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Recovery of Anhydrous Na{sub 2}SO{sub 4} from SO{sub 2}-Scrubbing Liquor by Extractive Crystallization: Liquid-Liquid Equilibria for Aqueous Solutions of Sodium Carbonate, Sulfate and/or Sulfite plus Acetone, 2-Propanol or {ital tert}-Butanol

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Recovery of Anhydrous Na_2SO_4 from SO_2-Scrubbing Liquor by Extractive Crystallization: Liquid-Liquid Equilibria for Aqueous Solutions of Sodium Carbonate, Sulfate and/or Sulfite plus Acetone, 2-Propanol or *tert*-Butanol.

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Abstract

Sodium carbonate is a superior scrubbing agent for removing SO_2 from combustion gases, but the resulting sodium sulfate (or sulfite) must be recovered for environmental reasons. Recovery by evaporative crystallization is energy-intensive; extractive crystallization (described below) is an attractive alternative when technically feasible. Liquid/liquid-equilibrium data were determined for two-phase mixtures containing aqueous solutions of sodium carbonate, sulfate, or sulfite and a polar organic solvent: acetone, 2-propanol and 2-methyl propan-2-ol (*i.e.*, *t*-butanol). In the salt-saturated two-phase region, data were obtained between the lower consolute temperature and 60 °C (50 °C for acetone). Data were also obtained at 35 °C for liquid/liquid systems that were subsaturated with their respective salts, and for liquid/liquid systems with overall molar ratios of sodium sulfite/sodium sulfate fixed at 25/75, 50/50 and 75/25. In the latter systems it was found that the sulfite/sulfate ratios in the organic and aqueous phases were the same; *i.e.*, there is no selectivity by these solvents for one salt relative to the other. The data show that any one of these solvents can be used to extract water from a concentrated solution of either sodium sulfite or sodium sulfate in a countercurrent extractor at 35 °C, causing the anhydrous salt to crystallize. The wet solvent can be dried for recycle in a similar countercurrent operation at 35 °C, using a saturated solution of Na_2CO_3 as the drying agent. The number of moles of carbonate required for drying does not exceed the moles of sulfite-plus-sulfate precipitated. The process energy required is low.

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Introduction

Formation of aqueous salt solutions is a common step in the manufacture and purification of inorganic compounds, and the recoery of these salts from solution after purification can be a major cost of their production. Depending upon the solubility of the salt in water, various techniques are available. If the solubility is a strong function of temperature, then simply heating or cooling the solution causes precipitation and the purified salt crystals can be filtered from the mother liquor. However, the solubility of some salts is relatively insensitive to temperature; in these cases precipitation of the solid salt requires evaporation of all of the water. Water has a large heat of vaporization, which makes evaporative crystallization an energy-intensive process. Multi- (usually triple-) effect evaporators are commonly used industrially to reduce the energy required for evaporation. The economics for multi-effect evaporation is better than for single-stage evaporation, but a process that caused crystallization of the salt without evaporation of water might provide an alternative with even lower energy costs.

One such process, in which an immiscible solvent is added to extract water from the salt solution, has been given the name extractive crystallization. Systems containing various salts and solvents have been studied prior to this work: 1-butanol and 1-propanol with sodium carbonate, and di-isopropylamine (DIPA) with sodium chloride (Weingaertner, *et al.*, 1991); N,N-diethylmethylamine (DEMA) with sodium chloride and sodium sulfate (Ting, *et al.*, 1992); and 1-propanol, 2-propanol, and 2-methyl propan-2-ol (*i.e.*, *t*-butanol) with sodium sulfate (Brenner, *et al.*, 1992). The individual characteristics of these ternary systems have dictated various overall process schemes, but the basic extractive-crystallization principle of using an immiscible solvent to extract water from the system is the same for each.

Flue-gas scrubbing operations result in the conversion of sodium carbonate to aqueous solutions containing sodium sulfate and sodium sulfite; the solubility behavior of these three salts

in the presence of water and acetone, 2-propanol or *t*-butanol is the subject of this research. Solubilities of the three salts in water are reported by Seidell (1958). All three form solid hydrates below a specific temperature. At higher temperatures, the solubilities of the salts are not a strong function of temperature, and the anhydrous crystal (or monohydrate in the case of Na_2CO_3) is the stable solid phase. For sodium sulfate, the decahydrate is formed below 32.4 °C, and for sodium sulfite, the heptahydrate is formed below 33.0 °C. With Na_2CO_3 the monohydrate is the stable solid between 35.4 °C and the normal boiling point; the heptahydrate is stable between 35.4 and 32 °C, while the decahydrate forms at all lower temperatures. When recovering either the sulfate or the sulfite from scrubbing liquor by extractive crystallization, one would normally want to produce the anhydrous salt.

Experimental Apparatus

The experimental apparatus used for all experimental work consisted of a flat-bottomed 300-mL flask submerged in a 12-L thermostatted water bath, as shown in Figure 1. A magnetic stirrer bar within the flask provided constant agitation of the liquid mixture. A Neoprene stopper in the top of the flask was outfitted with a three-way valve open to the atmosphere for pressure control during runs. (When working with Na_2SO_3, an atmosphere of N_2 was maintained within the sample flask to preclude oxidation.) Samples were obtained by immersing a sampling tube in one of the phases with the three-way valve in the stopper connected to an air (or N_2) supply. Closing the three-way valve created a pressure in the flask sufficient to force the sample to flow through the tube. After a rinse, the solutions were pumped directly into Fisherbrand screw-cap vials. The size of each sample varied from 1 to 10 g, according to the different analytical techniques to be used (Jaecksch, 1993).

The temperature of the water bath was monitored by a Hart-Scientific temperature

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controller. To maintain a wide range of temperatures, above and below ambient, the temperature controller was connected to a 500-watt immersion heater and a Forma-Scientific refrigeration bath that circulated coolant through coils submerged in the water bath. A stirrer in the bath helped to ensure a uniform temperature throughout.

Chemicals

The solvents used in this research were Fisher-Scientific acetone and 2-propanol, and Mallinckrodt *t*-butanol. Aldrich ethylene glycol was used in the gas-chromatography calibrations. All solvents had a guaranteed purity of at least 99.6% and were used without further purification. The salts used were Fisher-Scientific sodium sulfate, and Mallinckrodt sodium sulfite and sodium carbonate. All water used was distilled. The distilled water used for dilution purposes in the atomic absorption analyses was further purified with a Barnstead Nanopure ultrapure water system. For gas chromatography, the internal standard used in the aqueous samples was Aldrich anhydrous ethylene glycol (99+% pure).

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.

Analytical Techniques

a. Atomic Absorption

Atomic-absorption spectroscopy was the analytical technique chosen to quantify the amount of salt present in the organic-phase samples, which were generally dilute in salt, and for some of the aqueous-phase samples, particularly those that contained both sulfate and sulfite.

In atomic-absorption spectroscopy, a wavelength of light, characteristic of the analyzed element, is absorbed by ground-state atoms causing them to become excited. These ground-state atoms were generated by aspirating the sample into an air/acetylene flame, thereby vaporizing the sample. The temperature of the flame is about 2300 °C, as recommended for this type of analysis. The amount of light absorbed by the sample indicates the concentration of that element in the sample, and can be quantified. Quantitative measurements are based on Beer's Law, which assumes that absorbance is proportional to concentration. However, Beer's Law holds only for very low concentrations; therefore, all of the organic-phase samples analyzed by atomic absorption had to be diluted.

For this analysis, a Perkin-Elmer 2280 atomic-absorption spectrophotometer with a Perkin-Elmer Intensitron™ sodium lamp was used to measure the concentration of sodium present in the sample. The characteristic wavelength used for sodium is 589 nm. A standard stock solution was prepared by dissolving 2.542 g NaCl, and therefore 1.000 g of Na^+, in one liter of deionized water. Two dilute standards were then prepared that contained 0.5 and 1.0 mg Na^+ per liter. After dilution, 1 g of KCl was added to each of the dilute standard solutions to prevent ionization interference.

The organic-phase samples analyzed contain solvent, and therefore the effects of the solvent on the atomic-absorption analysis had to be tested. In three separate experiments, the addition of 1 g/L of one of the three solvents was shown to have no effect on the light absorption for a sample containing 1.0 mg Na^+/L. The solvent content of the samples could thus be ignored for this particular analysis.

Dilution of the samples had to be very precise to be in the range required by Beer's Law, and techniques were devised for estimating the salt concentration before dilution. Details of these procedures are given by Jaecksch (1993) and Schiozer (1994).

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b. Gas Chromatography (GC)

A Hewlett-Packard 5890A gas chromatograph with a thermal-conductivity detector (TCD) was used. The TCD detector was chosen because it allows analysis of water. A J&W Scientific water-compatible DB-624 column was used; a column 30 m in length with a 3.0-μm film thickness was chosen to separate the chromatograph peaks of the alcohols and water. The 0.53-mm inner diameter is quite large for these columns, but was necessitated by the large sample injections required for peak resolution. Helium, with a manufacturer's guaranteed purity of 99.995%, was chosen as both the carrier gas and the detector make-up gas. An Alltech oxygen trap was installed on the helium line, as well as a Molecular-Sieve 5 A chemical filter on the carrier gas flow line, to guard further against contamination. A packing material filter (2% OV-101 on 100/120 mesh chromasorb W-HP) was placed on the sample injection port to keep any salt in the sample from entering the column. The column flow and temperature ranges were those recommended by the manufacturers. Some changes were made in the flow rates throughout the study to enhance peak resolution, but the changes were small.

All samples were injected into the gas chromatograph with a Hamilton 1-microliter syringe 7001-N, using 0.2 μl for the calibration-standard samples, and 0.8 μl for the aqueous-phase samples. The increase in sample size was to compensate for the low concentrations of solvent and ethylene glycol in the aqueous-phase samples. Immediately before each injection the syringe was rinsed with the sample solution being tested at that time to diminish cross-sample contamination. Each calibration standard and each aqueous-phase sample was run six times; the results were averaged to increase the accuracy of the final results.

The gas chromatograph was connected to a Hewlett-Packard 3392A integrator that detected and analyzed the sample signal. The integrator reports its signal in units of area percent; to convert those numbers to weight percent, a calibration factor was determined. The

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calibration factors varied smoothly, and nearly linearly, with composition.

For the aqueous-phase samples, the solvent peak was usually very small in relation to the water peak, and therefore an internal standard was added to the sample to improve accuracy. An internal standard must not cause the samples to phase-split, and must also have a retention time different from those of the other components. Ethylene glycol was found to meet these criteria, and was also chosen because it kept those samples taken below ambient temperature from phase-splitting upon warming.

