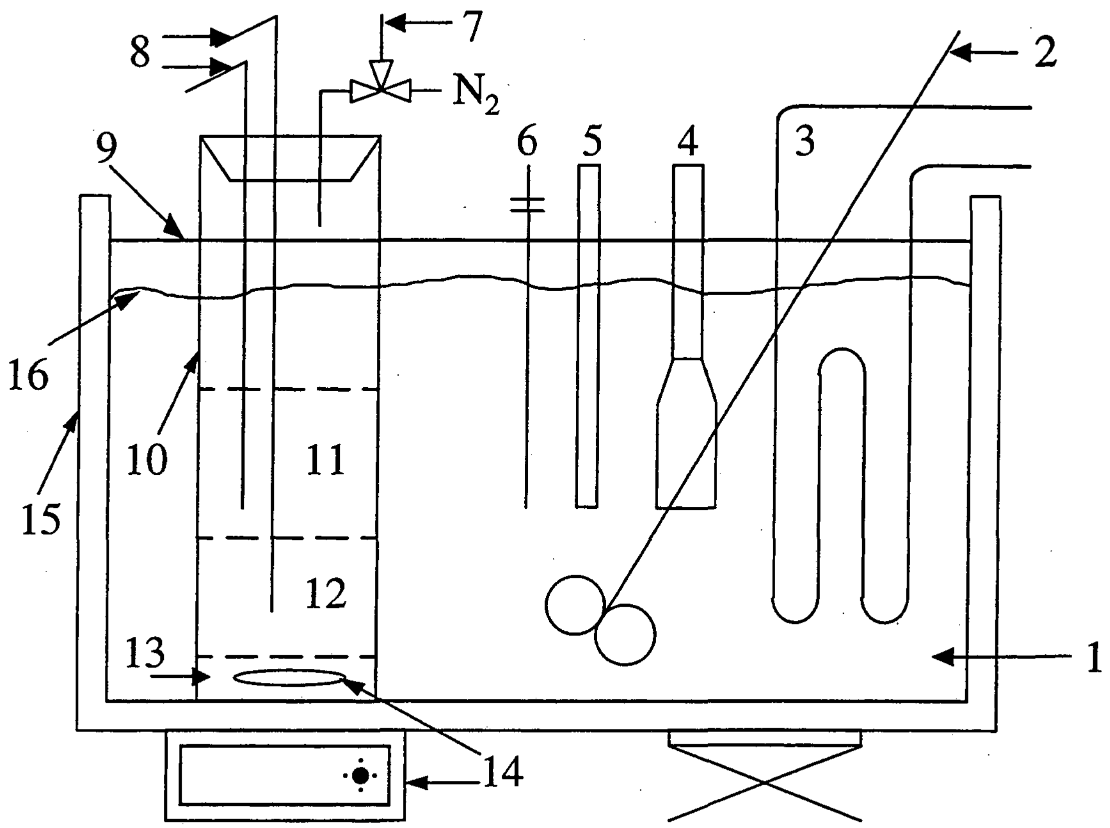


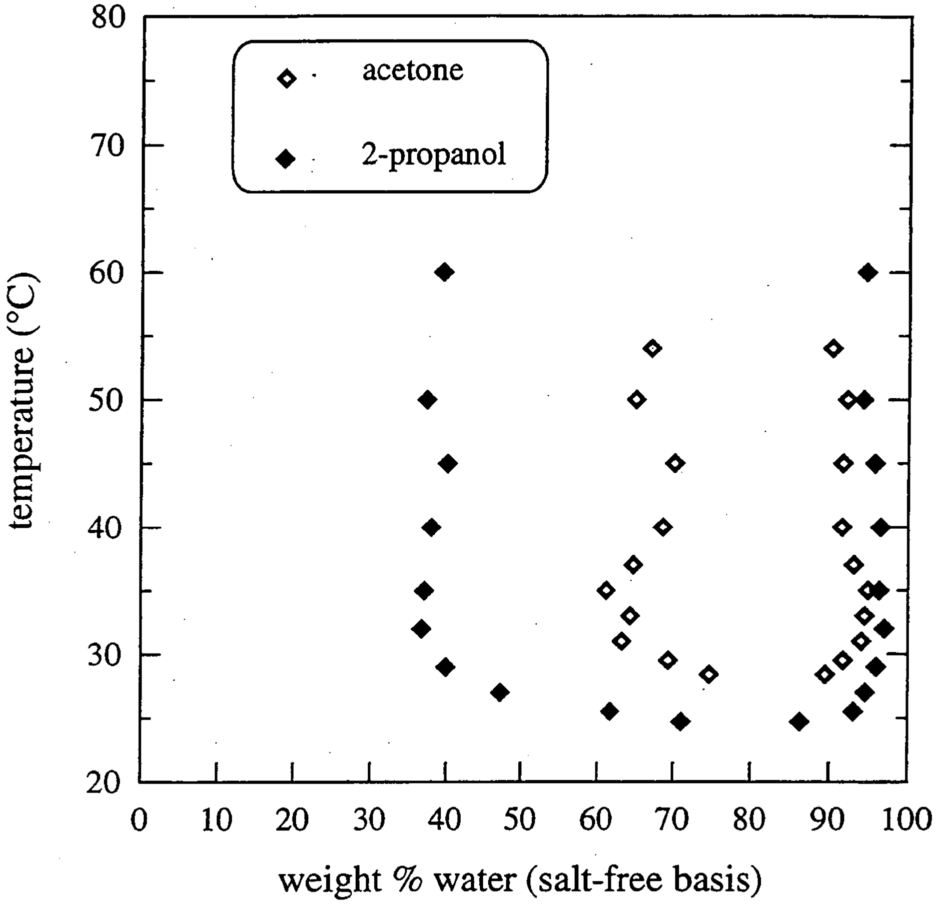
Fig. 3.1 Schematic Diagram of Experimental Apparatus.

covering a range of temperatures. The results for these experiments though, were not reproducible, and it was concluded that the main reason for the failure was the formation of metastable regions at certain temperatures due to the presence of sulfite crystals.

Because of the problems that occurred with the quaternary system, it was decided that the ternary system containing sulfite should be reconsidered. Ternary systems with sodium sulfite and three solvents had already been studied by Jaecksch (1993), and the results were quite unusual. The coexistence curves for the sodium sulfite with acetone, and 2-propanol are shown in Fig. 3.2. Instead of the characteristic U-shaped curve, Jaecksch (1993) detected an indentation on both sides of the curve. Before reaching any final conclusion from of the bizarre shape that seemed to be a characteristic of sulfite systems, it was decided that those experiments should be repeated.

According to Jaecksch (1993), acetone proved to be the best solvent, followed by 2-propanol. Acetone showed the greatest capacity to absorb water at temperatures above 30°C, and also presented the greatest potential as an economic method for removing the absorbed water. For this reason, it was decided to investigate whether the system sodium sulfite/water/acetone was reproducible. Finally the strange and unusual shape of the coexistence curve was repeated and the experiment was proved to be reproducible under the same conditions of the experiments performed previously by Jaecksch (1993), Brenner (1992), and Ting (1991).

Some authors, *e.g.*, Lewis (1923) and Rivett (1924), studied the system sodium sulfite/sodium sulfate/water and found irregularities for the systems containing sodium sulfite. They claimed that the results were quite satisfactory and consistent at all temperatures at which the solid phase in equilibrium with the liquid phase consisted of hydrated crystals, but in equilibria where anhydrous salt was formed, the most unexpected irregularities appeared; *i.e.*, points were obtained with no simple relation between the solubility of sulfite and the amount of sulfate present. Such irregularities, however, were no longer apparent when excess anhydrous sodium sulfite was used instead of hydrated crystals. Anhydrous sodium sulfite was added, with sodium sulfate, to warmed water, and the complex raised to 70 or 80°C before cooling to a suitable lower temperature. After


COEXISTENCE CURVES

Saturated Equilibrium Data for Na_2SO_3

Figure 3.2 Coexistence Curves for Aqueous Na_2SO_3 Systems (Jaecksch, 1993).

approximately one hour, the mixture was seeded with anhydrous sodium sulfite.

Further investigation was done of the ternary system sulfite/sulfate/water at temperatures at which only the anhydrous solid phases could exist (Rivett *et al*, 1924). For satisfactory results, since it was necessary to form the solid at the temperature of the experiment, it was decided to form the solids from homogeneous solutions. In such a system, this meant that water should be evaporated from unsaturated solutions of suitably chosen concentrations.

The application of such an idea to extractive crystallization is simple because the addition of the solvent to a subsaturated solution causes salt to crystallize from the solution. Subsaturated aqueous salt solutions must be formed with a concentration relatively close to saturation to obtain a solid phase at the temperature of the experiment; when the solvent is added, considerable amounts of salt should crystallize out of the solution.

The ternary system containing sulfite, water, and acetone was again studied using the technique described above. For the system containing sulfite, water, and 2-propanol, only a few points close to the perturbation were repeated. Water and enough sodium sulfite were mixed to form a subsaturated solution close to saturation. This was achieved by the addition of water to the sampling tube containing a certain amount of salt until a clear, subsaturated solution was obtained. Enough water was added, such that no solid salt could be seen in the bottom of the flask. Then an appropriate volume of solvent was added to force some salt to crystallize out of solution, obtaining a saturated ternary solution. Such a procedure was necessary to ensure that if the experiment was conducted in a temperature above 33°C, all the crystals formed would be anhydrous, with no trace of heptahydrate crystals. It was required always to have excess solid salt in the stirred experimental flask to ensure saturation.

The sampling flask was kept properly closed with a neoprene stopper during the experiment, and under a nitrogen atmosphere to prevent oxidation of sodium sulfite. The solution was stirred for at least 4 hours to ensure that equilibrium was reached, then the stirrer was turned off and the system was left in the constant temperature bath until the solid had all settled to the bottom of the sampling tube, and two well-defined phases of liquid were observed.

Samples were taken from each liquid phase, and kept in Fischerbrand screw-cap vials of different sizes. Vial sizes varied accordingly to the volume required for each technique employed. The vials were weighed on a Mettler H10 analytical balance before and after samples were taken. Samples were taken using two small-diameter glass tubes, each one located to withdraw one of the phases. A three-way valve was also attached to the sampling flask stopper. During the actual experiments the valve was connected to a nitrogen cylinder and to a trap keeping the sampling flask at atmosphere pressure. By the time samples were removed, the three-way valve was disconnected from the nitrogen cylinder and from the trap, and attached to an air supply. With one of the paths of the valve connected to the air supply, the other was then closed, creating a pressure gradient sufficient to remove the samples from the flask. The glass tubes were first flushed with the respective solution to reach the temperature of the experiment, preventing potential crystallization inside the tubes. After the flushing, the sample vials were filled with solution from each of the phases in the sampling flask. Extra samples were always taken in case any of the analyses gave erratic results.

Each set of experiments was repeated for the sodium sulfite/water/acetone ternary system at several temperatures. The range included the temperature where only one phase exists, the lower consolute temperature, and extended to a temperature far above the transition point (but not too close to the temperature that acetone boils, 56°C). In the case of the ternary system containing 2-propanol, only three temperatures were repeated. Such temperatures were those close to the perturbation, and the results obtained for the other temperatures were assumed to be correct.

Results for both systems will be discussed in Chapter 4.

3.1.2.2 Quaternary Systems

The biggest concern in working with quaternary systems was the instability of the sulfite crystals. To overcome that problem it was decided to perform the experiments under subsaturated conditions, near to saturation as much as possible at the beginning of the experiment, such that a complete two-phase envelope would be obtained. In this way, the first samples had a concentration very close to saturation. Additional water was then added and more samples were taken until the organic phase had disappeared and the system had only an aqueous phase.

Two quaternary systems were examined: sodium sulfate/sodium sulfite/water/2-propanol and sodium sulfate/sodium sulfite/water/acetone, both at a constant temperature of 35°C, that was maintained constant to within 0.02°C. The complexes, treated as indicated below, were stirred in closed tubes in the constant-temperature bath for varying periods of time, and the sampling solution was kept under a nitrogen atmosphere. The samples were taken from each phase using the same procedure discussed for the ternary systems.

For the quaternary systems, water, sodium sulfite, and sodium sulfate were brought together in the sampling tube to form a subsaturated solution close to saturation. Enough solvent was then added to the mixture such that salt crystallized out of the solution and an organic phase formed large enough to take several samples. At that point, the solution was stirred for enough time to get all the fresh, anhydrous salt crystals out of solution. Water was then added little by little until the solution became clear; it was easy to identify the two liquid phases in the absence of the solid phase. Such a procedure ensured that the total amount of salt dissolved in solution was derived from anhydrous crystals at 35°C. This procedure, although easy in concept, was time-consuming since the salt redissolves very slowly. Therefore, it was important to let the solution reach complete equilibrium before adding new portions of water, otherwise the solution would be more dilute than expected. Water should then be added until a subsaturated solution, very close to saturation was reached. This start-point was considered to be saturated, although it was saturated only with the less soluble salt for that solution composition.

The process resulting from this research was anticipated to be isothermal. The temperature chosen should be as close to ambient temperature as possible for energy purposes, and at the same time, as far from the lower consolute temperature as necessary to stay away from substantial composition changes due to temperature fluctuations. Since the hydrate-transition temperature for both salts is below 33°C, and above this temperature all the sodium sulfite and sodium sulfate in solution are derived from anhydrous materials, it was thought to be appropriate to choose 35°C as the temperature of the process. So all subsaturated experiments were held at this temperature.