The dissolved salt present in the aqueous-phase samples did not affect the GC results, but it did affect the performance of the injection syringes. When testing aqueous-phase samples, the syringes repeatedly plugged with salt. To alleviate this problem, the syringe was repeatedly flushed with hot water between each sample injection. The syringe was also cleaned and dried with a Hamilton syringe cleaner at the end of each day. These precautions helped considerably, but not totally. To increase accuracy further, each calibration standard and organic-phase sample was run five times, and the results averaged.

In the organic phase the solvent and water peaks were similar enough in size to be compared directly, without the use of an internal standard. As before, calibration standards were determined using each of the three solvents. The organic-phase calibration factors ranged from 1.13 to 1.26 on a weight/area basis. Since the solvent and water peaks were compared directly, the range of weight percents calibrated was much larger than that with the aqueous-phase samples.

c. Iodimetric Titration

Iodimetric titration was the technique chosen to quantify the amount of sulfite ions present in the organic and aqueous samples (Jeffery *et al*, 1991). Analyses were made immediately after samples were taken to minimize sulfite oxidation. Excess of standard 0.05M

iodine in KI solution was diluted with several volumes of water and acidified with hydrochloric acid. The volume of the sample was measured with calibrated pipettes 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.

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. Solutions of sodium thiosulfate prepared with highly purified water are perfectly stable. However, ordinary distilled water may contain carbon dioxide, as well as bacteria, that may cause slow decomposition. For these reasons, a small amount of sodium carbonate was employed to ensure the correct pH.

d. Oven Drying

Simple oven evaporation was the method chosen to determine the concentration of dissolved salt in the aqueous-phase samples because of the large amount of salt present in the aqueous phase. Drying of the samples was done slowly to avoid loss of spray by boiling and therefore the oven temperature was set below the boiling point of water, at about 85 - 90°C. Drying time was set at four days, about twice the time required for the samples to reach a constant weight.

Analytical Techniques for Ternary Systems

a. Aqueous-Phase Analyses

After samples were taken from the aqueous phase, they were analyzed separately for solvent and salt. The concentration of solvent was determined by using an internal standard and GC. A separate sample was weighed, dried in the laboratory oven and weighed again to determine the amount of salt present. (An analysis of the solids was unnecessary since, after

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oven drying above 80 °C, only anhydrous sodium carbonate, sulfate or sulfite could be present.) The respective quantities were expressed as mole or weight percent. The water content was obtained by difference. The analysis of water content was also done with a Karl-Fischer moisture titrator for a few samples for comparison with the difference method. Since the results were in very good agreement, the less-tedious GC-plus-drying method was chosen.

b. Organic-phase Analyses

To determine the organic-phase compositions, the amount of water relative to the amount of solvent in each sample was determined by GC. The salt content of each sample was determined by atomic-absorption spectroscopy.

Analytical Techniques for Quaternary Systems

a. Aqueous Phase

Quaternary systems contained both sodium sulfate and sulfite as the solutes, one of the organic solvents, and water. Separate samples were taken from the aqueous phase and analyzed for the solvent by GC using an internal standard, for the total amount of salt by oven drying, and for the sulfite content by iodimetric titration. The sulfate was obtained by difference as was the amount of water. For the systems containing acetone, it was necessary to evaporate the solvent before the actual titrations, as mentioned above.

b. 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, except that an internal standard was not necessary in the GC analyses since the peaks from the integrator had comparable sizes. The samples taken to be titrated and analyzed for sulfite were larger than those taken from the aqueous phase since the organic phase had a much lower salt concentration. A separate sample was analyzed by atomic absorption for

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sodium. From the two measurements the percentage of sodium sulfate present in each phase was readily calculated.

Experimental Procedure

a. Ternary salt-saturated systems

Liquid/liquid/solid-equilibrium experiments were conducted using acetone, 2-propanol, and *t*-butanol for solvents; sodium sulfate, sodium sulfite, and sodium carbonate for salts; and water. Equilibrium compositions were obtained using distilled water and each of the solvent/salt pairs, giving a total of nine ternary salt-saturated systems. In the first set of experiments, each system was saturated with the particular salt, and the temperature was varied. Thermal and chemical equilibrium were ensured by using the apparatus described above and the experimental procedure described below.

The liquid mixture contained the appropriate solvent, water, and salt, in proportions such that at the desired temperature the mixture split into two liquid phases of approximately equal size. The total liquid volume was 75 to 100 mL, and was sufficient to allow taking samples while permitting good mixing. Enough salt was added so that a solid phase was always present. Because the quantity of salt in the solid phase did not affect the liquid-phase compositions, it was not measured. However, the volume of solid salt was kept small enough to facilitate good mixing.

For each system the lower consolute temperature (below which only a single liquid phase can exist) was first determined. The lower consolute temperatures for these systems all lie between 15° and 30°C. The aqueous phase is always the denser of the two liquid phases, and is comprised mostly of water and salt. The lighter, organic phase consists mostly of solvent and water. Near the lower consolute temperature, the organic-rich phase for these systems has a solvent-to-water weight ratio less than one, but this ratio is usually greater than one at the higher

temperatures.

The two liquid phases were equilibrated for at least four hours after the desired temperature had been reached. Preliminary studies showed that equilibrium was reached within two hours or less, but that duration was doubled to reduce experimental error. After the four hours, agitation within the test flask was stopped and the phases were allowed to separate. Total separation of the phases and settling of the solid salt usually occurred within a few minutes; however, when the liquid phases approached each other in composition, up to 15 minutes was required for complete separation. The flask was then pressurized, and samples were withdrawn from the two liquid phases through the capillary tubes that extended into each. The first portion of each sample was discarded and the rest was used for analysis. The temperature was then increased to the next value and the process was repeated. Sufficient amounts of each component were added to the flask to compensate for the samples that had been withdrawn; the liquid phases were maintained approximately equal in size and the presence of solid salt ensured saturation.

Near the lower consolute temperature, phase composition is a strong function of temperature; the temperature increments between samples were small in that region. At about 35 °C the phase compositions became fairly constant, and the temperature increments between samples was increased. The temperature range for each system began at the lower consolute temperature and was increased to an upper value of 60 °C. However, because acetone boils at 56 °C, systems containing acetone had an upper limit of 50 °C.

b. Ternary Systems Subsaturated with Salt

The experimental apparatus and procedures detailed above were also used to gather data for the subsaturated systems. The temperature was kept constant at 35 °C. The initial liquid mixture was prepared by taking the saturated equilibrium compositions for the salt, water, and

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the solvent at 35 °C, and a total sample size of about 125 mL. Extra salt was added to ensure saturation, and the mixture was then heated to 35 °C. After four hours of stirring, the two liquid phases were decanted into another test flask, leaving behind the solid salt. The mixture was again allowed to equilibrate to 35 °C, and the first sample taken. Because of small losses the first samples were slightly less than fully saturated with the salt.

The system was rendered subsaturated in salt by adding an increment of water to the system after taking each set of samples. After the first set was taken, near salt-saturation, about 10 mL of water was added to the two-phase mixture, and the two phases were again allowed to equilibrate. Another set of samples was then taken, and another increment of water added. The volume of water added between sampling was decreased as the plait point was approached. The plait point is similar to the lower consolute temperature, in that it is the point at which the two liquid phases reach the same composition. At water contents higher than the plait point only one liquid phase exists in the system at that temperature. Thus at each temperature above the lower consolute temperature for a given salt-saturated system there is a unique plait-point composition for the subsaturated system.

The sample vials were first labeled and weighed on a Mettler H10 balance. Those vials designated to be used for oven samples were first dried in the laboratory oven for at least four hours before their initial weighing. This ensured that the weighing conditions of these samples were consistent throughout the experimental procedures. Samples dried in the oven were handled with tissues (rather than bare fingers) at all times to keep fingerprints off the vial surfaces.

Ethylene glycol was used as an internal standard for the gas-chromatographic analysis of the aqueous-phase sample, and was added at this time. That sample was again weighed so that the exact amount of ethylene glycol added was known.

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The analytical techniques used to determine exact compositions are described above. Analysis was completed as soon as possible to avoid degradation of the samples.

c. Quaternary Systems

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 $35 \pm 0.02\,°C$. The liquid mixtures, treated as indicated below, were stirred in closed flasks in the constant-temperature bath for varying periods of time under a nitrogen atmosphere. The samples were taken from each phase using the same procedure discussed for the ternary systems.

To prepare the quaternary systems, appropriate quantities water, sodium sulfite, and sodium sulfate were brought together in the test flask to form a slightly subsaturated aqueous solution. Enough solvent was then added to the mixture such that salt crystallized out of the solution and an organic phase formed that was large enough to allow taking several samples. At that point, the mixture was stirred until the fresh, anhydrous salt crystals finished precipitating. Water was then added little by little until both liquid phases 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 simple 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. Since the hydrate-transition temperature for both salts is below 33 °C, and above this temperature only anhydrous sodium sulfite and sodium sulfate are present as solids, 35 °C was chosen for the temperature of the experiments; all experiments subsaturated in salt were held at this temperature.

The apparatus of Figure 1 was also used for the quaternary systems; the technique used

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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 was determined by iodimetric titration. 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 the results were averaged. However, since acetone reacts readily with iodine, when it was the solvent it had first to be removed before the titration. For this procedure the samples were first transferred into Erlenmeyer flasks, where they were agitated at a temperature of about 35 °C while the acetone evaporated under reduced pressure into a continuous flow of nitrogen to avoid oxidation of the sulfite. This procedure was followed with all samples containing acetone that were to be titrated iodimetrically.

Discussion of Accuracy

Many factors, both human and mechanical, affect the accuracy of the results presented in this work. The experimental procedure and analytical techniques described so far have been designed to minimize that error, and some of these measures are described.

Ensuring chemical and thermal equilibrium of the samples was of prime importance, since composition and temperature are the main variables in this system. The temperature of the water bath was carefully monitored and controlled, and agitation of both the bath and the sample solution was continuous. The temperature could be set to within $\pm$ 0.1 °C; however, temperatures near ambient were sometimes more difficult to maintain. For this reason, an overall temperature accuracy should probably be given as $\pm$ 0.2 °C. Also, an excess of time was allowed to ensure that equilibrium had been reached. Thermal steady state of the water bath usually occurred within half an hour, and thermal and chemical equilibrium of the sample solution within two hours. As four or more hours were allowed between samples, and the presence of a solid salt was always maintained in the sample cylinder, the data represent salt-

saturated equilibrium conditions.