The apparatus of Fig. 3.1 was also used for the quaternary systems, so the technique used to take samples was the same except that in this case, extra samples were withdrawn to detect the amount of sulfite present in the phases. The sulfite determination was performed with iodimetric titrations.

For the systems containing 2-propanol, three samples were withdrawn from the sampling tube and run directly into an excess of 0.5-normal iodine to detect the amount of sulfite present. They were then analyzed and averaged. However, when acetone was used as the organic solvent, this procedure could not be used since acetone reacts readily with iodine according to Reaction 3.1.

$$CH_3CH_3CO + I_2 \leftrightarrow CH_3CH_2ICO + H^+ + I^- \qquad 3.1$$

To overcome this problem, acetone was evaporated under reduced pressure with a continuous flow of nitrogen into the solution to avoid any possible oxidation of the sulfite. The samples were transferred into Erlenmeyer flasks where they were agitated and kept at a temperature of about 35°C. This procedure was followed with all samples containing acetone that were to be titrated for iodine.

3.1.3 Chemicals

The solvents used for the experiments were Fisher-Scientific spectranalyzed acetone (99.7% pure) and 2-propanol (99.9% pure). Distilled water was used in all experiments.

In the gas chromatograph, the standard used in the aqueous samples was Aldrich anhydrous ethylene glycol (99+% pure). The salts used were Fisher-Scientific anhydrous sodium sulfite and J.T. Baker analyzed anhydrous sodium sulfate.

For the dilutions in the atomic absorption, distilled water was purified with a Barnstead Nanopure ultrapure water system.

In the iodimetric titrations, Mallinckrodt resublimed iodine and Fisher-Scientific iodate-free potassium iodide were used. The thiosulfate solution was prepared with Mallinckrodt sodium thiosulfate, and anhydrous sodium carbonate. The thiosulfate standardization was done with Mallinckrodt potassium iodate, and Fisher-Scientific potassium iodide, and sulfuric acid. Fisher-Scientific hydrochloric acid was used to acidify the samples to be titrated.

3.2 Analytical Techniques for Ternary Systems

3.2.1 Aqueous phase

After samples were taken from the aqueous phase, they were weighed and then analyzed for the solvent and salt; the respective quantities were expressed as mole or weight percent. The water content was obtained by difference. The analysis for the water content was also done with a Karl Fisher moisture titrator for a few samples for comparison with the difference method. Since they were in very good agreement, it was chosen to use the former method.

The solvent content was obtained by gas chromatography using an internal standard. The salt content was determined by drying the samples in the oven.

An examination of the solids was unnecessary for the present purpose since it has been known that, above 33°C, only anhydrous sodium sulfite precipitates from solution.

3.2.1.1 Gas Chromatograph

A Hewlett-Packard 5890A gas chromatograph with a thermal conductivity detector (TCD) was used to detect the amount of solvent in each sample. Gas chromatography is a method of separation that uses an unreactive carrier gas as the mobile phase to drive the mixture through the column. The inner walls of the column are coated with a nonvolatile liquid acting as the stationary phase.

Since the components of the mixture interact to different extents with the stationary phase, they move along the column at different rates, and separation occurs. As they exit the column, the components pass through a detector that signals their presence.

The column used was J & W Scientific water compatible DB-624. As the inert carrier gas, helium was chosen since it is a gas with very high thermal conductivity. When using a capillary column, HP 5890A detectors that are designed for compatibility with packed columns, generally require higher carrier gas flow rates, therefore, a separate make-up gas system is provided to bring total flow into a given detector up to the optimal rate required to insure optimal detector sensitivity. In this case, helium was also used as the make-up gas. An Alltech oxygen trap was required in the helium line to remove oxygen and trace impurities. As further protection for solid impurities, a Molecular-Sieve 5A chemical filter was installed.

The gas chromatograph operating conditions are summarized in Appendix A. The gas chromatograph was connected to a Hewlett-Packard 3392A integrator that detected and analyzed the sample signal, converting that to area percent. A calibration curve was required to convert area percent to weight percent of solvent. Calibration factors had been obtained and plotted against area percent of solvent. The curves are very near to straight lines.

For aqueous-phase samples, an internal standard was added to the sample since the solvent peak was very small and difficult to compare to the water peak with enough precision. Ethylene glycol was chosen as the internal standard since it does not cause phase-splitting of the sample at ambient temperature; moreover, it has a retention time different from those of water and the solvent.

It was decided to calibrate the internal standard to the solvent peak because it would be inaccurate to compare it with the water peak since the salts studied form hydrated crystals that precipitate at ambient temperature, changing the water content of the liquid sample.

The calibration curve was obtained by preparing standards containing known amounts of solvent and ethylene glycol (e.g.). Calibration factors (CF) were then calculated using Equation 3.2.

$$\text{CF} = \frac{\text{weight solvent (g)}}{\text{weight e.g. (g)}} \times \frac{\text{area \% e.g}}{\text{area \% solvent}} \qquad 3.2$$

Where e.g. stands for ethylene glycol.

The calibration factor was plotted against area percent, and with the calibration factor and weight of ethylene glycol known, the weight of solvent relative to the total weight of the sample could be determined for each sample by rearranging Equation 3.2.

All the samples were injected in the gas chromatograph using a Hamilton 1 ml syringe 7001-N. The size of the aqueous samples was around 0.5 ml, bigger than that for organic samples to compensate for the small peaks of the solvent and the internal standard.

The ethylene glycol peak was about the same size as the solvent peak. For that reason, an initial estimate of the solvent content in the aqueous phase was obtained by running the sample before it was weighed. With the result, an appropriate amount of ethylene glycol was added to the sample. This procedure increased the accuracy of the analysis. Because the aqueous samples were very concentrated, part of the routine procedure was to wash the syringe with hot water after injections to prevent them from becoming clogged.

3.2.1.2 Oven Drying

Because of the large amount of salt in the aqueous phase, evaporation was used to analyze its contents. Samples were introduced into the oven at a temperature between 80 and 85°C. Although acetone has a low boiling point, it was not necessary to stay below that temperature since the solvent content was very small compared to the water and salt contents.

More than one sample per experiment was taken to be dried in the oven. After two days, they were weighed; knowing the initial tare weight, it was possible to obtain the salt content relative to the total sample. The samples were then brought back to the oven and left for two more days to see if any change in weight occurred; usually that was negligible.

The salt contents of the samples were averaged for each set of experiments and the results were very consistent.

3.2.2 Organic Phase

After samples were taken from the organic phase, they were weighed and then analyzed for the solvent and salt, obtaining their respective amounts either in weight or mole percent. The water content was obtained by difference. The solvent content was obtained by gas chromatography whereas the salt content was determined by atomic-absorption spectroscopy.

3.2.2.1 Gas Chromatograph

Gas chromatography was used for measuring the amount of solvent in the organic phase. The system operating parameters are equivalent to those for the aqueous-phase analysis.

In the organic phase, the amounts of water and solvent are not so different from each other as to require the use of an internal standard and, as a result, the peaks could be compared directly. For this procedure the calibration factor had to be redefined, and it was found that a simple relationship between the area percent obtained from the integrator and the weight percent would provide a better curve, closer to a straight line. The calibration factor for the organic phase is defined as:

$$\text{CF} = \frac{\text{weight solvent (\%)}}{\text{area solvent (\%)}} \qquad 3.3$$

The samples were injected in the gas chromatograph using the same type of syringe described before, but with injections of only 0.2 ml for this case. Samples were run at least 5 times or until a stable answer from the integrator was obtained.

3.2.2.2 Atomic Absorption

Atomic absorption spectroscopy was the analytical technique used to detect the amount of salt in the aqueous phase. Atomic absorption spectroscopy is a standard technique that involves exciting the electrons of the element in question and measuring the emitted radiation as the atom relaxes to its ground state. Liquid samples are aspirated into an acetylene/air flame that vaporizes them, then excites the electrons. The flame temperature is about 2300°C, sufficiently high for the determination of sodium salts.

A Perkin-Elmer 2280 atomic absorption spectrophotometer was used for this analysis. A Perkin-Elmer Intensitron™ sodium lamp was used to detect the amount of sodium present in the sample. The wavelength used for sodium is 589 nm. The operating conditions used in this system are summarized in Appendix A.

Quantitative measurements in atomic absorption are based on Beer's law, which states that absorbance is proportional to concentration. The law, however, applies only for very small concentrations. For this reason, the samples were all diluted to fall within a suitable concentration.

Upon calibration it was found that, for sodium, Beer's law is valid only up to 1 mg of salt per liter of solution. Therefore the samples were diluted to a concentration below that value.

A standard stock solution was prepared by dissolving 2.542 g of NaCl in one liter of deionized distilled water, that is the same as having 1 g of Na diluted in 1 liter of water. Two standards were prepared from this solution; 0.5 and 1.0 mg sodium per liter of solution. To prevent ionization interferences, 1 g of KCl was added to each standard solution.

The samples to be diluted and analyzed by atomic absorption spectroscopy contain solvents, and for this reason, standard solutions were tested containing traces of the solvent to be used in the experiments and the results compared to others not containing solvents. Because the results were the same, it was decided to neglect the amount of solvent in the samples.

The samples were diluted in class-A volumetric flasks previously cleaned with dilute sulfuric acid solution and washed with abundant distilled water. After the dilution, the samples were transferred to small plastic bottles and then analyzed in the spectrophotometer.

The result of the analysis is expressed as the absorbance, which can be readily translated into units of concentration of sodium using the calibration curve prepared at the beginning of each set of samples to be analyzed. The concentrations were multiplied by the volume of the total diluted sample to give the weight of sodium in the original sample, and subsequently the weight of the salt.

3.3 Analytical Techniques for Quaternary Systems

3.3.1 Aqueous Phase

Samples were taken from the aqueous phase and analyzed for the solvent, for the total amount of salt, and for the sulfite present. The sulfate was obtained by difference as was the amount of water.

The amount of solvent was again obtained using an internal standard in a gas chromatograph. Some quantities withdrawn were run into an excess of a 0.5-normal solution of iodine in which the sulfite was rapidly oxidized to sulfate. The excess iodine was titrated with deci-normal thiosulfate, and the percentage of sulfite deduced. Again, for the systems containing acetone, it was necessary to evaporate the solvent before the actual titrations, as mentioned earlier. A separate sample was analyzed by atomic absorption for sodium. From the two measurements the percentage of sodium sulfate present in each phase was readily calculated.

3.3.1.1 Gas Chromatograph

Gas chromatography was the technique chosen to determine the amount of solvent in the aqueous phase when working with a quaternary system. The system and operating conditions are the same as those outlined for ternary systems (Section 3.2.1.1).

3.3.1.2 Atomic Absorption

Atomic-absorption spectroscopy was the analytical technique used to determine the total amount of salt in the aqueous phase. Evaporation was used for the ternary system; however, a more accurate procedure was necessary for quaternary systems, *i.e.*, a technique that would guarantee that sulfite would not oxidize to sulfate, since now both salts are present, and the ratio between them is very important.

The atomic-absorption technique is equivalent to the procedure discussed in Section 3.2.2.2 for the organic phase. However, in this case, samples were diluted many more times since the aqueous phase was much more concentrated in salt.

3.3.1.3 Iodimetric Titration

There are several methods to quantify the amount of sulfite ions present in the organic and aqueous samples (Clesceri *et al*, 1988; and Jeffery *et al*, 1989). Iodimetric titration was the technique chosen for this work and it is based upon Reactions 3.4 and 3.5 (Jeffery *et al*, 1989).

$$SO_3^{2-} + I_3^- + H_2O \rightarrow SO_4^{2-} + 2\ H^+ + 3\ I^- \qquad 3.4$$

$$HSO_3^{2-} + I_3^- + H_2O \rightarrow SO_4^{2-} + 3\ H^+ + 3\ I^- \qquad 3.5$$

Analyses were made immediately after samples were taken to minimize sulfite oxidation. Excess of standard 0.05M iodine was diluted with several volumes of water and acidified with hydrochloric acid. The volume of the sample was measured with calibrated pipet and added slowly with the jet close to the surface of the iodine solution. The excess of iodine was then titrated with standard 0.1M sodium thiosulfate solution.

In addition to a low solubility (only 0.335 g of iodine dissolves in 1 liter of water at 25°C), aqueous solutions of iodine have an appreciable vapor pressure of iodine, and therefore decrease slightly in concentration because of volatilization when handled. Both difficulties are overcome by adding to the iodine an aqueous solution of potassium iodide: the more concentrated the iodide solution, the greater the solubility of the iodine. The increase in the solubility is due to the formation of the tri-iodide ion. The resulting solution has a much lower vapor pressure than a solution of iodine in pure water, although it is still considerable. Precautions must be taken to keep vessels containing iodine closed and in the dark, except during the actual titrations.

Resublimed iodine and iodate-free potassium iodide were employed for the preparation of standard iodine solutions. The solution was standardized with sodium thiosulfate solution that had recently been standardized against potassium iodate.