Guarding against sample contamination was also incorporated into the experimental procedures. The liquid volume of each phase was large enough to allow withdrawal of all the necessary samples, and to ensure that none of the solid or other liquid phase was inadvertently taken up with the sample. The sampling tubes were also rinsed with the sample liquid before they were pumped into the sample vials. Cross contamination was also minimized by having a sampling tube for each phase.

All samples and sample vials were weighed on a Mettler H10 balance, accurate to within $\pm$ 0.0005 grams.

The GC analysis procedures were also carefully controlled. Calibration factors were determined for each phase; they spanned the entire range of sample results. For the aqueous-phase analysis, an internal standard of ethylene glycol was added to the sample, in an amount proportional to the concentration of the solvent. Because the formation of hydrated salt crystals could change the water concentration within the sample liquid, the internal standard was calibrated to the smaller solvent peak. This comparison lowered the precision of the results, and for this reason six runs were performed and averaged for each data point. The GC analysis of the aqueous-phase samples gives results with a standard deviation of $\pm$ 0.4 wt%.

The organic-phase samples had much more evenly-sized water and solvent GC peaks, and therefore direct analysis was performed. The results from these analyses were much less variable than those for the aqueous-phase samples, and for this reason only five runs were performed and averaged for each data point. This increase in precision gave results with a standard deviation of $\pm$ 0.3 wt%.

Accuracy of the atomic-absorption analysis is mainly dependent upon dilution precision, and signal fluctuations during testing. Dilution errors were minimized, and samples of known

concentrations were prepared and tested so that all sample dilutions would lie within the linear absorbance-versus-concentration range. Signal-fluctuation errors were minimized by testing each sample three times, and zeroing the absorbance signal with deionized water between each test. After all samples had been tested, each was run once more, to ensure an accurate result. The atomic- absorption analysis gives results with a standard deviation of $\pm$ 0.02 wt%.

The oven analysis performed on the aqueous-phase samples gave very good results as long as the weight percent was above about 10% salt. After analysis of all the aqueous-phase samples had been completed, the reserve aqueous-phase sample would be placed into the laboratory oven and its weight-percent salt calculated and compared to the previous sample result. The results always matched well, and the oven analysis gave results with a standard deviation of $\pm$ 0.05 wt%.

The standard deviations given so far relate to the specific procedures and analytical techniques discussed so far. However, if a fresh sample solution was prepared and analyzed, then not only analytical variations, but also sampling, weighing, and temperature variations had to be taken into consideration. Table 1 gives the final standard deviations expected from a complete analysis of this type.

EXPERIMENTAL RESULTS

Salt-Saturated Systems

The following sections give salt-saturated equilibrium compositions for the nine systems investigated. The data are tabulated in units of weight percent for each component for each of the liquid phases versus temperature. To retain as much information on a two-dimensional graph as possible, one may plot the weight-percent water on a salt-free basis in each phase as a function of temperature. These plots of liquid/liquid composition form a two-phase envelope, or coexistence curve, meeting at the temperature called the lower consolute point. Salt-saturated

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mixtures with a water/solvent ratio that lies inside the envelope will split into two liquid phases, while those outside the envelope remain as one liquid phase. All mixtures have only one liquid phase below the lower consolute point. Such a graph gives no indication of the salt content in either liquid phase; this information is available in the tables. However, the organic phases consistently have less than 10 wt% salt, and the aqueous phases usually have between 15 and 35 wt% salt.

The precise phase compositions vary from system to system, but the overall trends are similar. At the higher temperatures, the aqueous phase has very little solvent, and therefore the salt concentration is very close to the solubility of that salt in water at that particular temperature. Conversely, at the higher temperatures, the organic phase has its lowest water content, and therefore salt solubility is almost zero. Both phase compositions remain fairly constant until the temperature is decreased below the transition temperature for polyhydrate formation, about 32° to 35 °C, at which point the polyhydrated form of the salt becomes the stable solid phase. (Ting, *et al.*, (1992) showed that the transition temperature for these salts is not affected by the presence of a solvent.) As the temperature is decreased further, the aqueous solubility of the salt drops rapidly; the aqueous phase therefore absorbs more solvent, which depresses salt solubility still more, and the organic phase absorbs more water, causing an increase in its salt content. As the temperature continues to fall, this trend is followed until the two liquid phases become identical and hence only one liquid phase exists. The point at which the two liquid-phase compositions become equal is called the lower consolute point. Near the lower consolute point the compositions are such a strong function of temperature that it is nearly impossible to pinpoint consolute-point composition and temperature accurately. At the lowest temperature for which composition was determined for a given system, the aqueous-phase and organic-phase compositions are already decidedly different. This means that the lower

consolute-point temperature is necessarily lower than that lowest reported temperature. However, since the temperatures reported are accurate to within $\pm$ 0.2 °C, the lower consolute point temperature ($t_{consolute}$) is listed as 0.2 °C below the lowest reported two-phase temperature.

a. Sodium Sulfate, Na$_2$SO$_4$

The overall shape of these coexistence curves is a direct reflection of the salt-solubility behavior in pure water. For example, Figure 2 shows the solubility/temperature curve for sodium sulfate. The solubility is relatively constant at higher temperatures, where the solid phase is the anhydrous crystal, whereas below the transition temperature the decahydrate is stable and salt solubility is a strong function of temperature. (A corollary of this behavior is that the heat of solution of the anhydrous salt is quite small while the molar heat of solution of the decahydrate is somewhat greater than ten times the molar heat of fusion of ice.) This pattern is reflected in the ternary-phase behavior of the solvent/sulfate/water systems shown in Figure 3.

The relatively straight sides of the U-shaped curves in Figure 3 result from the reduced dependence of salt solubility on temperature above the transition temperature. The aqueous phase at these temperatures contains little solvent, its composition is nearly constant, and hence the composition of the organic phase is also nearly fixed. At temperatures between the anhydrite/polyhydrate-transition temperature and the lower consolute temperature, where salt solubility drops rapidly as the temperature falls, the compositions of the liquid phases become a strong function of temperature. This is reflected in the U-shape of the coexistence curves; as salt is removed from the aqueous phase the solvent can take its place.

Saturated equilibrium systems containing water, solvent, and sodium sulfate have been studied by previous researchers (Ting, *et al.*, 1992; Brenner, *et al.*, 1993). The data presented with 2-propanol and *t*-butanol as solvents with this salt (Brenner, 1992) are added to this work to show full comparison of all systems. Acetone was introduced as a new solvent because its

higher volatility is an advantage in some extractive-crystallization processes. Tables 2, 3 and 4 show saturated equilibrium data for the Na_2SO_4/water systems, with acetone, 2-propanol, and *t*-butanol, respectively, as solvents.

A solvent's ability to hydrogen-bond with water is a good measure of the behavior to expect in these systems. The three solvents studied here are all related structurally to propane. Acetone is the most hydrophilic because of its highly polar carbonyl oxygen; at the higher temperatures, the organic phase is about 50% water on a salt-free basis. 2-Propanol, a secondary alcohol, is less hydrophilic than acetone, and *t*-butanol, with its additional methyl group, is the least hydrophilic of the three. Molecular-thermodynamic modeling of these systems has not yet been accomplished, but the qualitative results follow expected trends.

The lower consolute temperature for all three solvents is near ambient, with acetone at 29.8 °C, 2-propanol at 28.8 °C, and *t*-butanol at 22.8 °C. Figure 3 also shows that above 35 °C the phase compositions remain nearly constant.

b. Sodium Sulfite, Na_2SO_3

Tables 5, 6 and 7 and Figure 4 show salt-saturated equilibrium data for the sodium sulfite/water systems, with acetone, 2-propanol, and *t*-butanol, respectively, as solvents, and upon first glance are similar to the sodium sulfate data presented above. The ability of these solvents to extract water from Na_2SO_3 solutions appears to follow the same order as that found for Na_2SO_4 solutions. Acetone extracts more water than 2-propanol, and more than twice as much as *t*-butanol, at temperatures above 30 °C. The order of lower consolute temperatures is also consistent with the Na_2SO_4 data; however, all dropped at least 2 °C, and the lower consolute temperature for *t*-butanol, 14.8 °C, is well below ambient temperature. This behavior is a reflection of the higher aqueous solubility of Na_2SO_3 at temperatures below 32 °C, shown in

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Figure 5 when compared to Figure 2. As was true with the Na_2SO_4 systems, the liquid-phase compositions change little with temperature above 35 °C.

c. Sodium Carbonate

Sodium carbonate is a more hydrophilic salt than either sodium sulfate or sodium sulfite, as is seen from the salt-saturated equilibrium data for Na_2CO_3 and the three solvents. Tables 8, 9, and 10 show saturated equilibrium data for the Na_2CO_3 systems, with acetone, 2-propanol, and t-butanol, respectively.

Because Na_2CO_3 is the more hydrophilic, an organic phase in equilibrium with its saturated aqueous solution will contain less water than an organic phase in equilibrium with a saturated aqueous solution containing either of the other two salts. This means that a saturated solution of sodium carbonate could be used to "dry" a stream of organic solvent that had been equilibrated with a saturated solution of either sodium sulfate or sulfite. "Dry" in this case is only a relative term; it is used to emphasize that, since water has been extracted from the solvent stream, that same solvent stream can then be recycled back to an extractive crystallizer to extract more water. This method of solvent regeneration has the advantage of operating isothermally, with relatively little heat effect, and therefore could give significant economic savings over simple distillation.

The order of the solvents' abilities to extract water from Na_2CO_3 solutions remains consistent, although at some temperatures the acetone and 2-propanol systems show very similar results. In common with the sulfate and sulfite systems, the phase compositions in equilibrium with $Na_2CO_3 \bullet H_2O$ remain relatively constant above about 33 °C, meaning that the extraction capacity of the solvent has been reached. The lower consolute temperatures are 24.8, 23.8, and 17.8 °C, for acetone, 2-propanol, and t-butanol, respectively. These temperatures are on the low side of ambient, and fall between the temperatures reported for sodium sulfate and sodium

sulfite. Figure 6, when compared to Figures 3 and 4, shows graphically the lower consolute

temperatures and drier solvent compositions shown by the sodium carbonate systems.

Subsaturated Systems

All of the equilibrium data presented thus far have been for salt-saturated liquid/liquid

systems, where saturation was ensured by having solid salt present in excess. However, in a

countercurrent liquid/liquid extractor, in which a concentrated aqueous solution is used to dry

a solvent-rich stream, subsaturation conditions will exist. For the extraction to proceed, there

must always be two distinct liquid phases present. Subsaturated liquid/liquid equilibrium data

were therefore obtained for each of the three salts, water, and each of the three solvents. The

resulting nine subsaturated two-phase envelopes determine the operating region for a liquid/liquid

extractor for a given salt/water/solvent system.