The standardization is done by adding standardized thiosulfate solution to the iodine solution. Reaction 3.6 occurs rapidly under acid conditions.

$$2\ S_2O_3^{2-} + I_3^- \rightarrow S_4O_6^{2-} + 3\ I^- \qquad 3.6$$

The colorless intermediate $S_2O_3I^-$ forms by a rapid reversible reaction, as follows:

$$S_2O_3^{2-} + I_3^- \leftrightarrow S_2O_3I^- + 2\ I^- \qquad 3.7$$

The intermediate reacts with thiosulfate ion to provide the main course of the overall reaction:

$$S_2O_3I^- + S_2O_3^{2-} \rightarrow S_4O_6^{2-} + I^- \qquad 3.8$$

The intermediate also reacts with iodide ion:

$$2\ S_2O_3I^- + I^- \rightarrow S_4O_6^{2-} + I_3^- \qquad 3.9$$

Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) is readily obtainable in a state of high purity, but there is always some uncertainty as to the exact water content because of the efflorescent nature of the salt. The substance is therefore unsuitable as a primary standard.

Solutions prepared with conductivity water are perfectly stable. However, ordinary distilled water usually contains an excess of carbon dioxide that may cause slow decomposition with the formation of sulfur in Reaction 3.10.

$$S_2O_3^{2-} + H^+ \rightarrow HSO_3^- + S \qquad 3.10$$

Decomposition may also be caused by bacterial action. For these reasons, a small amount of sodium carbonate is employed to ensure a high pH.

The standardization of sodium thiosulfate was done with potassium iodate. Potassium iodate reacts with potassium iodide in acid solution to liberate iodine, this is illustrated in Equation 3.11.

$$IO_3^- + 8\ I^- + 6\ H^+ \rightarrow 3\ I_3^- + 3\ H_2O \qquad 3.11$$

3.3.2 Organic Phase

Samples were taken from the organic phase and analyzed for the solvent, for the total amount of salt, and for the sulfite present. The determinations were the same as those described for the aqueous phase. However, in this case, an internal standard was not necessary in the samples analyzed in the gas chromatograph since the peaks coming out from the integrator had comparable sizes. The samples taken to be titrated and analyzed for the sulfite were bigger than those taken from the aqueous phase for analysis since the organic phase had a much lower salt concentration; therefore a larger sample was employed to minimize errors.

CHAPTER 4: EXPERIMENTAL RESULTS

The experimental results are divided into two sections. In the first section, results for the saturated ternary systems sodium sulfite/acetone/water and sodium sulfite/2-propanol/water covering a temperature range are presented and discussed. Results for the quaternary systems sodium sulfate/sodium sulfite/acetone/water, and sodium sulfate/sodium sulfite/2-propanol/water are discussed in the second section. The experiments for the quaternary systems were performed under subsaturation conditions starting at saturation relative to salts, at a constant temperature for three sulfite/sulfate ratios, and covering a range of concentrations from saturation to the one-phase region.

4.1 Ternary Systems

As explained in Section 3.1.2.1, the ternary systems sodium sulfite/acetone/water and sodium sulfite/2-propanol/water were studied and results are presented in this section.

The presence of salt separates the two miscible solvents into two liquid phases, and since the system is saturated, a solid phase consisting of sodium sulfite also forms. One of the liquid phases is rich in organic solvent; it is called organic phase. The other is rich in water and salt; it is named the aqueous phase. Both liquid phases in this case are saturated with sodium sulfite.

Tables 4.1 and 4.2 show how the saturated equilibrium compositions of the two liquid phases change with temperature. Because acetone boils at 56°C, the highest temperature examined for the system containing this solvent was 48.6°C. However, when 2-propanol is the solvent, the highest temperature was 60°C.

In Fig. 4.1, concentrations of water in a salt-free basis for the aqueous and organic phases are plotted as a function of temperature for both systems containing acetone and 2-propanol. These compositions form a two-phase envelope meeting at the lower critical

Table 4.1 Saturated Equilibrium Data for Na_2SO_3/Acetone/Water

	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
Temp. (°C)	Na_2SO_3	Water	Acetone	Na_2SO_3	Water	Acetone
28.5	15.31	76.13	8.56	4.39	71.23	24.38
30.0	20.25	75.32	4.43	2.50	60.19	37.31
35.0	21.79	74.85	3.36	1.56	55.49	42.95
40.1	19.80	75.47	4.73	1.96	56.87	41.17
45.0	18.29	76.73	4.98	2.07	57.23	40.70
48.6	16.96	76.88	6.16	2.33	57.96	39.71

Table 4.2 Saturated Equilibrium Data for Na_2SO_3/2-Propanol/Water.
* Data determined by Jaecksch, 1993.

	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
Temp. (°C)	Na_2SO_3	Water	2-Propanol	Na_2SO_3	Water	2-Propanol
24.7*	11.8	76.21	11.99	4.32	67.93	27.75
25.5*	15.62	78.57	5.81	1.93	60.48	37.59
27.0*	21.43	74.36	4.21	0.73	46.82	52.45
29.0*	23.34	73.63	3.03	0.42	39.71	59.87
32.0*	24.43	73.33	2.24	0.29	36.61	63.10
35.0	23.41	73.92	2.67	0.24	35.79	63.97
40.0	22.15	74.94	2.91	0.25	35.84	63.91
45.0	21.39	75.15	3.46	0.26	36.12	63.62
50.0*	21.84	73.69	4.47	0.24	37.23	62.53
60.0*	19.91	75.77	4.32	0.30	39.21	60.49

solution temperature. This type of plot is called a coexistence curve. The left and right-hand sides of the curve refer to the organic and aqueous phases, respectively.

Solutions having compositions outside the envelope exist as a single liquid phase, while those inside the envelope split into two liquid phases. Both phase compositions remain roughly constant at temperatures higher than the transition temperature. (Below this temperature the anhydrous form of the salt becomes hydrated (Fig. 3.1)). As the temperature falls below the transition temperature, the solubility of the salt in water drops, causing an increase of solvent in the aqueous phase and an increased water content in the organic phase, resulting in a considerable transfer of salt from the aqueous to the organic phase. This trend continuous as the temperature decreases further until the composition of the two phases are the same and they combine to form one phase. The minimum temperature at which two phases can exist is called the lower critical solution temperature (LCST). The LCST was 28.2°C for the ternary system sodium sulfite/acetone/water, and 24.5°C (Jaecksch, 1993) for the system sodium sulfite/2-propanol/water.

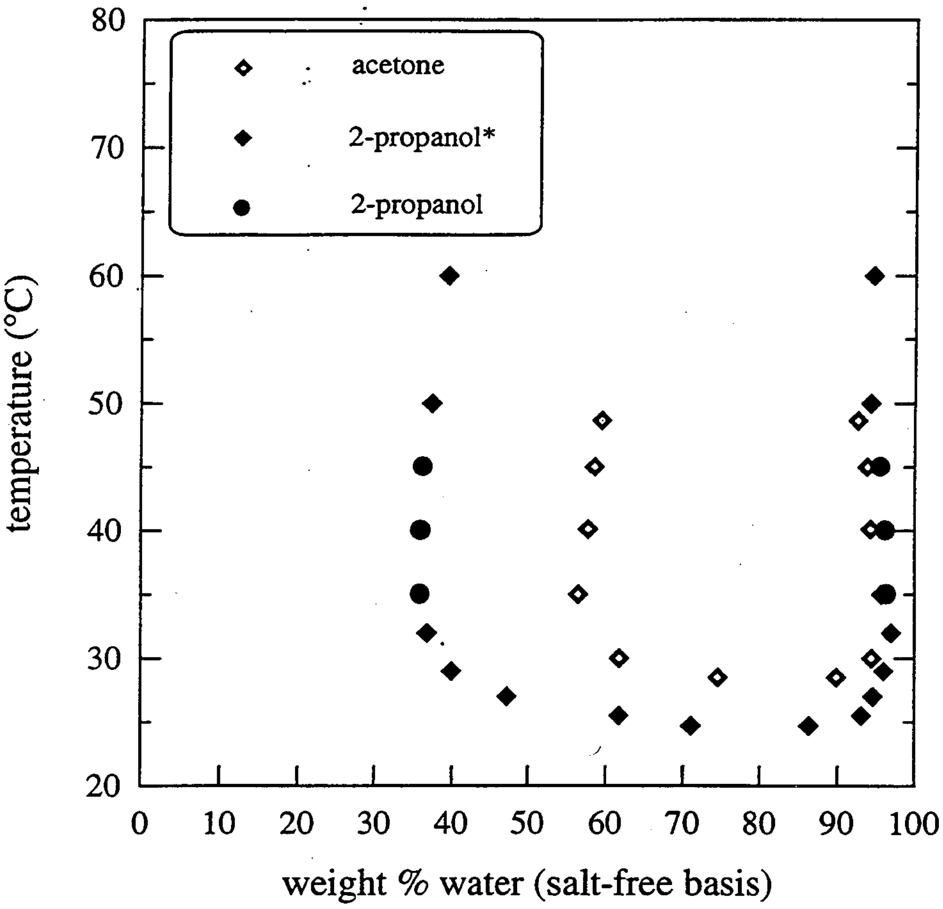
For the system sodium sulfite/2-propanol/water in Fig. 4.1, the points close to the perturbation in Fig. 3.2 were repeated using the same procedure used for the system with acetone. The points were plotted and a smooth result was found. Those points together with the points obtained by Jaecksch (1993) that were assumed to be correct are plotted in Fig. 4.1 together with the acetone curve.

Upon comparing the two curves in Fig. 4.1, it is clear that acetone shows the greater capacity to absorb water at temperatures above 30°C. From this result it can be concluded, as was already posited by Jaecksch (1993), that acetone is the most desirable of the solvents studied so far for the extractive crystallization of sodium sulfite.

Sodium sulfate has been studied extensively with a wide range of solvents. Fig. 4.2 presents the results obtained by Jaecksch (1993) and Brenner (1992) for the system sodium sulfate/water with two solvents: acetone and 2-propanol. The sulfate systems

COEXISTENCE CURVES

Saturated Equilibrium data for Na_2SO_3



* Data determined by Jaecksch, 1993

Fig. 4.1 Coexistence Curves for Aqueous Na_2SO_3 Systems.

follow approximately the same trend as the sulfite systems in the sense that acetone continues to present the greater capacity to absorb water.

Acetone proved to be the best solvent for extractive crystallization of solutions containing either sodium sulfite or sodium sulfate. These results are not conclusive, however. Other factors must be taken into account before an economically feasible process is proposed. Following this section, results for quaternary systems with acetone and 2-propanol as solvents are presented.

4.2 Quaternary Systems

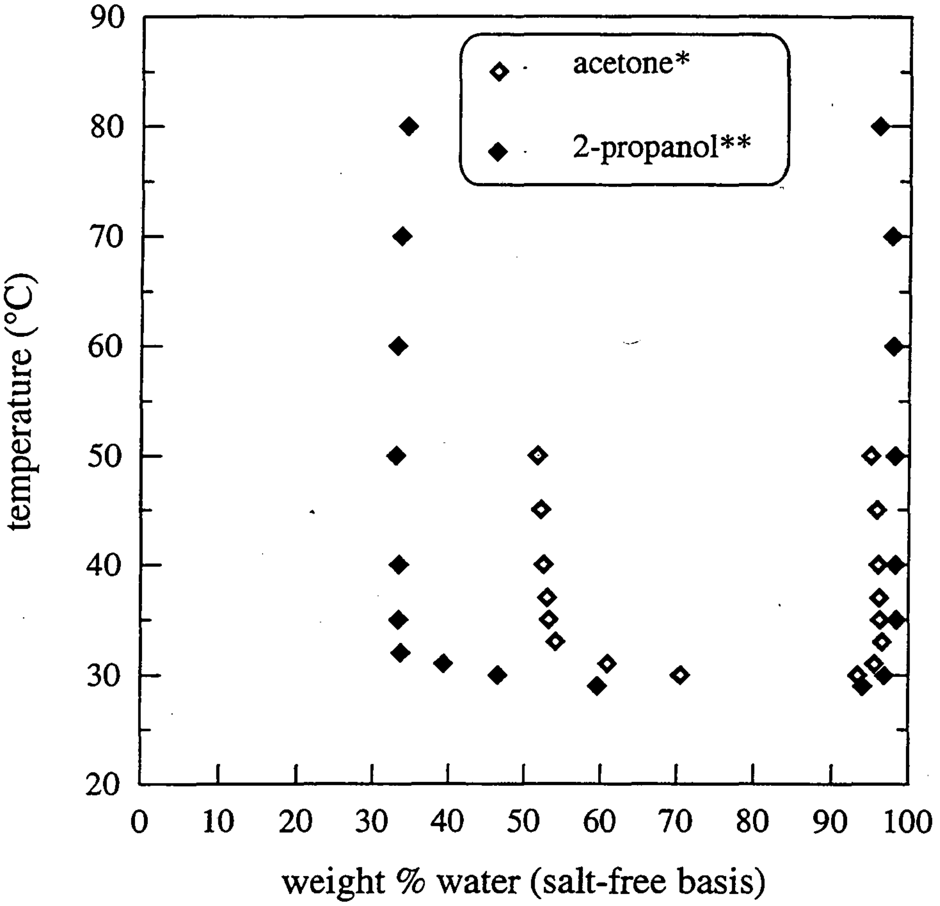
The compositions of the quaternary systems can be represented by points within a regular tetrahedron. However, to simplify interpretation of the results, a triangular diagram was used where one of the corners is the sum of the compositions of the two salts. Such representation is very suitable since what we want to compare is the ability of the solvent to extract water and precipitate salt out of the aqueous solution. The relative amounts of sulfite and sulfate are then presented in separate plots.