The temperature chosen was as close to ambient as possible while still far enough above

the lower consolute temperature to ensure that small temperature fluctuations did not result in

large composition changes. For all of the salts in this study a temperature of 35 °C met these

criteria.

a. Sodium Sulfate

Subsaturated data for the systems Na_2SO_4/water/ and acetone, 2-propanol and t-butanol

are presented in Tables 11, 12 and 13, respectively. Figure 7 is a ternary diagram of the data

for the 2-propanol system; tie lines connect the co-existing phase compositions. The estimated

plait point for this system is at a composition of about 7 wt% Na_2SO_4, 20 wt% 2-propanol and

73 wt% water.

b. Sodium Sulfite

Subsaturated data for the systems Na_2SO_3/water/ and acetone, 2-propanol and t-butanol

are presented in Tables 14, 15 and 16, respectively. Figure 8 is a ternary diagram of the data

for the acetone system, with tie lines connecting three of the co-existing phase compositions. In addition, saturation data for this system taken at a variety of temperatures are plotted on the same diagram. The purpose of this plot is to show that the composition of co-existing liquid phases depends more strongly on the water/solvent ratio than it does on the temperature. This observation can be useful in estimating unknown phase compositions under some conditions.

c. Sodium Carbonate

Tables 17, 18 and 19 give subsaturated equilibrium data for the sodium carbonate/water systems, with acetone, 2-propanol, and t-butanol, respectively, as solvents at 35 °C. All three subsaturated systems exhibit similar trends as the plait point is approached, where both the aqueous and organic-phase compositions show an increase in the weight fraction of water. Looking at the aqueous-phase compositions, the increase in the water content of that phase is accompanied by an increase in the weight fraction of solvent. However, the solubility of sodium carbonate in the pure solvent is very small, and therefore, as the solvent content increases, the weight fraction of Na_2CO_3 falls considerably. Considering the organic-phase behavior, increased water content and decreased solvent content lead to increased Na_2CO_3 solubility; however, the solvent content remains large enough to keep the weight fraction of Na_2CO_3 relatively low. The one exception to these trends is the aqueous-phase data presented in Table 18 for 2-propanol. Within the standard deviation limits stated in Table 1 the water content of aqueous-phase samples 5 through 8 remains approximately constant while the sodium-carbonate and 2-propanol compositions follow the aforementioned trends.

Quaternary Systems

As noted in the Experimental Section, the data on solubilities for systems containing both sodium sulfate and sulfite were taken at a single temperature, 35 °C; concentrations ranged from salt-saturated to near the plait point; and the solvents studied were limited to acetone and 2-

propanol since both were substantially more attractive from a process standpoint. The total amounts of the two salts added to the system in each case were in the molar ratios 75/25, 50/50 and 25/75. The solubility data for these systems are presented in Tables 20 and 21. The compositions of the quaternary systems could be represented by points within a regular tetrahedron. However, it simplifies interpretation of the results to use a ternary diagram where one of the corners is the sum of the weight fractions of the two salts. Such representation is useful for comparing the ability of the solvent to extract water and precipitate salt from the aqueous solution. The relative amounts of sulfite and sulfate are presented in separate columns in the two tables as their molar ratios in the aque

The phase compositions shown in Tables 20 and 21 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 lowest 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. The plait point is not easy to detect because in the region close to this point, small amounts of water added to the system cause large changes in the compositions of the two liquid phases. Ternary composition diagrams of these quaternary systems (the salts are combined as a single pseudocomponent) closely resemble the diagrams for the ternary systems but are not presented here because of space limitations. Again, acetone has the higher capacity to extract water. The data also show that in a system containing less sulfite than sulfate, more water can

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be extracted using a smaller amount of solvent.

The data presented in Tables 20 and 21 were analyzed to determine whether either solvent is effective for separating sulfite from sulfite. The separation factor for the distribution of the two salts between the organic and aqueous phases can be defined as:

$$\text{Separation Factor} \equiv ([SO_3^{-2}]/[SO_4^{-2}])_{Org.}/([SO_3^{-2}]/[SO_4^{-2}])_{Aq.}$$

where the terms in square brackets are concentrations in moles per liter and the numerator and denominator are simply the molar ratios listed in Tables 20 and 21. The separation factors for the acetone system, Table 20, are listed in Table 22. Within the scatter of the data there is no trend with concentration and the separation factor is unity. The separation factors for the 2-propanol system, Table 21, are listed in Table 23. Again, within the scatter of the data the separation factor is one. For both solvents, in other words, there is no tendency to separate sodium sulfite from sodium sulfate when either of these two solvents is used for extractive crystallization. It appears 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 two salts to be more soluble in either of the phases. This result is important because in many cases the feed to be treated will be a mixture of the two salts.

Conclusions

The data presented here show the technical feasibility of a low-energy process for recovering anhydrous sodium sulfate from an SO_2-scrubbing system such as shown in Figure 9, and provide the basis for the design of such a system. The SO_2 is produced by burning a high-sulfur fuel for process heat, and a solution (14) of soda ash (Na_2CO_3) is used to scrub it from the combustion gas. A portion of the bottoms product from the scrubber is recycled to the top, and the net feed of carbonate solution is controlled by monitoring the pH of the bottoms product. The scrubber is operated with minimal excess water in the liquor, as would also be done for

evaporative recovery of the sodium sulfate/sulfite from it. The spent scrubbing liquor is first aerated in a gas/liquid contactor to convert sulfite to sulfate, as needed, then fed (1) to the extractive-crystallization system together with regenerated solvent (3), either acetone or 2-propanol. This system would be operated at 35 to 50°C, and produce anhydrous sodium sulfate as product. (The product slurry (4) is filtered to separate the crystals (5) from the mother liquor (2); a portion of feed (1) is used to wash the crystals free of solvent.) The crystallizer operates at a temperature about 5 °C lower than that of the solvent drier. If the feed solution is significantly subsaturated with respect to sodium sulfate, then the feed would enter the top of the crystallizer and the upper section of the crystallizer would serve as a countercurrent extractor. The wet solvent (6) leaving the crystallizer is dried by countercurrent contact with a saturated solution of sodium carbonate (7) in a liquid/liquid extraction operation operated at about the same temperature as that for the extractive crystallization step. The dried solvent (8) is returned to the crystallizer while the diluted carbonate solution (9) is stripped of solvent. The feed (9) to the stripper is preheated by heat exchange with the bottoms product (11) in HX 1; streams (12) and (13) are the preheated feed and cooled product, respectively. The high activity coefficient of either solvent in a relatively concentrated solution of sodium carbonate leads to minimal energy consumption in the stripper. The vapor (10) leaving the top of the stripper is condensed and a portion is returned to the stripper to act as reflux; liquid stream 10) is thus nearly pure solvent. A portion of the stripper-bottoms stream (15) is used to dissolve additional soda ash (16) while the remainder (14) is returned to the scrubber. A water stream (not shown) must also be added to stream (15) to make up for water evaporated in the scrubber and the gas/liquid contactor, and entrained in the product crystals.

For a system in which the feed to the crystallizer is a 28 wt% solution of sodium sulfate and the solvent is acetone, the following compositions and flow ratios are found: The dried

solvent contains 25 wt% water and the ratio of dried solvent to feed solution is 1.2 on a weight basis. The wet solvent leaving the crystallizer contains 53 wt% water and 0.5 wt% Na_2SO_4 and has a flow of 1.9 kg/kg of feed solution. The flow of saturated (31 wt%) carbonate to the solvent drier is almost exactly equal to the flow of the entering wet solvent on a weight basis. The dilute carbonate solution leaving the solvent drier contains 22 wt% Na_2CO_3, 1.8 wt% acetone and 1.0 wt% Na_2SO_4 and has a flow of 2.6 kg/kg of feed solution. As noted above, after this solution is stripped of acetone, 65% is resaturated with soda ash and recycled to the solvent drier while the rest is sent to the SO_2 absorber. The steam consumption in the stripper reboiler is 1.5 kg/kg acetone in the stripper feed, or 0.07 kg/kq of feed solution to the system.

The energy required for the stripper reboiler for the system above is a very small fraction of the energy that would be required to recover anhydrous sodium sulfate from the feed solution by evaporative crystallization (or any other conventional process). The only other energy requirements are for pumping power and general utilities. This application is a special case of a more general process described by Lynn and Hanson (1986).

Acknowledgments

Literature Cited

Brenner, Doris K.; Eric W. Anderson, Scott Lynn and John M. Prausnitz "Liquid-Liquid Equilibria for Saturated Aqueous Solutions of Sodium Sulfate + 1-Propanol, 2-Propanol, or 2-Methylpropan-2-ol". *Journal of Chemical & Engineering Data* 37 419-422 (1992).

Jaecksch, Wendy L., "Liquid/Liquid/Solid Equilibria of Sodium Sulfate, Sodium Sulfite and Sodium Carbonate; Water; Acetone, 2-Propanol and t-Butanol" M.S. Thesis, Department of Chemical Engineering, University of California, Berkeley; (1993)

Jeffery, G.H.;J. Bassett; J Mendham; and R.C. Denney; "Vogel's Textbook of Quantitative Chemical Analysis"; Fifth Edition, John Wiley & Sons, Inc., New York, 1989, 389-398.
Lynn, Scott; Donald M. Hanson, "Method of Treating Aqueous Solutions". U.S. Patent 4,632,760, December 30, 1986.

Schiozer, Adriana L., "Quaternary Liquid/Liquid Equilibria of Sodium Sulfate, Sodium Sulfite and Water with Two Solvents: Acetone and 2-Propanol". M.S. Thesis, Department of Chemical Engineering, University of California, Berkeley; (1994)

Seidell, A.; "Solubilities of Inorganic and Metal-Organic Compounds"; Fourth Edition, Vol. 2, D. Van Nostrand Company, Inc.: New York, 1965; pp. 1117 - 1123

Weingaertner, David A.; Donald N. Hanson and Scott Lynn, "Extractive Crystallization of Salts from Concentrated Aqueous Solutions". *I. & E.C. Research* 30 490 - 501 (1991).