Quaternary systems are expressed in ternary planar diagrams at a constant temperature of 35°C. The data from Tables 4.3 to 4.8 are plotted in Figs. 4.3 to 4.8. Saturated and subsaturated data are shown for sodium sulfate/sodium sulfite/water systems with acetone, and 2-propanol, respectively, as solvents. Again, each corner of the equilateral triangles represents a pure component, except for the salts corner, which represents the sum of the two salts, sodium sulfate and sodium sulfite. In this way, the quaternary systems are considered as ternary systems.

In the ternary planar diagrams, the phase compositions in equilibrium are joined by a dashed tie line which passes through the overall mixture composition. Just a few tie lines are shown for each sulfite/sulfate ratio per solvent since others can easily be obtained by interpolation.

COEXISTENCE CURVES

Saturated Equilibrium data for Na_2SO_4



* Data determined by Jaecksch, 1993

** Data determined by Brenner, 1991

Fig. 4.2 Coexistence Curves for Aqueous Na_2SO_4 Systems.

The phase compositions vary from one system to another but it is clear that the overall trend is similar. At concentrations close to saturation, the aqueous phase has very little solvent, and therefore, the salt concentration is very close to the solubility of the mixture of salts in pure water at 35°C. Correspondingly, the organic phase has its lower water content at concentrations close to saturation, resulting in a minimum amount of salt in solution. With the addition of water to the mixture of solvent/water/salts, the salt concentration in the aqueous phase drops, allowing the solvent content of that phase to increase. The organic phase, on the contrary, absorbs more water, increasing its salt content. As water continues to be added, the compositions of the two phases approach each other and become the same at the plait point where the two phases merge forming one phase. The plait point is not easy to detect because in the region close to this point, small amounts of water added to the system yield drastic changes in composition.

The tie lines slope down to the right; the organic phase is richer in organic solvent than the aqueous phase. This suggests that water can be extracted from the aqueous phase using a moderate amount of solvent.

In the cases where acetone is used as solvent, the tie lines have a steeper slope than the tie lines obtained when 2-propanol is used as the organic solvent. This confirms that acetone has the higher capacity to extract water.

Phase compositions are plotted for three different sulfite/sulfate ratios established at the beginning of each experiment. The mol % sulfite/mol % sulfate ratios chosen were 25/75, 50/50, and 75/25. In Figs. 4.3 to 4.5, and in Figs. 4.6 to 4.8, results for those ratios are plotted for acetone and 2-propanol, respectively.

The slopes of the lines for each ratio increases as the sulfite concentration decreases. Such a result proves that a system containing less sulfite than sulfate would be able to extract more water using a smaller amount of solvent.

Results of the analyses of sulfite and sulfate in both aqueous and organic phases, shown as the mole ratio of sulfite to sulfate for acetone and 2-propanol, respectively, are shown in Tables 4.9 and 4.10 and plotted in Figs. 4.9 and 4.10. The data points show the results of all concentrations for the three salt ratios, *i.e.*, each set of data shows all the results analyzed and represented in each ternary diagram. Each single point represents the result of each experiment at a different concentration, and each group of points refers to a different salt ratio.

The results are then plotted in Figs. 4.9 and 4.10. Table 4.9 and Fig. 4.9, and Table 4.10 and Fig. 4.10 refer to the systems with acetone and 2-propanol, respectively.

There is no selectivity for either salt between the phases, *i.e.*, the ratios between the two salts in each phase obtained after equilibrium are very close to the ratios established at the beginning of the experiments, as shown in Figs. 4.9 and 4.10. Such results confirm that the salt concentrations in both phases are functions only of the quantity of water in the phase, and there is no particular competition between the salts to be more soluble in either of the phases.

The plots show that for each of the three salt ratios chosen at the beginning of the experiments, the same ratio is found in each phase, after equilibrium had been reached. Moreover, the results in both phases show that there is no selectivity of the salts between the phases as indicated by the localization of the data points close to the three salt ratios established for the experiments. This result is very important for process' purposes when the feed to be considered is a mixture of both salts.

Chapter 5 presents a comparison of two extractive crystallization processes where the feed to one is a mixture of sodium sulfite and sulfate and the feed to the other is a fully oxidized sulfate feed.

Table 4.3 Equilibrium Data: Na_2SO_3/Na_2SO_4/Acetone/Water at 35°C with a Salt Ratio of 25 mol % Sulfite to 75 mol % Sulfate.

	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
Sample No.	Na_2SO_3+Na_2SO_4	Water	Acetone	Na_2SO_3+Na_2SO_4	Water	Acetone
1	29.10	69.83	1.07	0.35	43.10	56.55
2	27.78	70.97	1.25	0.72	50.12	49.16
3	25.86	72.50	1.64	1.26	57.21	41.53
4	23.53	73.65	2.82	2.29	64.61	33.10
5	22.07	75.14	2.79			
6	17.44	80.62	1.94			

Table 4.4 Equilibrium Data: Na_2SO_3/Na_2SO_4/Acetone/Water at 35°C with a Salt Ratio of 50 mol % Sulfite to 50 mol % Sulfate.

	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
Sample No.	Na_2SO_3+Na_2SO_4	Water	Acetone	Na_2SO_3+Na_2SO_4	Water	Acetone
1	28.78	70.00	1.22	0.38	45.23	54.39
2	26.37	71.71	1.92	0.80	48.98	50.22
3	23.75	73.61	2.64	1.31	54.75	43.94
4	20.60	75.10	4.30	3.41	61.70	34.89
5	18.20	77.72	4.08			
6	15.94	80.60	3.45			

Table 4.5 Equilibrium Data: Na_2SO_3/Na_2SO_4/Acetone/Water at 35°C with a Salt Ratio of 75 mol % Sulfite to 25 mol % Sulfate.

	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
Sample No.	Na_2SO_3+Na_2SO_4	Water	Acetone	Na_2SO_3+Na_2SO_4	Water	Acetone
1	26.21	72.30	1.49	0.45	49.07	50.48
2	23.81	74.15	2.04	0.88	55.48	43.64
3	21.35	75.99	2.66	2.01	60.04	37.95
4	18.69	77.49	3.82	2.99	64.11	32.90
5	18.34	78.33	3.33			
6	16.63	80.16	3.21			

Table 4.6 Equilibrium Data: Na_2SO_3/Na_2SO_4/2-propanol/water at 35°C with a Salt Ratio of 25 mol % sulfite to 75 mol % sulfate.

	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
Sample No.	Na_2SO_3+Na_2SO_4	Water	2-Propanol	Na_2SO_3+Na_2SO_4	Water	2-Propanol
1	32.14	67.20	0.66	0.11	25.43	74.46
2	27.79	71.04	1.18	0.24	31.43	68.33
3	25.62	72.93	1.45	0.38	35.78	63.84
4	23.97	74.36	1.67	0.41	38.95	60.63
5	21.77	75.97	2.26	0.81	45.15	54.04
6	20.98	76.21	2.81	0.89	46.50	52.61
7	16.05	78.54	5.41			

Table 4.7 Equilibrium Data: Na_2SO_3/Na_2SO_4/2-propanol/water at 35°C with a Salt Ratio of 50 mol % sulfite to 50 mol % sulfate.

	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
Sample No.	Na_2SO_3+Na_2SO_4	Water	2-Propanol	Na_2SO_3+Na_2SO_4	Water	2-Propanol
1	28.94	69.97	1.10	0.13	27.85	72.02
2	25.79	72.83	1.38	0.24	33.51	66.25
3	22.86	75.29	1.86	0.45	39.59	59.96
4	21.50	76.10	2.40	0.65	42.73	56.62
5	20.16	76.80	3.05	0.87	46.03	53.10
6	14.97	80.27	4.76			

Table 4.8 Equilibrium Data: Na_2SO_3/Na_2SO_4/2-propanol/water at 35°C with a Salt Ratio of 75 mol % sulfite to 25 mol % sulfate.

	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
Sample No.	Na_2SO_3+Na_2SO_4	Water	2-Propanol	Na_2SO_3+Na_2SO_4	Water	2-Propanol
1	26.39	72.18	1.43	0.14	28.01	71.85
2	25.22	73.29	1.49	0.16	29.43	70.41
3	24.95	73.53	1.52	0.17	30.24	69.59
4	23.43	74.56	2.01	0.33	34.61	65.06
5	21.81	75.38	2.81	0.44	38.57	60.99
6	21.36	75.57	3.07	0.49	39.61	59.90
7	17.57	78.42	4.01			

Table 4.9 Molar Sulfite/Sulfate Salt Ratios for Na_2SO_3/Na_2SO_4/Acetone/Water at 35°C.

Sample No.	Sulfite/Sulfate in the Organic Phase	Sulfite/Sulfate in the Aqueous Phase
1	0.261	0.245
2	0.250	0.235
3	0.255	0.229
4	0.242	0.254
5	0.233	0.233
6	0.248	0.248

Table 4.10 Molar Sulfite/Sulfate Salt Ratios for Na_2SO_3/Na_2SO_4/Acetone/Water at 35°C.

Sample No.	Sulfite/Sulfate in the Organic Phase	Sulfite/Sulfate in the Aqueous Phase
1	0.511	0.492
2	0.515	0.482
3	0.482	0.512
4	0.491	0.497
5	0.508	0.508
6	0.483	0.483

Table 4.11 Molar Sulfite/Sulfate Salt Ratios for Na_2SO_3/Na_2SO_4/Acetone/Water at 35°C.

Sample No.	Sulfite/Sulfate in the Organic Phase	Sulfite/Sulfate in the Aqueous Phase
1	0.725	0.740
2	0.735	0.749
3	0.736	0.727
4	0.742	0.756
5	0.739	0.739
6	0.752	0.752

Table 4.12 Molar Sulfite/Sulfate Salt Ratios for Na_2SO_3/Na_2SO_4/2-Propanol/Water at 35°C.

Sample No.	Sulfite/Sulfate in the Organic Phase	Sulfite/Sulfate in the Aqueous Phase
1	0.257	0.223
2	0.248	0.242
3	0.243	0.249
4	0.268	0.252
5	0.257	0.268
6	0.241	0.262
7	0.244	0.244

Table 4.13 Molar Sulfite/Sulfate Salt Ratios for Na_2SO_3/Na_2SO_4/2-Propanol/Water at 35°C.

Sample No.	Sulfite/Sulfate in the Organic Phase	Sulfite/Sulfate in the Aqueous Phase
1	0.493	0.486
2	0.522	0.501
3	0.515	0.491
4	0.505	0.475
5	0.489	0.498
6	0.472	0.472

Table 4.14 Molar Sulfite/Sulfate Salt Ratios for Na_2SO_3/Na_2SO_4/2-Propanol/Water at 35°C.

Sample No.	Sulfite/Sulfate in the Organic Phase	Sulfite/Sulfate in the Aqueous Phase
1	0.753	0.771
2	0.759	0.781
3	0.768	0.749
4	0.757	0.747
5	0.752	0.761
6	0.741	0.764
7	0.762	0.762

TERNARY DIAGRAM

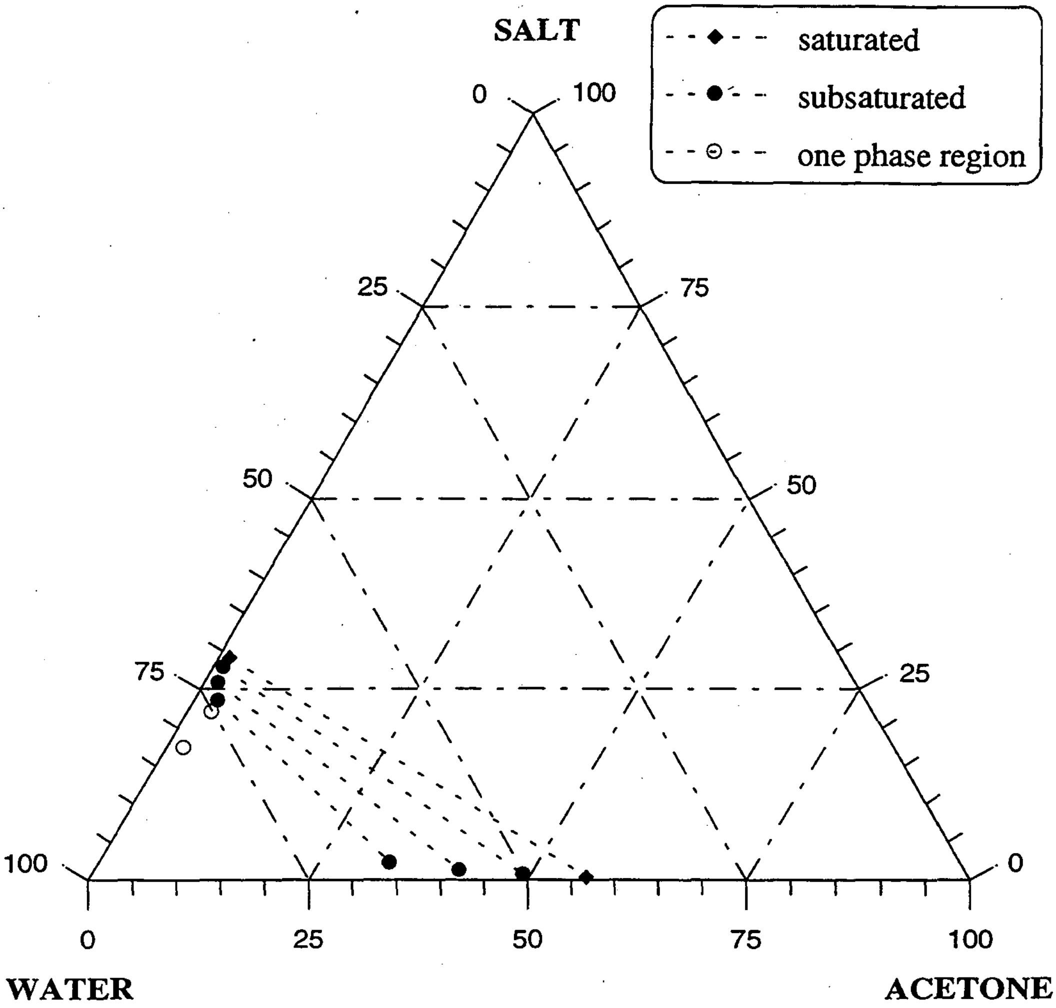


Fig. 4.3 Ternary Diagram: Na_2SO_3-Na_2SO_4/Acetone/Water at 35°C with a Salt Ratio of 25 mol % Sulfite to 75 mol % Sulfate.

TERNARY DIAGRAM

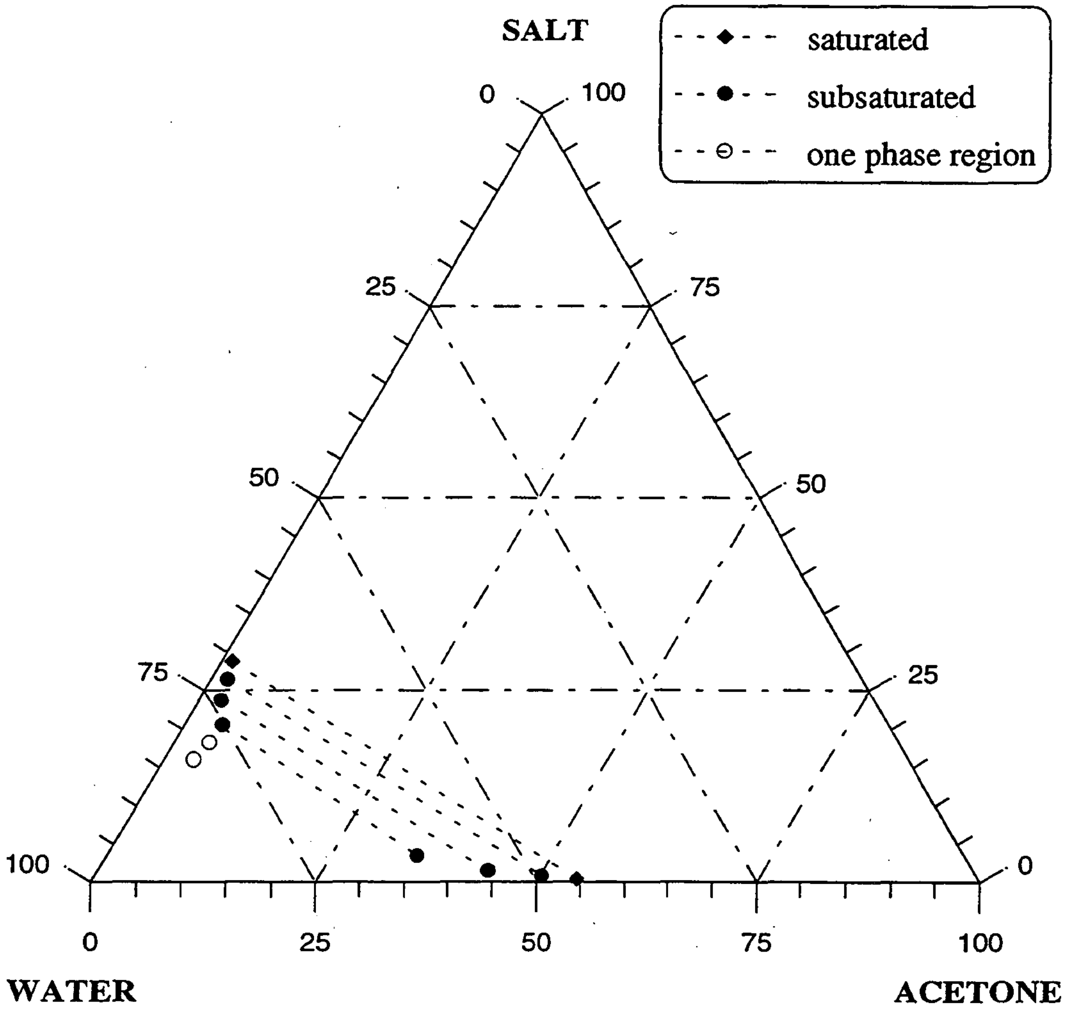


Fig. 4.4 Ternary Diagram: Na_2SO_3-Na_2SO_4/Acetone/Water at 35°C with a Salt Ratio of 50 mol % Sulfite to 50 mol % Sulfate.

TERNARY DIAGRAM

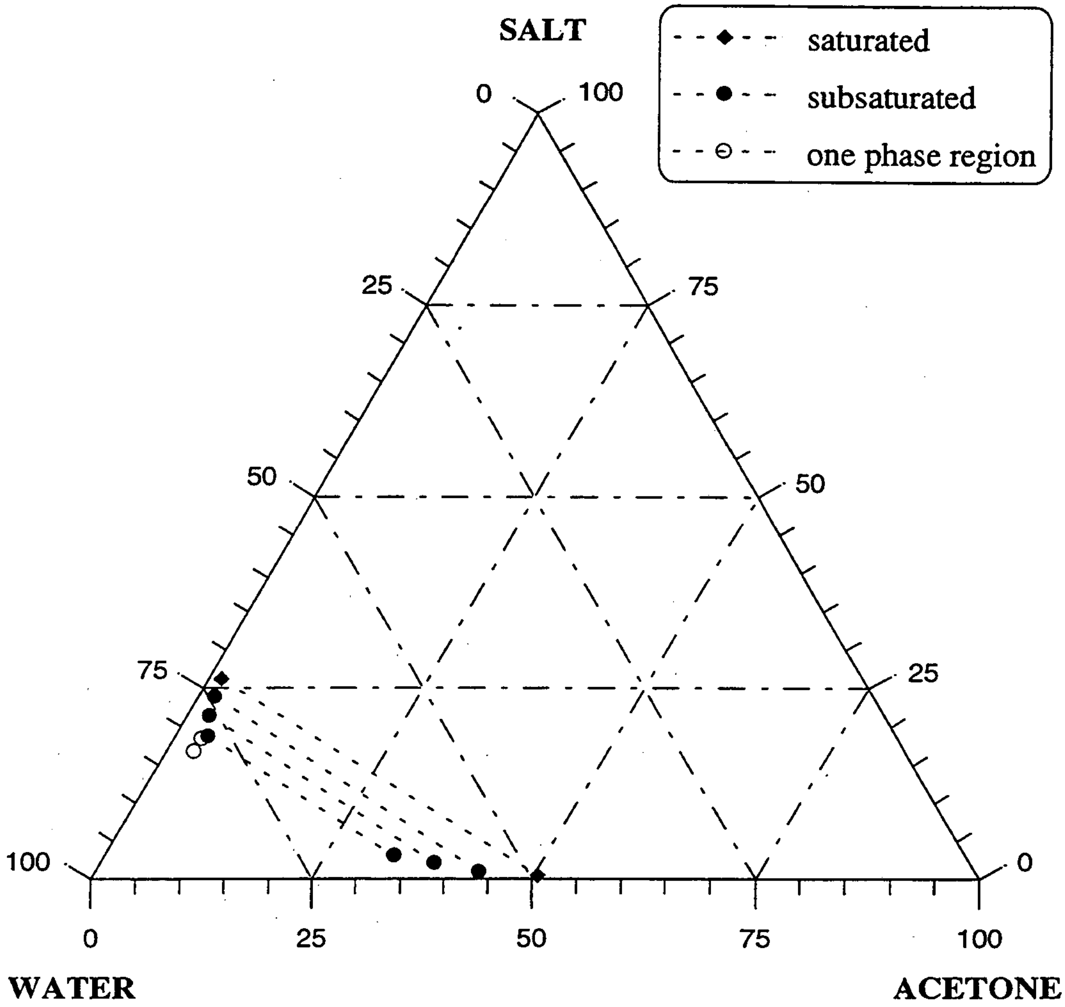


Fig. 4.5 Ternary Diagram: Na_2SO_3-Na_2SO_4/Acetone/Water at 35°C with a Salt Ratio of 75 mol % Sulfite to 25 mol % Sulfate.

TERNARY DIAGRAM

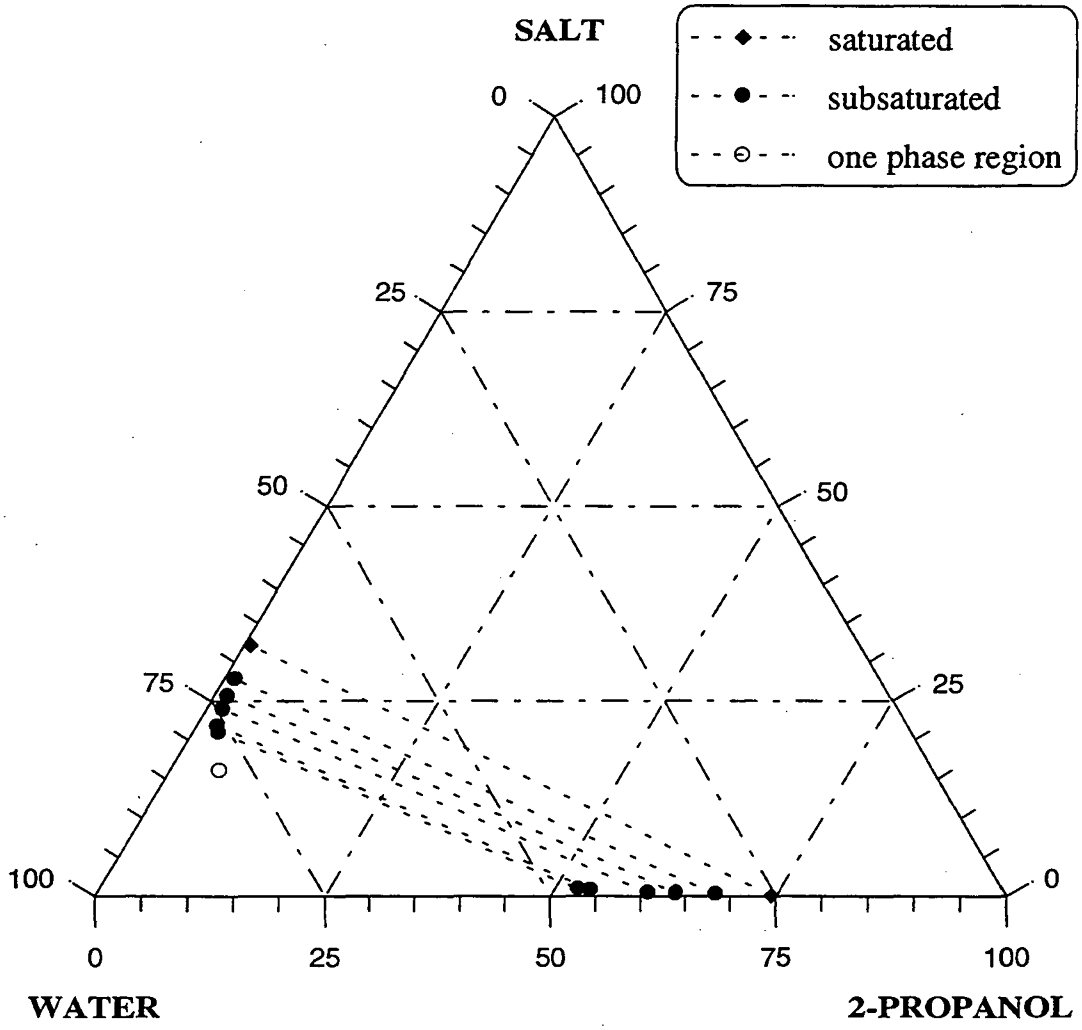


Fig. 4.6 Ternary Diagram: Na_2SO_3-Na_2SO_4/2-Propanol/Water at 35°C with a Salt Ratio of 25 mol % Sulfite to 75 mol % Sulfate.