Ting, Andrew M.; Lynn, Scott; and Prausnitz, John M.; "Liquid-Liquid Equilibria for Aqueous Systems Containing N,N-diethylmethylamine and Sodium Chloride or Sodium Sulfate"; *J. Chem. Eng. Data* 37, 252-259 (1992)

List of Figures

Figure 1: Experimental Apparatus

1	insulation	8	Neoprene stopper
2	water bath	9	glass capillary
3	magnetic stirrer	10	air/nitrogen-supply tube
4	stir bar	11	organic phase
5	immersion heater	12	aqueous phase
6	stirrer	13	temperature controller
7	mixing tube	14	quartz thermometer
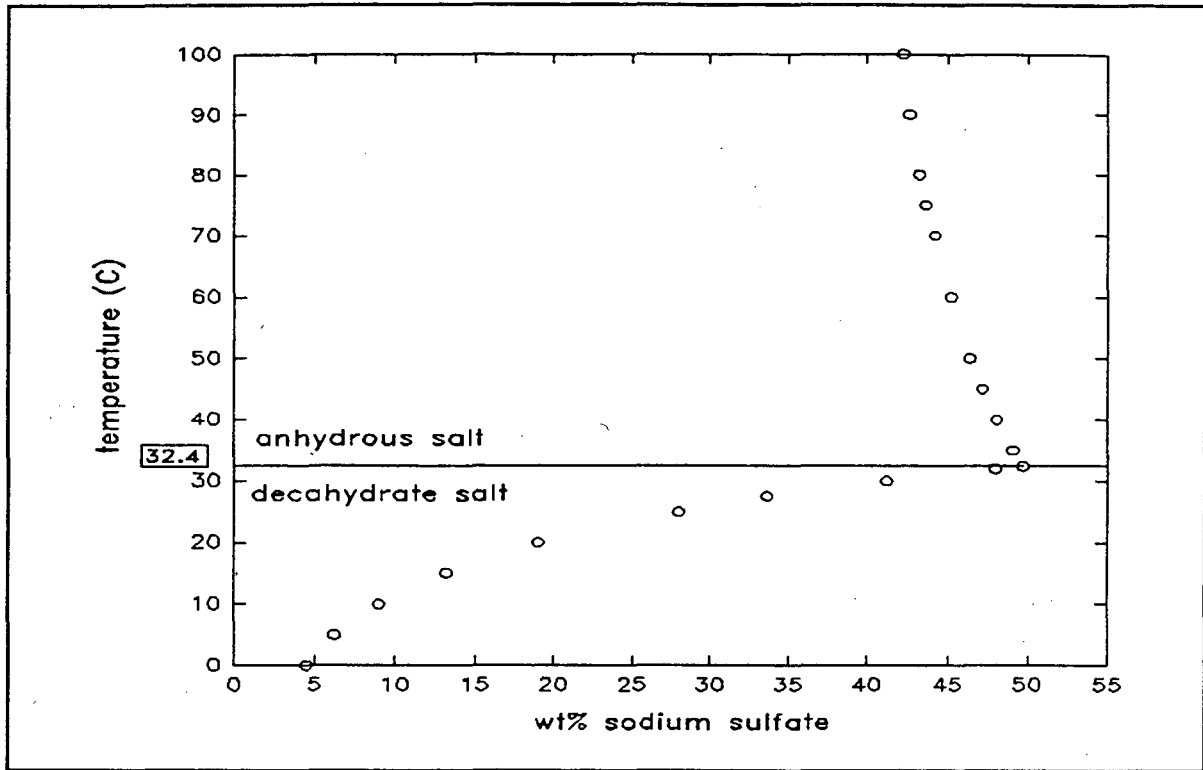
Figure 2
Solubility of Sodium Sulfate in Water (Seidell, 1958)

Coexistence Curves

Saturated Equilibrium data for Na_2SO_4
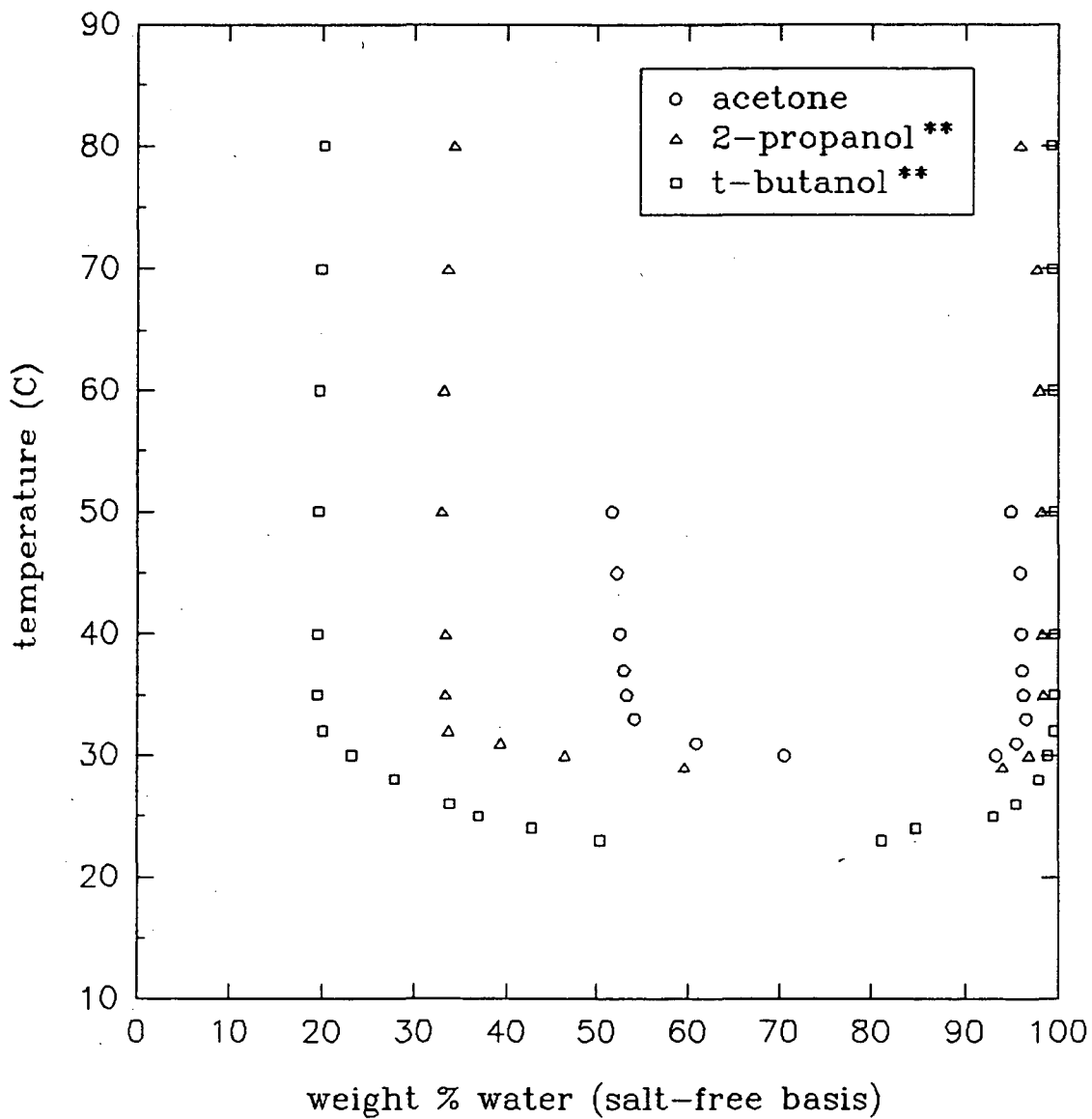
** Data determined by Brenner, 1992