TERNARY DIAGRAM

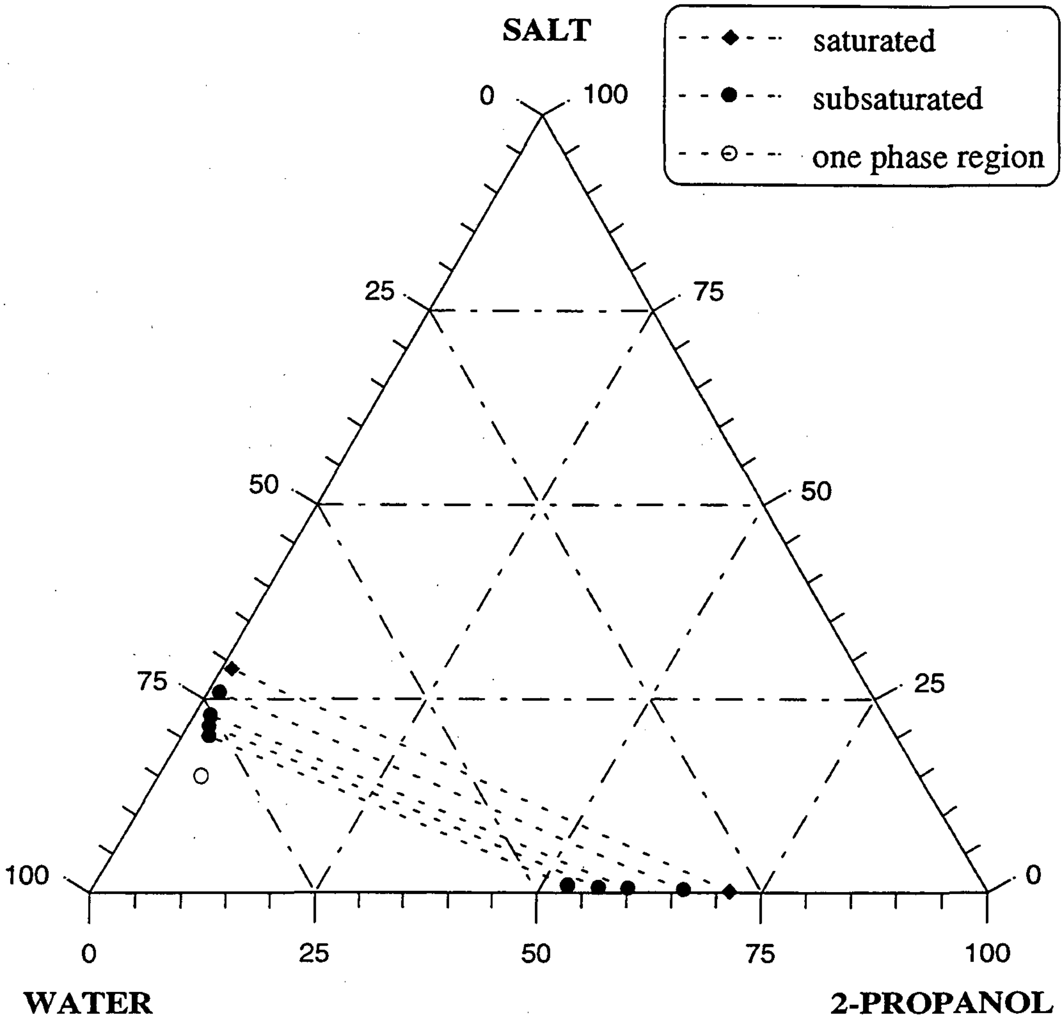


Fig. 4.7 Ternary Diagram: Na_2SO_3-Na_2SO_4/2-Propanol/Water at 35°C with a Salt Ratio of 50 mol % Sulfite to 50 mol % Sulfate.

TERNARY DIAGRAM

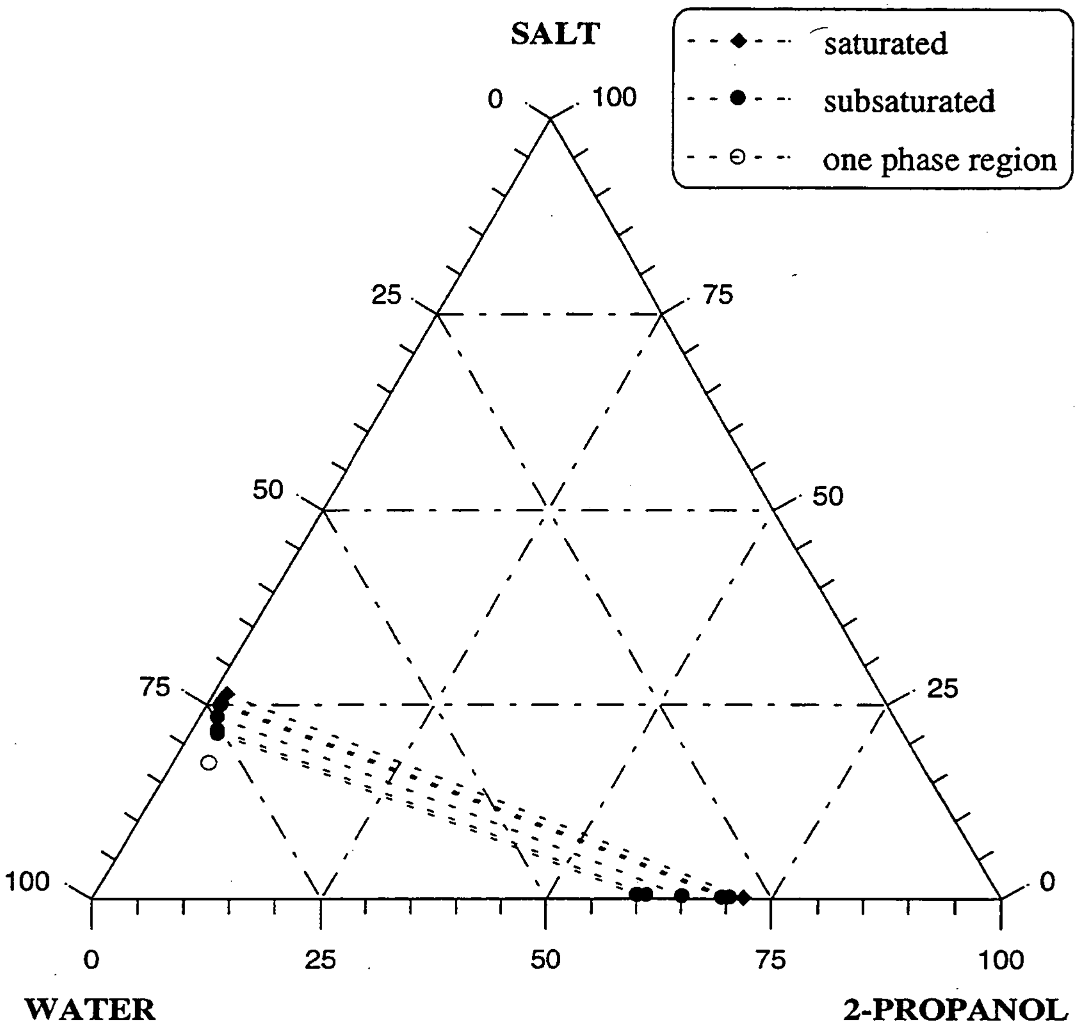


Fig. 4.8 Ternary Diagram: Na_2SO_3-Na_2SO_4/2-Propanol/Water at 35°C with a Salt Ratio of 75 mol % Sulfite to 25 mol % Sulfate.

SALT RATIOS IN THE ORGANIC AND AQUEOUS PHASES

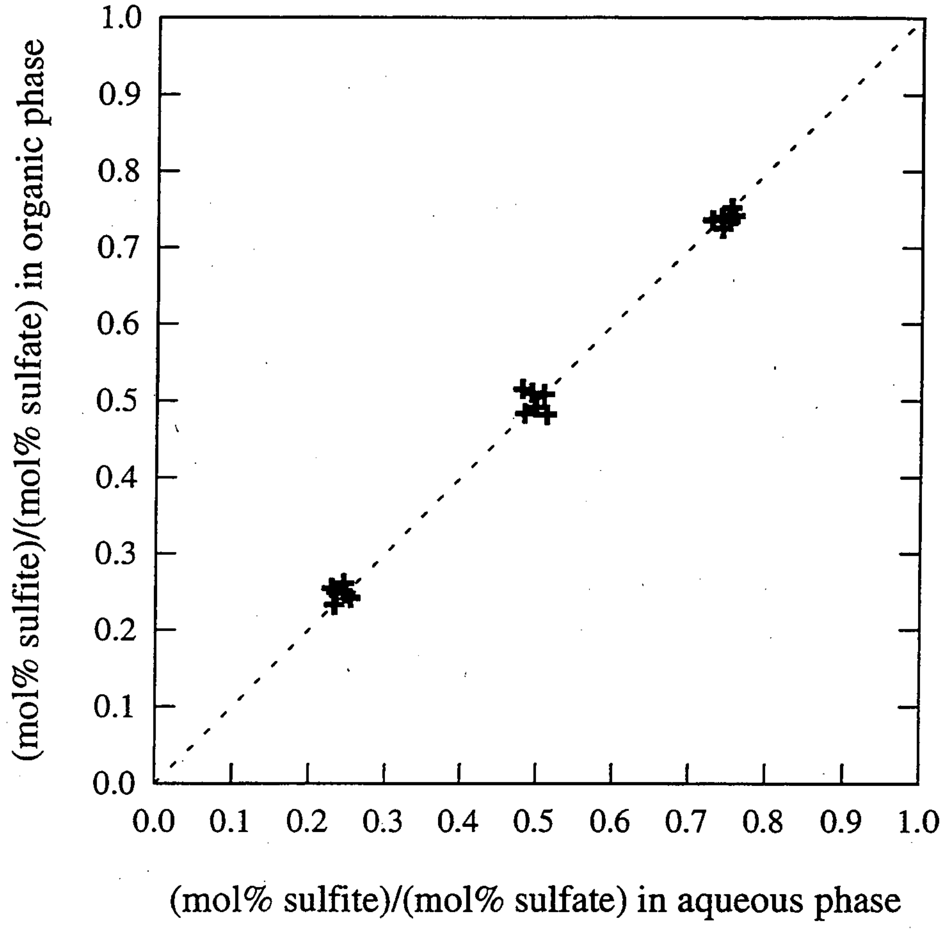
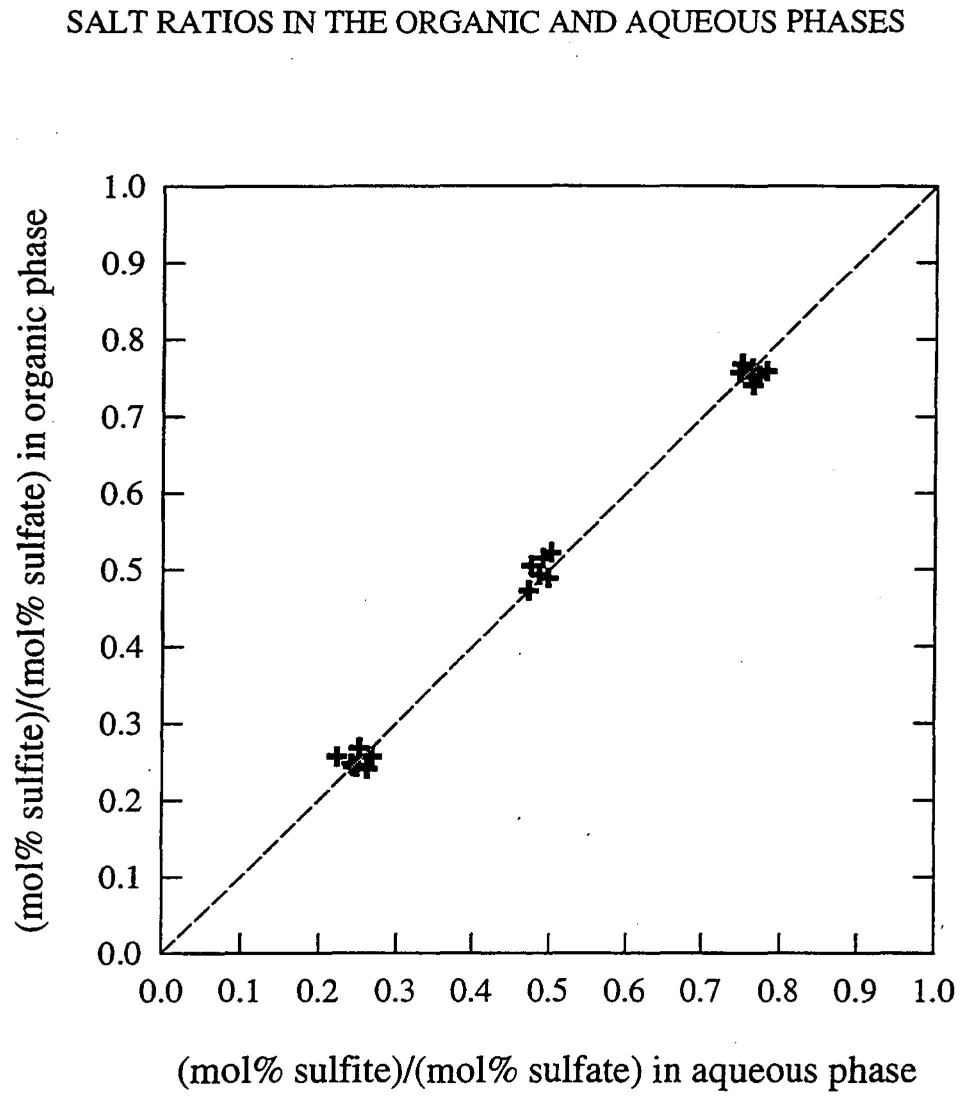


Fig. 4.9 Salt Ratios for Na_2SO_3/Na_2SO_4/Acetone/Water.



SALT RATIOS IN THE ORGANIC AND AQUEOUS PHASES

Fig. 4.10 Salt Ratios for Na_2SO_3/Na_2SO_4/2-Propanol/Water.

4.3 Uncertainties in Measurements

The analyses of the experiments presented in this work are based on results of measurements. Every measurement has an inherent uncertainty. If we use the results of the measurements to reach conclusions, we must estimate the size of these uncertainties.