Figure 3
Coexistence Curves for Na_2SO_4/Water/Solvent Systems
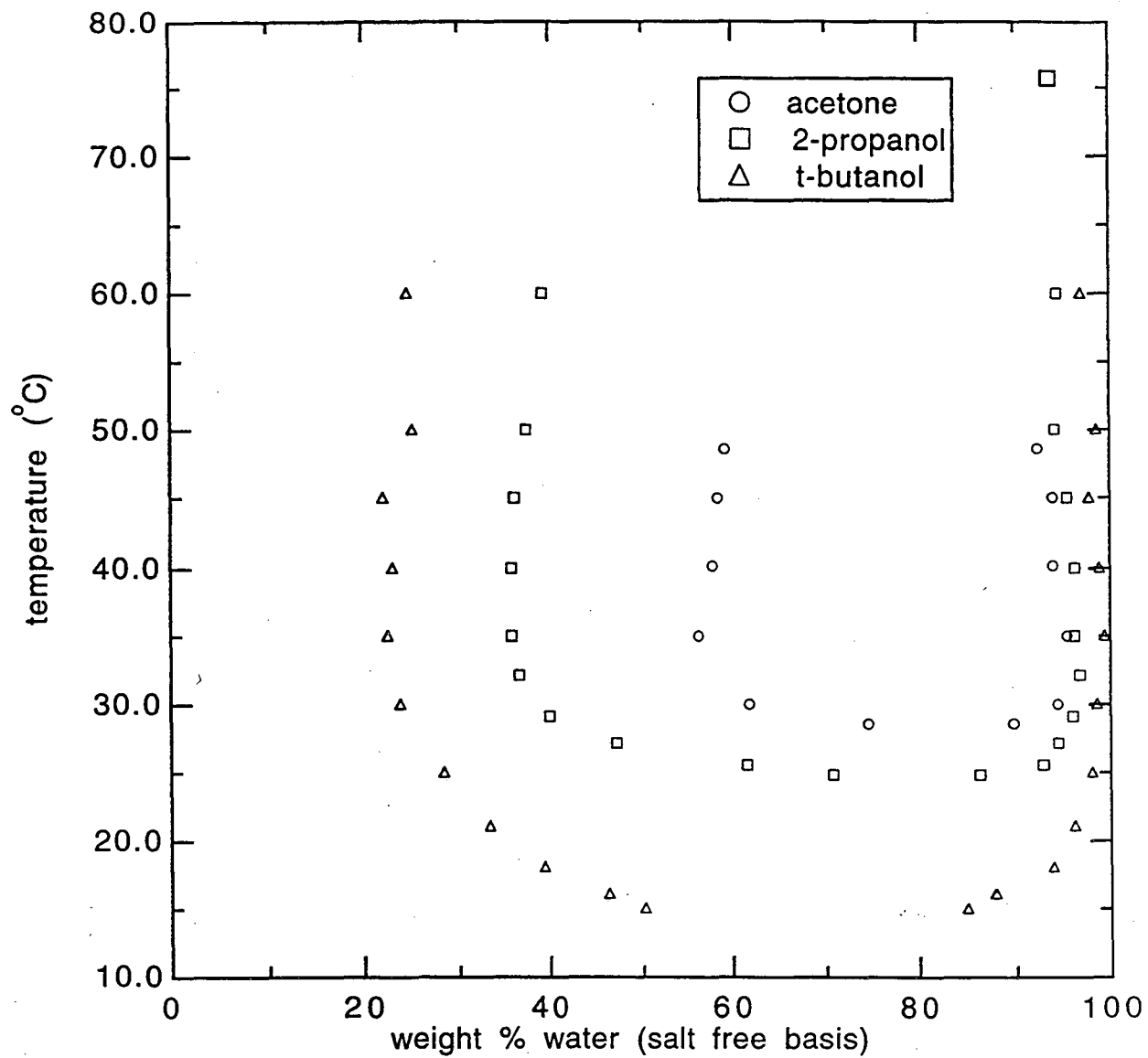
Figure 4
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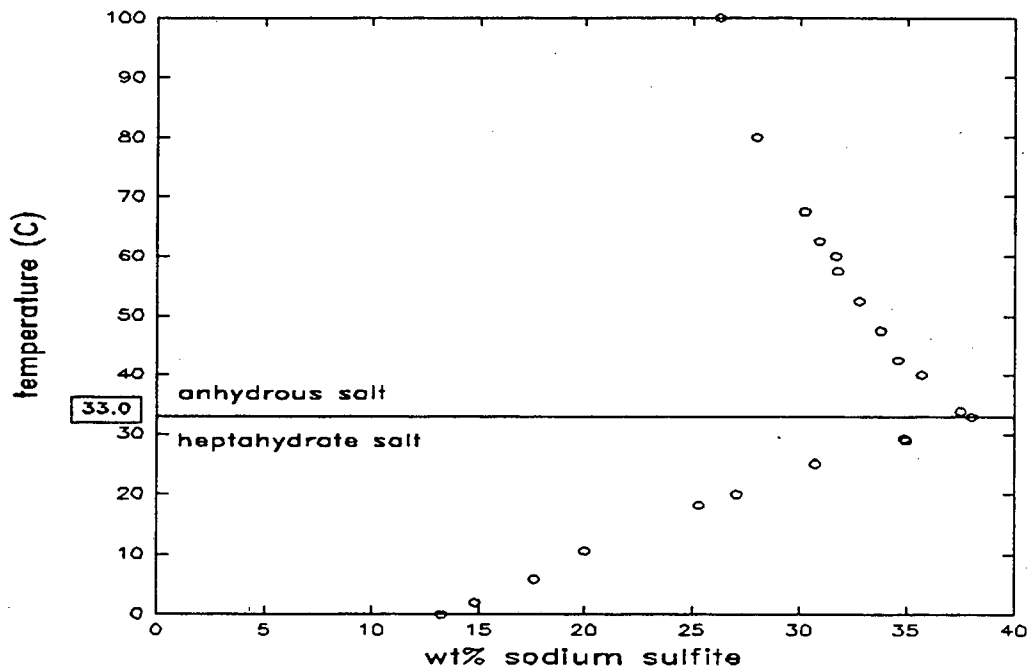
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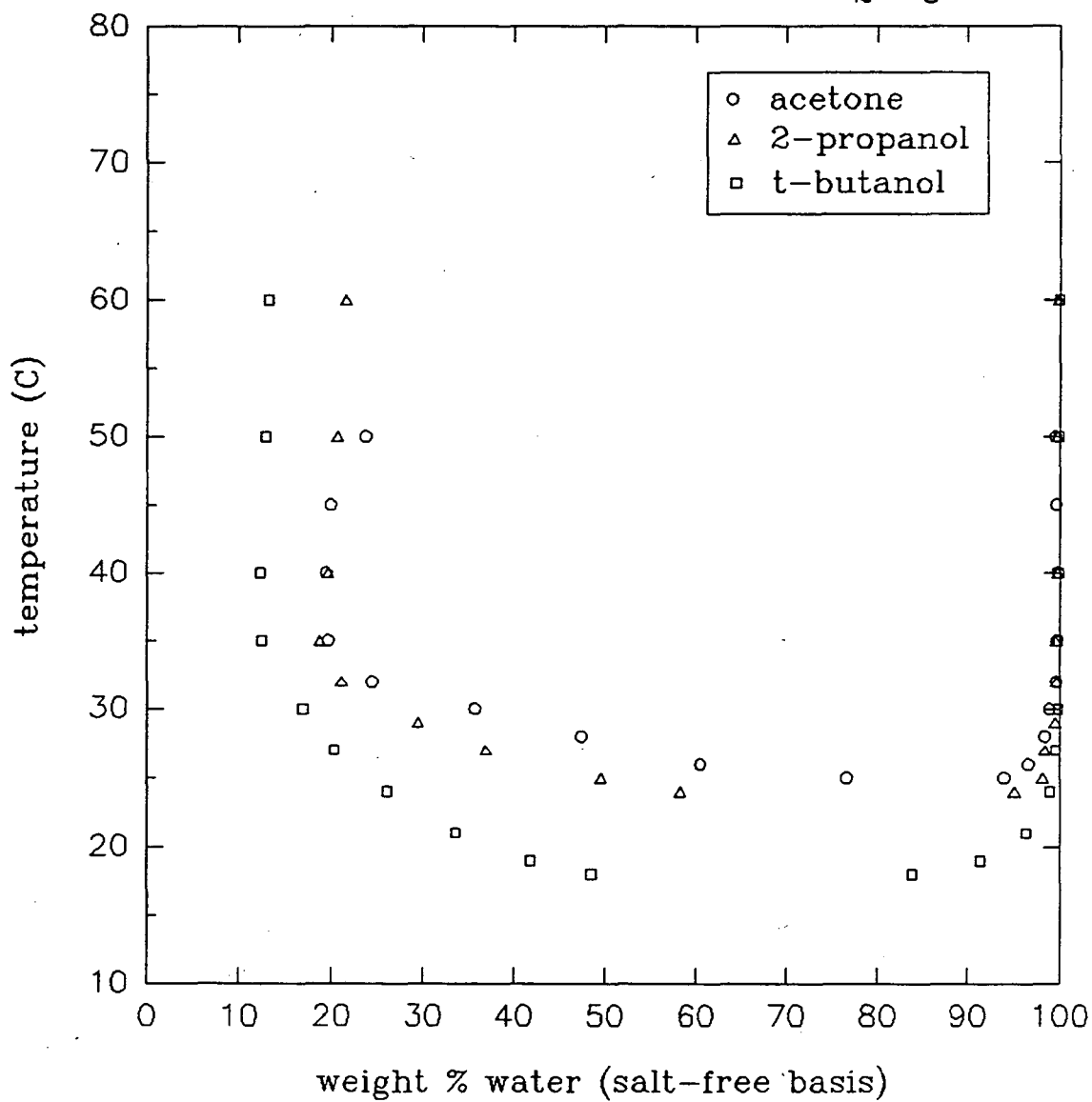
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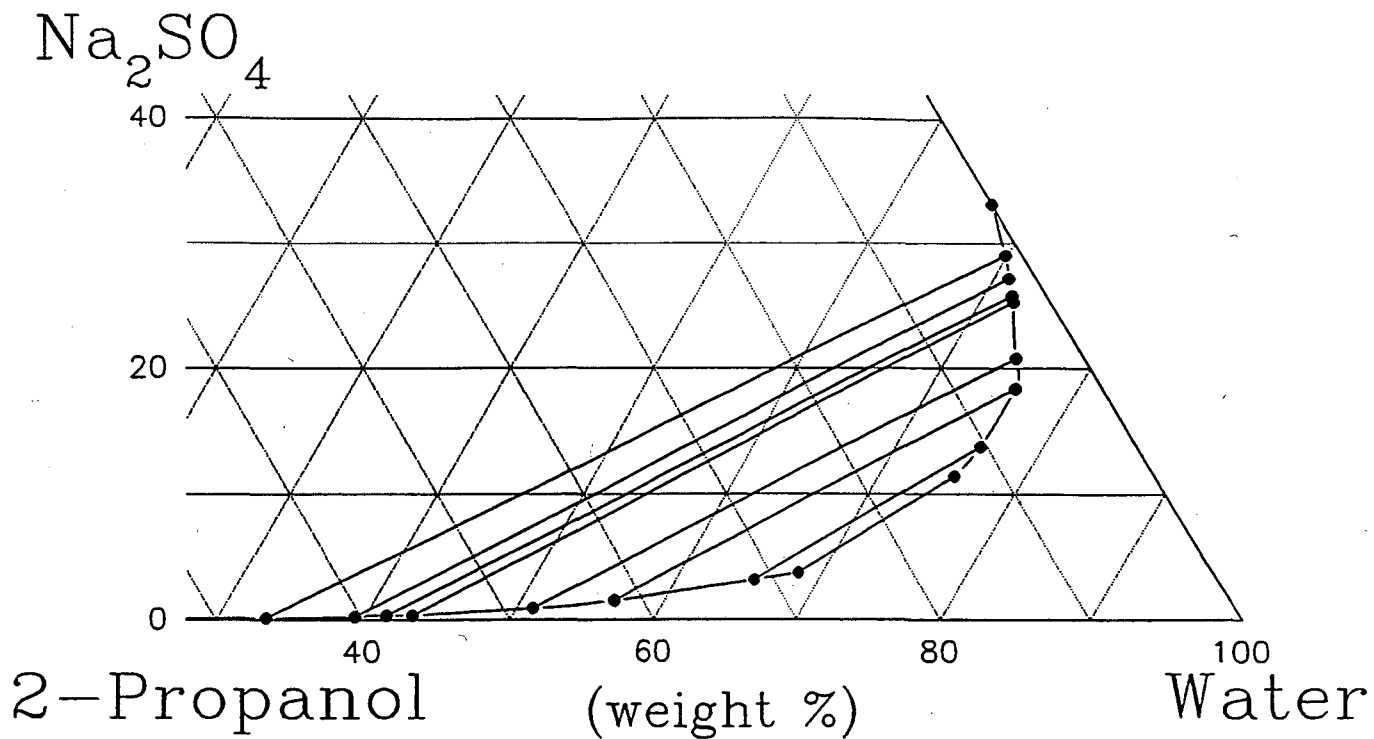
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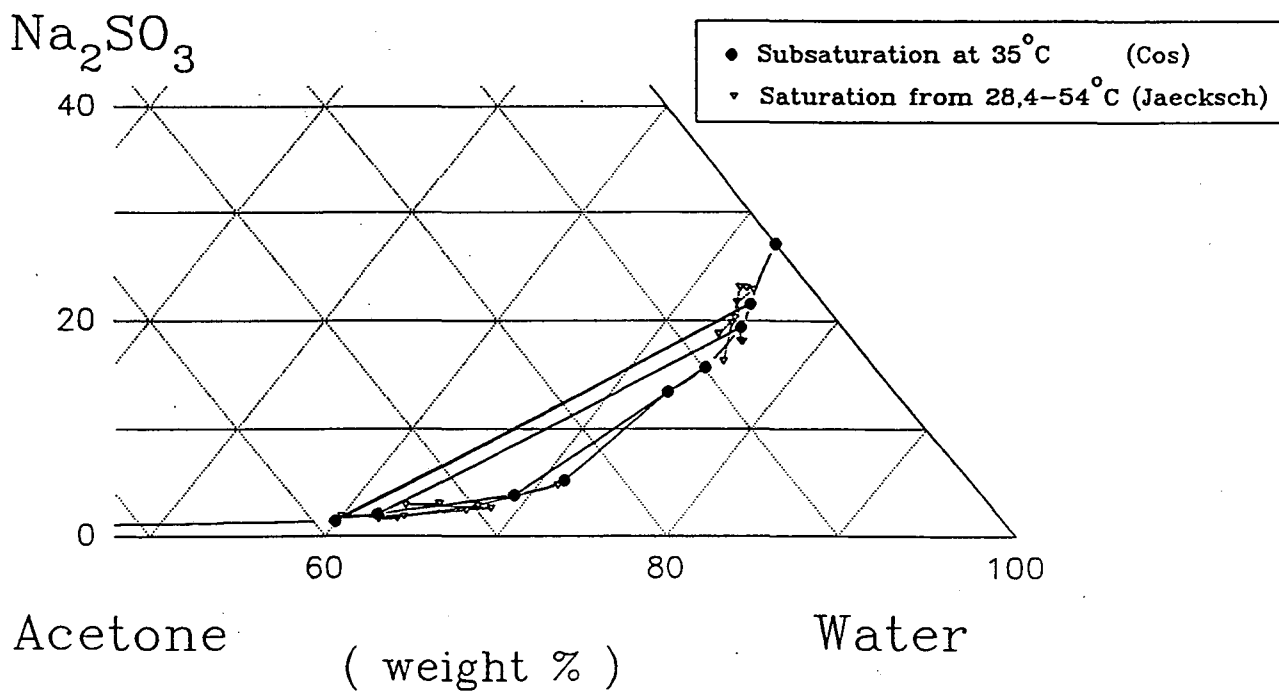
Figure 8: Subsaturation Equilibrium Data at 35 °C for Na₂SO₃/Water/Acetone
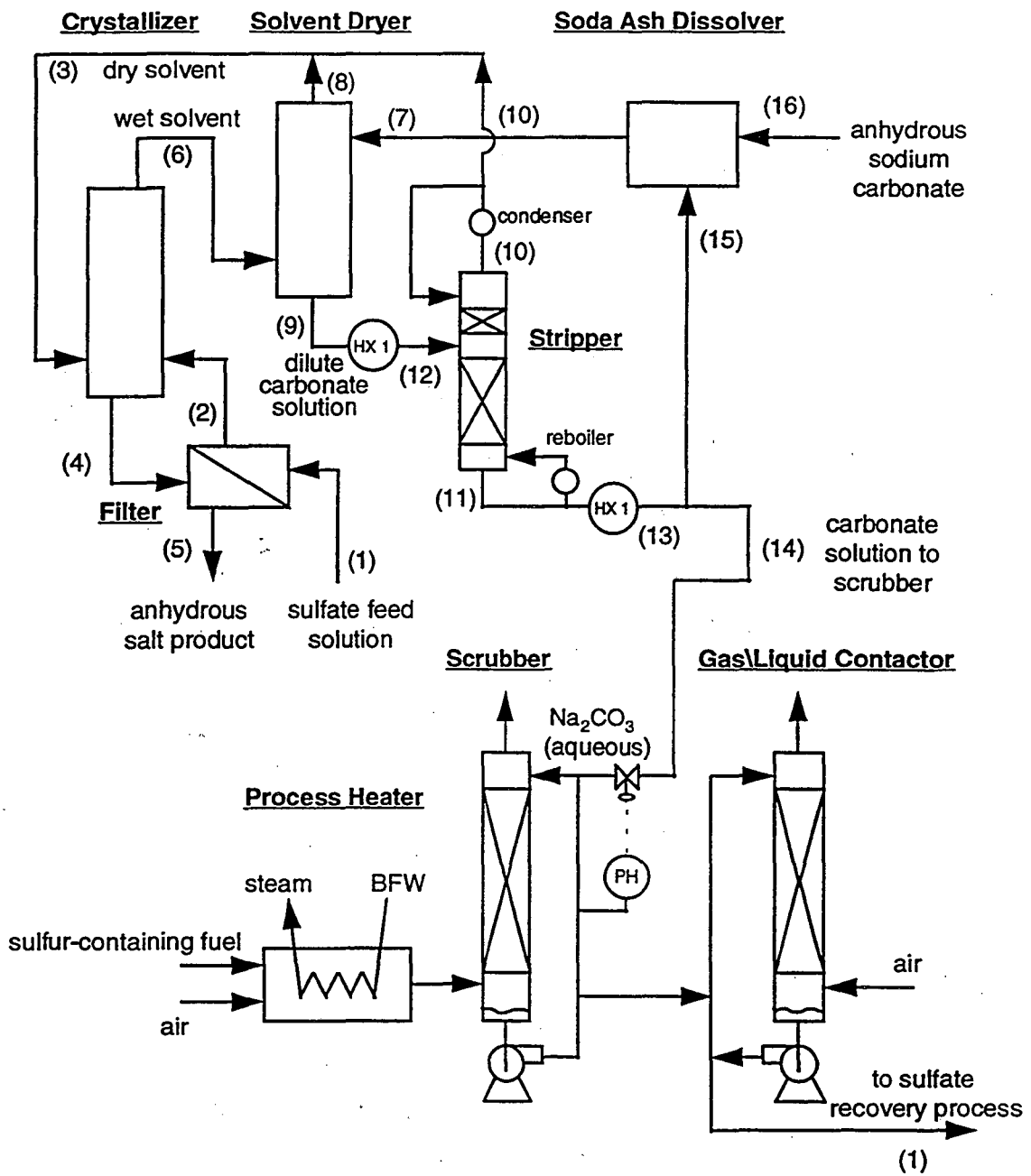
Figure 9