The accuracy of a measurement refers to how close it is to the true value. An inaccurate result occurs as a consequence of some systematic error in the measurement, *e.g.*, the presence of an interfering substance, an incorrect calibration of an instrument, or an operator error. One of the goals of chemical analysis is to eliminate systematic errors, but random errors can only be minimized. In practice, an experiment is almost always done to find an unknown value (the true value is not known). In this case the precision of several replicate determinations is used to represent the accuracy of the results. The results of the replicate analysis are expressed as an average (which is assumed to be close to the true value) with an uncertainty that gives some indication of how close the average value may be to the true value. The error limit gives the uncertainty of the experimental result.

Once several measurements are performed, the results should express first: the average of the measurements, and second, the size of the uncertainty. In this work, the mean was used to express the average value for a series of results, and the precision was represented by the standard deviation.

The standard deviation describes the precision of a type of determination using a series of replicate results. However, in this study, it is important to estimate the precision of a procedure involving several kinds of measurements, which is accomplished by combining the precisions of the individual steps.

The experiments were performed to ensure that thermal and chemical equilibria were achieved for each sampling solution. For this reason, it was important that the temperature of the sampling solution was kept constant during the experiments. The temperature measured had an uncertainty of ±0.2°C.

The sample vials were weighed on a Mettler H10 balance giving an uncertainty of ±0.0001 grams for each measurement.

The analyses with the gas chromatograph were performed for the aqueous and organic phases. The uncertainty in the results came from both the calibration curve and from the peak's area percent obtained from the integrator. The results from one run to another were not the same and, for this reason, several injections from the same sample were run until a consistent result was obtained.

For the aqueous-phase analysis, an internal standard was used and its peak was compared with the lowest-concentration component, the organic solvent. This comparison lowered the precision of the results; several runs were performed and averaged to obtain results for each data point. The points obtained for the aqueous phase had a relative standard deviation of ±1.0% of the weight percent.

The gas chromatograph analysis for the organic-phase samples were performed directly, without the use of an internal standard. The peak sizes for the solvents were close enough to be compared with each other. In this case, an increase in precision was noted and a standard deviation of ±0.5% of the weight percent was obtained in most cases.

The analyses with atomic absorption spectroscopy were performed to detect the total amount of salt in the organic phase and in the aqueous phase[1]. The uncertainty in the results came mainly from the dilutions, from the accuracy of the standard solutions concentrations, and from eventual signal fluctuations of the instrument. Dilution errors were minimized by taking sample volumes greater than 20 ml for further dilutions. The samples together with the standard solutions were tested at least three times; in some cases, an extra sample was diluted and tested to compare the results. A standard deviation of ±0.3% of the weight percent was found for the worst cases analyzed in the

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[1] Atomic-absorption spectroscopy was used to detect the total amount of salt in the aqueous phase only for quaternary systems. For ternary systems, oven evaporation was used for this purpose.

spectrophotometer.

Oven evaporation was used to detect the amount of salt in the aqueous phase for ternary systems. Two samples were placed in the oven for each data point and a standard deviation of ±0.5% of the weight percent was usually obtained.

Iodimetric titrations were used to determine sulfite concentrations in the organic and aqueous phases. The uncertainty in the results came from several instrument measurements that take place in usual titrations; in this case more than in others, operator errors can count substantially. The results were good and a precision ranging from ± 0.25% to ±0.90% of the weight percent standard deviation was found when 2-propanol was used as the solvent. When acetone was used, good results were also found despite the involved procedure required to evaporate the solvent before the titrations. The standard deviation in the latter case ranged from ±0.4% to ±1.3% of the weight percent.

Tables 4.15 to 4.17 give final standard deviations expected from a complete analysis for ternary and quaternary systems.

Table 4.15 Standard Deviations of Aqueous and Organic Phases for Ternary systems

Phase	Component	Standard deviation (% of the weight percent)
Aqueous	Salt	± 0.5
	Solvent	± 1.0
Organic	Salt	± 0.3
	Solvent	± 0.5

Table 4.16 Standard Deviations of Aqueous and Organic Phases for Quaternary Systems with Acetone as the Solvent

Phase	Component	Standard Deviation (% of the weight percent)
Aqueous	Sodium sulfite	± 1.0
	Sodium sulfite + sulfate	± 0.3
	Acetone	± 1.0
Organic	Sodium sulfite	± 1.0
	Sodium sulfite + sulfate	± 0.3
	Solvent	± 0.5

Table 4.17 Standard Deviations of Aqueous and Organic Phases for Quaternary Systems with 2-Propanol as the Solvent

Phase	Component	Standard Deviation (% of the weight percent)
Aqueous	Sodium sulfite	± 0.7
	Sodium sulfite + sulfate	± 0.3
	Acetone	± 1.0
Organic	Sodium sulfite	± 0.7
	Sodium sulfite + sulfate	± 0.3
	Solvent	± 0.5

CHAPTER 5: PROCESS CONSIDERATIONS

5.1 Prior Process Development

The extractive-crystallization process scheme for the recovery of anhydrous sodium sulfate (Jaecksch, 1993) is presented in the top part of Fig. 5.1. The sodium sulfate solution comes from a flue-gas scrubbing operation wherein SO_2-containing flue gas is scrubbed with a sodium carbonate solution, resulting in the formation of an aqueous sodium sulfite solution that is further oxidized to sulfate in a gas-liquid contactor.

In the extractive-crystallization process for recovering anhydrous sodium sulfate, Jaecksch (1993) used three solvents: acetone, 2-propanol, and t-butanol. She found that the solvent with the highest capacity to extract water from this salt solution is acetone. The process is isothermal, operating at 35°C. The process yields sulfate salt crystallized directly as anhydrous crystal.

Sodium carbonate is used as the drying agent for regenerating the wet organic solvent. In the process, aqueous sulfate solution coming from a flue-gas scrubbing operation (1) is used as the feed. The concentration of the feed solution should be as high as possible to avoid the need for pre-evaporation. The feed solution washes the salt slurry (4) from the crystallizer to recover any solvent traces that might be present in the anhydrous solid crystals (5). The anhydrous sodium sulfate (5) is removed from the filter, and the two entering liquid streams are combined, and fed back into the crystallizer (2).

In the crystallizer, the liquid feed (2) coming from the filter is contacted with the relatively dry solvent stream (3), which extracts water from the aqueous feed, causes most of the salt to crystallize, and forms wet solvent stream (6). The crystallizer and the filter together constitute the basis for the extractive crystallization process. However, an industrially attractive process must include a way to regenerate the solvent for recycle to the crystallizer.

Regeneration of the solvent takes place in a liquid/liquid extractor, where a saturated sodium carbonate solution (7) is countercurrently contacted with the wet solvent (6). This yields a relatively dry organic phase (8) that is recycled to the crystallizer. The resulting aqueous phase (9), containing mostly water and sodium carbonate with traces of solvent and sodium sulfate, is fed into a stripper to remove the remaining solvent. To improve operating efficiency, it is necessary to heat the incoming stripper feed (12) in a heat exchanger, while countercurrently cooling the liquid stream leaving the stripper (11) to reach the temperature of the process.

It is assumed that all of the solvent entering the stripper in stream (12) leaves in stream (10), which is eventually condensed, combined with stream (8) and returned to the crystallizer. Part of the carbonate solution leaving the stripper, stream (15), containing mainly water, sodium carbonate and traces of sodium sulfate, is combined with anhydrous sodium carbonate (16) in the soda-ash dissolver, where a saturated solution is formed (7). Stream (14), the remaining carbonate solution leaving the bottom of the stripper, is recycled to the flue-gas scrubber.

The anhydrous sodium-sulfate product (5) can be sold for use in paper-pulp manufacturing. The kraft paper industry consumes two-thirds of the total U.S. sodium sulfate production.

Jaecksch (1993) presents some process considerations as well as assumptions for the mass and energy balances for the isothermal process. Her analysis shows that all three solvents, acetone, 2-propanol, and t-butanol can compete with triple-effect evaporation in terms of energy requirements only. Based only on energy considerations, 2-propanol and t-butanol show an advantage over acetone; however, acetone is more advantageous as a solvent for extracting water from a sulfate solution because of the lower solvent flow necessary to produce the desired output of anhydrous sodium sulfate.

The sodium-sulfate process described above only becomes applicable when combined with a desulfurization process for flue gas. In this way, the sodium carbonate stream coming from the sulfate process is used as the absorber feed for the scrubber in the flue-gas desulfurization.

5.2 Sodium-based Desulfurization Processes

Nearly half of the energy used in industry in the United States is consumed in combustion systems, either boilers or fired heaters, to provide process heat. Much of the fuel contains some sulfur. To achieve good combustion efficiency, every molecule of combustible material in the fuel must react with the required number of oxygen molecules. Excess air, as a source of oxygen, is introduced into the combustion system to permit complete oxidation of the components of the fuel. The excess air has to be minimized, because a dilution of the combustion gas lowers the temperature of the flame, reducing radiant heat transfer. The additional air must also be heated to exhaust-gas temperature, which reduces the thermal efficiency of the system.

In Fig. 5.1, the desulfurization process for the flue gas is shown in combination with the sodium-sulfate process. The sulfur-containing combustion fuel and excess air are introduced into a heater to burn the fuel and to produce steam for industrial purposes. Flue gas containing CO_2, N_2, H_2O, O_2, and SO_2 is generated as the product of combustion.

Many processes have been developed for sulfur-dioxide removal by absorption in an aqueous solution of a soluble alkali metal compound. Sodium compounds are preferred over potassium or other alkali metals strictly on the basis of cost. The process consists of contacting the gas with a solution of sodium hydroxide or sodium carbonate to form sodium sulfite. Part or all of the sulfite is oxidized to sulfate by excess oxygen in the combustion gas.

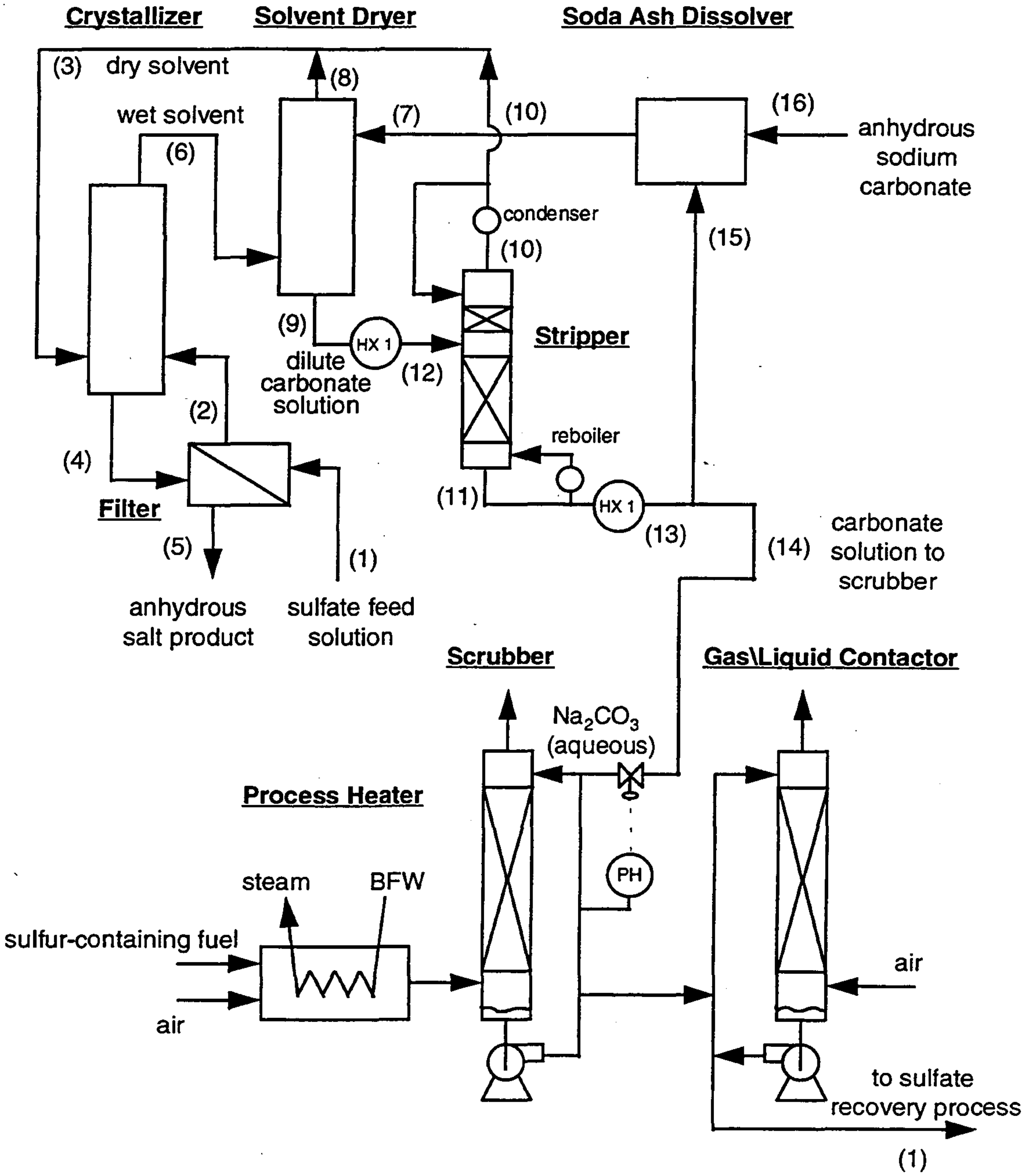

Fig. 5.1 Process Flow Diagram.

preferred over potassium or other alkali metals strictly on the basis of cost. The process consists of contacting the gas with a solution of sodium hydroxide or sodium carbonate to form sodium sulfite. Part or all of the sulfite is oxidized to sulfate by excess oxygen in the combustion gas.