Low-Energy Extractive-Crystallization Process for Recovering
Anhydrous Na$_2$SO$_4$ from an SO$_2$-Scrubbing Liquor

PH = pH controller; BFW = boiler feed water.

Units marked HX 1 are the hot and cold sides of a single heat exchanger.

Table 1

Standard deviations of aqueous and organic samples

Phase	Component	Standard deviation (weight percent)
Aqueous	Salt	± 0.1
	Water	± 0.7
	Solvent	± 0.5
Organic	Salt	± 0.05
	Water	± 0.5
	Solvent	± 0.5

Table 2

Salt-Saturated Equilibrium Data: Na_2SO_4/Water/Acetone

$t_{consolute} \cong 29.8\,°C$

Temp. (°C)	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
	Na_2SO_4	Water	Acetone	Na_2SO_4	Water	Acetone
30	20.79	73.98	5.23	3.55	68.06	28.39
31	25.21	71.49	3.31	1.35	60.06	38.62
33	28.01	69.52	2.48	0.44	53.80	45.76
35	28.17	69.16	2.67	0.50	52.91	46.59
37	28.58	68.69	2.73	0.54	52.61	46.85
40	28.13	69.01	2.87	0.61	52.12	47.27
45	27.27	69.75	2.99	0.79	51.69	47.52
50	26.48	69.84	3.67	0.91	51.14	47.96

Table 3

Salt-Saturated Equilibrium Data: Na_2SO_4/Water/2-Propanol (Brenner, 1992)

$t_{consolute} \cong 28.8\,°C$

Temp. (°C)	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
	Na_2SO_4	Water	2-Propanol	Na_2SO_4	Water	2-Propanol
29	19.1	76.1	4.8	2.1	58.3	39.6
30	23.4	74.2	2.4	0.67	46.1	53.2
31	---	---	---	0.28	39.2	60.5
32	---	---	---	0.14	33.6	66.3
35	29.0	69.9	1.1	0.15	33.3	66.6
40	28.5	70.3	1.2	0.15	33.3	66.6
50	27.7	71.0	1.3	0.16	32.9	66.9
60	26.9	71.6	1.5	0.16	33.1	66.7
70	26.2	72.1	1.7	0.185	33.5	66.3
80	25.7	71.3	3.0	0.20	34.2	65.6

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Table 4

Salt-Saturated Equilibrium Data: Na_2SO_4/Water/t-Butanol (Brenner, 1992)

$$t_{consolute} \cong 22.8\,°C$$

Temp. (°C)	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
	Na_2SO_4	Water	t-Butanol	Na_2SO_4	Water	t-Butanol
23	4.6	77.4	18.0	0.88	49.9	49.2
24	8.2	77.8	14.0	0.37	42.6	57.0
25	13.6	80.4	6.0	0.20	36.9	62.9
26	16.2	80.0	3.8	0.13	33.8	66.1
28	21.5	76.9	1.6	0.07	27.8	72.1
30	27.1	72.07	0.83	0.04	23.2	76.8
32	30.9	68.76	0.34	0.035	20.1	79.9
35	31.5	68.24	0.26	0.025	19.5	80.5
40	30.8	68.93	0.27	0.04	19.5	80.5
50	30.0	69.66	0.34	0.02	19.6	80.4
60	28.9	70.7	0.40	0.02	19.7	80.3
70	28.7	70.81	0.49	0.02	19.9	80.1
80	28.0	71.46	0.54	0.02	20.2	79.8

Table 5

Salt-Saturated Equilibrium Data: Na_2SO_3/Water/Acetone

$t_{consolute} \cong 28.2\,°C$

Temp. (°C)	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
	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 6

Salt-Saturated Equilibrium Data: Na_2SO_3/Water/2-Propanol

$t_{consolute} \cong 24.5\,°C$

Temp. (°C)	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
	Na_2SO_3	Water	2-Propanol	Na_2SO_3	Water	2-Propanol
24.7	11.80	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	21.43	74.36	4.21	0.73	46.82	52.45
29	23.34	73.63	3.03	0.42	39.71	59.87
32	24.43	73.33	2.24	0.29	36.61	63.10
35	23.41	73.92	2.67	0.24	35.79	63.97
40	22.15	74.94	2.91	0.25	35.84	63.91
45	21.39	75.15	3.46	0.26	36.12	63.63
50	21.84	73.69	4.47	0.24	37.23	62.53
60	19.91	75.77	4.32	0.30	39.21	60.49