For the desulfurization of the combustion exhaust gas, one of the choices is to use a packaged wet-scrubbing system to remove sulfur dioxide when high-sulfur fuel is burned. Such a system utilizes a sodium compound as the absorbent and produces sodium sulfite and sodium sulfate as byproducts; such a system can achieve sulfur dioxide removals in excess of 99%.

The hot flue gas at about 150°C is introduced into a quench section where the gas is cooled to a temperature between 50 and 60°C, evaporating water during this adiabatic cooling. Once the gas has reached saturation temperature, it enters the absorption section where the scrubbing liquid containing the carbonate is introduced to absorb sulfur dioxide. Brady (1984) designed a scrubbing system specifically for this application.

The reactions taking place in the scrubber during the absorption of sulfur dioxide are:

$$SO_2(g) + CO_3^{2-} \rightarrow SO_3^{2-} + CO_2 \qquad 5.1$$

$$SO_3^{2-} + 1/2\ O_2(g) \rightarrow SO_4^{2-} \qquad 5.2$$

A pH controller monitors the liquid stream leaving the scrubber to control the rate at which sodium carbonate is added to the system. The absorber solution has a pH between 6.2 and 6.9 (Brady, 1984), and the pH is maintained by a proportional controller which holds it within plus or minus 0.1 pH units of the setpoint. Ando (1977) describes cases in Japan where an estimated 335 such plants exist, producing sodium sulfite or sodium sulfate. Ando (1977) gives operating data for a typical plant that treats 190,000

Nm^3/hr of flue-gas containing 1,400 ppm sulfur dioxide in a packed tower and produces an outlet gas containing 6 ppm sulfur dioxide. A liquor pH of 6.5 is used in this case.

5.3 Oxidation of sulfite to sulfate

Absorption of sulfur dioxide in the scrubbing system is relatively rapid when compared to oxidation of sodium sulfite to sulfate at the scrubber temperature, Reaction 5.2. The kinetics of the homogeneous reaction of dissolved oxygen with sulfite ions has been studied by many workers. However, there is wide disagreement in the reported data, and the kinetics of the reaction are still not well understood as the reaction is complex. In several cases, the results of different workers appear to contradict one another.

The reaction is very sensitive to catalysts of both positive and negative ion species. Furthermore, experimental results seem to depend upon the type of equipment used to study the reaction, purity of sulfite used, pH of the solution, and concentrations of oxygen and sulfite solution. The reaction rate has been found to increase with increasing pH up to 9.1 (Linek and Mayrhoferová, 1970; Chen and Barron, 1972), but beyond this pH value, studies are limited.

Sivaji and Murty (1982) measured the pH of sodium-sulfite solutions in the presence and absence of sodium sulfate and cobaltous sulfate, as the catalyst, for various concentrations of sodium sulfite. No significant variation of the rate with pH was noticed. The authors used a liquid droplet of sodium-sulfite solution (mixed with catalyst) suspended freely in air to study the kinetics of the reaction. From this study, it was found that for a concentration of sulfite of 0.39 mol/L the order of reaction in sulfite is zero, and that the sulfite oxidation reaction is fast and second-order in oxygen. At the same concentration, they found that the absorption rate increases with the square root of catalyst concentration (cobaltous sulfate was used as the catalyst), indicating that the second-order rate constant is proportional to the cobalt catalyst concentration. The absorption rate of oxygen also increases with increase in catalyst concentration, but only up to a limiting value. They concluded that the reaction is normally fast second-order, but when the sulfite concentration in the droplet falls below about 0.16 mol/L, there may be a possibility for the reaction to become fast pseudo first-order. This conclusion is based on experimental results with a sulfite concentration of 0.15 mol/L, which shows that the reaction is first-order in both the solute gas and the reacting species.

Linek and Mayrhoferová (1970) found that a model employing first-order reaction kinetics in oxygen is suitable for higher oxygen concentrations, and that second-order reaction kinetics fits better for lower oxygen concentrations in the presence of cobalt catalyst. Their results showed the reaction to be independent of pH, temperature, cobalt catalyst, and sulfite concentrations within the intervals covered. They also studied the influence of pH, temperature, and cobalt sulfate concentration on the oxygen absorption rate to find the influence of those parameters upon the reaction rate constant. They showed that the absorption rate is a linear function of pH at a constant catalyst concentration whereas it is linearly dependent on the square root of cobalt catalyst concentration with a negligible additive constant at a constant pH within the interval studied. The authors also presented an expression for the temperature dependence of the reaction rate constant of the Arrhenius type, which fit their data well. They stated that the higher the concentration of the sulfite solution, the higher the concentration of impurities and, therefore, the lower is the value of the reaction-rate constant.

Danckwerts (1970), measured the rate of absorption of oxygen from air by sulfite solutions in a packed column. The column used was the same to that used by Danckwerts and Gillham described in the Part I of the paper by Danckwerts (1971). Absorption experiments were performed with various heights of packing. He showed that the effect of gas-side resistance was negligible in all experiments. The column used for the experiments was about 4 m high and 0.5 m in internal diameter. The air was blown into the top, and flowed downwards, leaving through a pair of openings in the wall of the column. The liquid level was adjusted by an overflow device, immediately below the openings through which the gas left. There were a number of such pairs of openings, and the effective height of the column was varied by changing the exit from one pair to another and adjusting the liquid level accordingly. The results compared the specific effective interfacial area for various packings; they are useful for the design of the gas/liquid contactor, where all the sulfite left is oxidazed to sulfate.

5.4 Process Implications of this research

In Tables 5.1 and 5.2, the results for the feed streams containing sodium sulfite and sodium sulfate are compared with feed streams containing either pure sodium sulfate or pure sodium sulfite. The results are shown in wt % (Tables 5.1 and 5.2) and in mol % (Tables 5.3 and 5.4). Tables 5.1 and 5.3 are for saturated systems containing acetone and Tables 5.2 and 5.4 are for those containing 2-propanol.

From the quaternary data presented in Chapter 4 as well as in Tables 5.1 to 5.4, acetone shows the greater capacity to absorb water at 35°C compared to 2-propanol. This can be noted by the amount of water absorbed into the organic phase for the different systems with acetone and with 2-propanol. This work shows that acetone is the more desirable solvent for extractive crystallization when the feed stream contains a mixture of sulfite and sulfate at any ratio. Therefore, in terms of the extractive-crystallization step only, without any other considerations, acetone is the solvent of choice. Moreover, to produce a similar quantity of anhydrous mixture of sodium sulfite and sodium sulfate, a larger solvent stream would have to be used in a process employing 2-propanol than in one using acetone.

Table 5.1 Saturated Equilibrium Data at 35°C, Using 2-Propanol as the Organic Solvent (all compositions in weight %)

	Aqueous-Phase Compositions (weight %)				Organic-Phase Compositions (weight %)		
	Salt	Water	2-Propanol		Salt	Water	2-Propanol
Na_2SO_4	29.00	69.90	1.10		0.15	33.3	66.6
25 mol % Na_2SO_3+ Na_2SO_4	32.14	67.20	0.66		0.11	25.43	74.46
50 mol % Na_2SO_3+ Na_2SO_4	28.94	69.97	1.10		0.13	27.85	72.02
75 mol % Na_2SO_3+ Na_2SO_4	26.39	72.18	1.43		0.14	28.01	71.85
Na_2SO_3	23.41	73.92	2.67		0.24	35.79	63.97

Table 5.2 Saturated Equilibrium Data at 35°C, Using Acetone as the Organic Solvent (all compositions in weight %)

	Aqueous-Phase Compositions (weight %)				Organic-Phase Compositions (weight %)		
	Salt	Water	Acetone		Salt	Water	Acetone
Na_2SO_4	28.17	69.16	2.67		0.50	52.91	46.59
25 mol % Na_2SO_3+ Na_2SO_4	29.10	69.83	1.07		0.35	43.10	56.55
50 mol % Na_2SO_3+ Na_2SO_4	28.78	70.00	1.22		0.38	45.23	54.39
75 mol % Na_2SO_3+ Na_2SO_4	26.21	72.30	1.49		0.45	49.07	50.48
Na_2SO_3	21.79	74.85	3.35		1.56	55.49	42.95

Table 5.3 Saturated Equilibrium Data at 35°C, Using 2-Propanol as the Organic Solvent (all compositions in mol %)

	Aqueous-Phase Compositions (mol %)				Organic-Phase Compositions (mol %)		
	Salt	Water	2-Propanol		Salt	Water	2-Propanol
Na_2SO_4	4.98	94.57	0.45		0.036	62.50	37.46
25 mol % Na_2SO_3+ Na_2SO_4	5.87	93.85	0.28		0.030	53.24	46.73
50 mol % Na_2SO_3+ Na_2SO_4	5.26	94.30	0.44		0.035	56.31	43.65
75 mol % Na_2SO_3+ Na_2SO_4	4.81	94.63	0.56		0.039	56.51	43.45
Na_2SO_3	4.29	94.69	1.02		0.062	65.07	34.87

Table 5.4 Saturated Equilibrium Data at 35°C, Using Acetone as the Organic Solvent (all compositions in mol %)

	Aqueous-Phase Compositions (mol %)				Organic-Phase Compositions (mol %)		
	Salt	Water	Acetone		Salt	Water	Acetone
Na_2SO_4	4.85	94.02	1.13		0.094	78.47	21.44
25 mol % Na_2SO_3+ Na_2SO_4	5.15	94.40	0.45		0.075	71.01	28.91
50 mol % Na_2SO_3+ Na_2SO_4	5.23	94.26	0.51		0.082	72.76	27.16
75 mol % Na_2SO_3+ Na_2SO_4	4.76	94.63	0.61		0.096	75.72	24.18
Na_2SO_3	3.94	94.74	1.32		0.32	80.37	19.31

Results in Tables 5.1 to 5.4 show that the largest amount of water is extracted from the aqueous phase into the organic phase when the former contains pure sodium sulfite; the next largest is extracted from a solution of pure sodium sulfate, and the least amount of water is extracted from the various mixtures of the two salts. The process cannot be considered feasible for a feed stream containing only sodium sulfite, since the stream comes from a process for the removal of sulfur dioxide from a flue gas that always contains an excess of oxygen[1]. Sodium sulfite oxidizes in the presence of oxygen, and because the reaction is not very fast, as already discussed, it yields a mixture of sulfite and sulfate. The second option then seems to be to operate with a feed stream containing only sodium sulfate, which can be obtained by sufficient aeration of the sulfite/sulfate solution. As shown in the process scheme of Fig. 5.1, the stream containing sodium sulfite and the sodium sulfate produced by the presence of excess oxygen in the flue-gas stream leaves the scrubber and enters a gas absorber where the remaining sulfite is oxidized to sulfate. The outlet stream concentration is relatively high and is suitable for feed to the sulfate extractive-crystallization process; the feed should be as concentrated as possible.

A goal of this work was to evaluate the possibility of introducing a feed coming from a flue-gas scrubbing process directly to an extractive-crystallization process without the need for further oxidation. Quaternary-systems experiments were performed and the results were compared with sodium sulfate ternary-systems (Tables 5.1 and 5.2). From a comparison of the results, there is a small disadvantage when a feed containing a mixture of the two salts is used, since less water is extracted to the organic phase with this mixed feed. It can be concluded that for the extractive crystallization process, a 100 % sulfate feed is better than a feed containing a mixture of the sulfite and sulfate salts.

In industry, sodium sulfate is more commonly used than sodium sulfite because of its inertness at low temperatures and its reactivity at high temperatures. The principal uses

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[1] The excess oxygen is enough to oxidize only some of the sulfite.

for sodium sulfate is in the Kraft paper industry. Much of the sodium sulfite produced also goes into pulp applications, although its production is much smaller than the production of sodium sulfate. These factors make a process for production of anhydrous soldium sulfate even more atractive.

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APPENDIX A: Operating Conditions for Analytical Instruments

Table A.1 Gas Chromatograph Operating Conditions.

Chromatograph Type:	Hewlett-Packard 5890A
Detector:	Thermal Conductivity
Detector Temperature:	180°C
Injector:	Split Capillary Inlet
Injector Temperature:	190°C
Oven Temperature:	120°C
Carrier Gas:	Helium
Carrier Gas Flow:	120 ml/min
Split Ratio:	25
Initial Head Pressure:	2 psi
Column Flow Rate:	4 ml/min
Purge Gas Flow Rate:	5 ml/min
Make-Up Gas Flow Rate:	6 ml/min
Reference Gas Flow Rate:	25 ml/min
Signal Attenuation 2^( ):	4
Signal Range 2^( ):	7-10
Syringe:	Hamilton 1-Microliter Syringe 7001-N
Integrator Type	Hewlett-Packard 3392A

Table A.2 Operating Conditions for Atomic-Absorption Spectroscopy

Spectrophotometer Type:	Perkin-Elmer 2280
Lamp Type:	Perkin-Elmer Intensitron™ Sodium Lamp
Lamp Current:	8 mA
Analytical Wavelength:	589 nm
Slit Width:	0.1 nm
Oxidant:	Air
Air Pressure:	80 psi
Air Flow Rate:	20 ml/min
Fuel:	Acetylene
Acetylene Pressure:	12 psi
Acetylene Flow Rate:	50 ml/min

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