Table 7

Salt-Saturated Equilibrium Data: Na_2SO_3/Water/t-Butanol

$$t_{consolute} \cong 14.8\,°C$$

Temp. (°C)	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
	Na_2SO_3	Water	t-Butanol	Na_2SO_3	Water	t-Butanol
15	8.11	78.36	13.53	0.63	50.02	49.35
16	9.65	79.44	10.91	0.42	46.35	53.23
18	14.15	80.67	5.18	0.02	39.47	60.51
21	17.97	78.99	3.04	0.08	33.58	66.34
25	21.60	76.98	1.42	0.04	28.49	71.47
30	25.09	73.95	0.96	0.02	23.89	76.09
35	26.32	73.28	0.40	0.02	22.68	77.30
40	24.48	74.67	0.85	0.02	23.13	76.85
45	25.20	73.25	1.55	0.02	22.10	77.88
50	23.16	75.94	0.90	0.02	25.11	74.87
60	22.64	75.24	2.12	0.02	24.61	75.37

Table 8

Salt-Saturated Equilibrium Data: Na_2CO_3/Water/Acetone

$t_{consolute} \cong 24.8\,°C$

Temp. (°C)	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
	Na_2CO_3	Water	Acetone	Na_2CO_3	Water	Acetone
25	16.54	78.44	5.02	3.15	74.27	22.58
26	20.16	77.05	2.79	1.48	59.61	38.91
28	24.32	74.41	1.27	0.40	47.19	52.41
30	30.02	69.12	0.86	0.10	35.62	64.28
32	30.72	68.98	0.30	0.03	24.36	75.61
35	31.57	68.16	0.27	0.02	19.65	80.33
40	31.31	68.49	0.20	0.02	19.42	80.56
45	30.99	68.72	0.29	0.02	19.86	80.12
50	30.64	69.06	0.30	0.01	23.67	76.32

Table 9

Salt-Saturated Equilibrium Data: Na_2CO_3/Water/2-Propanol

$t_{consolute} \cong 23.8\,°C$

Temp. (°C)	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
	Na_2CO_3	Water	2-Propanol	Na_2CO_3	Water	2-Propanol
24	16.25	79.53	4.22	1.46	57.32	41.22
25	23.60	74.94	1.46	0.69	49.18	50.13
27	25.85	72.90	1.25	0.17	36.85	62.98
29	26.16	73.40	0.42	0.06	29.36	70.58
32	30.70	68.99	0.31	0.03	21.04	78.93
35	32.57	67.07	0.36	0.01	18.69	81.30
40	31.50	68.31	0.19	0.01	19.60	80.39
50	30.99	68.82	0.19	0.03	20.59	79.38
60	30.46	69.39	0.15	0.04	21.51	78.45

Table 10

Salt-Saturated Equilibrium Data: Na$_2$CO$_3$/Water/t-Butanol

$t_{consolute} \cong 17.8\,^\circ$C

Temp. (°C)	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
	Na$_2$CO$_3$	Water	t-Butanol	Na$_2$CO$_3$	Water	t-Butanol
18	6.25	78.62	15.13	0.51	48.26	51.23
19	9.87	82.35	7.78	0.25	41.71	58.04
21	15.59	81.28	3.13	0.09	33.57	66.34
24	20.37	78.70	0.93	0.03	25.96	74.01
27	24.55	75.10	0.35	0.02	20.36	79.62
30	28.15	71.69	0.16	0.01	16.89	83.10
35	32.56	67.30	0.14	0.005	12.51	87.49
40	32.04	67.85	0.11	0.005	12.35	87.65
50	31.49	68.42	0.09	0.005	12.90	87.10
60	30.76	69.16	0.08	0.006	13.15	86.84

Table 11
Subsaturation Equilibrium Data at 35°C: Na_2SO_4/Acetone/Water (Cos)

	Aqueous-Phase Compositions [wt %]			Organic-Phase Compositions [wt %]		
	Na_2SO_4	Acetone	Water	Na_2SO_4	Acetone	Water
binary[1]	33.1	---	66.9	---	---	---
sat.	28.96	2.04	69.00	0.79	44.72	54.49
	26.92	2.62	70.46	1.16	39.71	59.13
	24.68	2.87	72.45	2.16	33.51	64.33
	22.82	3.72	73.46	2.76	30.09	67.15
	20.16	6.25	73.59	3.90	24.65	71.45
	17.11	7.95	74.94	5.76	20.81	73.43

[1] Seidell

Table 12
Subsaturation Equilibrium Data at 35°C: Na_2SO_4/2-Propanol/Water (Cos)

	Aqueous-Phase Compositions [wt %]			Organic-Phase Compositions [wt %]		
	Na_2SO_4	2-PrOH	Water	Na_2SO_4	2-PrOH	Water
binary[1]	33.1	---	66.9	---	---	---
sat.[2]	29.0	1.1	69.9	0.15	66.55	33.30
	27.13	1.8	71.07	0.249	60.42	39.33
	25.79	2.28	71.93	0.359	58.22	41.42
	25.27	2.45	72.28	0.363	56.50	43.14
	20.75	4.52	74.73	0.911	47.97	51.12
	18.37	5.75	75.88	1.515	42.03	56.46
	13.79	10.43	75.78	3.17	31.38	65.45
	11.43	13.36	75.21	3.74	27.94	68.32

[1] Seidell
[2] Brenner

Table 13
Subsaturation Equilibrium Data at 35°C: Na_2SO_4/t-Butanol/Water (Cos)

	Aqueous-Phase Compositions [wt %]			Organic-Phase Compositions [wt %]		
	Na_2SO_4	t-Butanol	Water	Na_2SO_4	t-Butanol	Water
binary[1]	33.1	---	66.9	---	---	---
sat.[2]	31.5	0.26	68.24	0.0257	80.5	19.5
	28.41	0.349	71.24	0.0262	77.37	22.60
	25.92	0.905	73.17	0.0258	75.02	24.95
	21.84	1.68	76.48	0.0349	72.41	27.55
	18.52	3.09	78.39	0.0564	69.41	30.53
	13.81	5.37	80.82	0.101	65.95	33.95
	13.77	5.44	80.79	0.117	64.88	35.00
	11.74	6.48	81.78	0.121	64.43	35.45
	9.46	8.61	81.93	0.193	61.74	38.07
	7.32	12.45	80.23	0.299	57.31	42.39
	6.68	14.08	79.24	0.328	55.83	43.84
	6.74	13.68	79.58	0.351	55.01	44.64

[1] Seidell
[2] Brenner

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Table 14
Subsaturation Equilibrium Data at 35 °C: Na_2SO_3/Acetone/Water

	Aqueous-Phase Compositions [wt %]			Organic-Phase Compositions [wt %]		
	Na_2SO_3	Acetone	Water	Na_2SO_3	Acetone	Water
binary[1]	27.09	----	72.91	---	---	---
sat.	21.58	4.22	74.20	1.36	38.74	59.90
	19.42	5.84	74.74	2.06	35.94	62.00
	15.73	9.85	74.42	3.84	27.08	69.08
	13.48	13.15	73.37	5.19	23.47	71.34

[1] Seidell

Table 15
Subsaturation Equilibrium Data at 35 °C: Na_2SO_3/2-Propanol/Water

	Aqueous-Phase Compositions [wt %]			Organic-Phase Compositions [wt %]		
	Na_2SO_3	2-PrOH	Water	Na_2SO_3	2-PrOH	Water
binary[1]	27.09	---	72.91	---	---	---
sat.	23.41	2.67	73.92	0.24	63.97	35.79
	21.17	3.59	75.24	0.304	61.74	37.95
	18.22	5.55	76.23	0.553	54.90	44.54
	15.19	8.07	76.74	1.04	48.50	50.46
	13.76	10.04	76.20	1.33	44.56	54.11
	9.93	16.43	73.64	2.9	34.43	62.67

[1] Seidell

Table 16
Subsaturation Equilibrium Data at 35 °C: Na_2SO_3/t-Butanol/Water

	Aqueous-Phase Compositions [wt %]			Organic-Phase Compositions [wt %]		
	Na_2SO_3	t-Butanol	Water	Na_2SO_3	t-Butanol	Water
binary[1]	27.09	---	72.91	---	---	---
sat.	26.32	0.40	73.28	0.0168	77.3	22.68
	24.21	0.77	75.02	0.0145	78.24	21.75
	22.48	1.18	76.35	0.0350	76.42	23.54
	20.93	1.52	77.55	0.0163	76.41	23.57
	17.26	2.56	80.18	0.0480	71.52	28.43
	13.13	4.72	82.15	0.0750	67.46	32.47
	10.36	7.30	82.34	0.113	64.50	35.39
	7.98	10.55	81.48	0.183	60.90	38.91
	7.02	11.64	81.34	0.227	60.32	39.45

[1] Seidell

Table 17
Subsaturated Equilibrium Data at 35 °C: Na_2CO_3/Water/Acetone

Sample No.	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
	Na_2CO_3	Water	Acetone	Na_2CO_3	Water	Acetone
1	30.71	68.79	0.50	0.01	25.98	74.01
2	29.66	69.85	0.49	0.02	30.42	69.56
3	25.51	73.30	1.19	0.02	37.62	62.36
4	24.31	74.46	1.23	0.04	43.91	56.05
5	22.01	75.74	2.25	0.12	52.11	47.77
6	18.56	77.50	3.94	0.38	59.29	40.33
7	15.27	78.56	6.17	1.89	66.41	31.70

Table 18

Subsaturated Equilibrium Data at 35 °C: Na_2CO_3/Water/2-Propanol

Sample No.	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
	Na_2CO_3	Water	2-Propanol	Na_2CO_3	Water	2-Propanol
1	26.70	72.79	0.51	0.03	24.71	75.26
2	25.84	73.39	0.77	0.06	28.44	71.50
3	23.89	74.58	1.53	0.11	32.79	67.10
4	21.56	76.71	1.73	0.15	37.15	62.70
5	18.40	79.12	2.48	0.27	43.28	56.45
6	17.02	78.54	4.44	0.54	48.22	51.24
7	14.67	79.31	6.02	0.95	54.82	44.23
8	12.14	78.00	9.86	1.56	60.48	37.96

Table 19

Subsaturated Equilibrium Data at 35 °C: Na_2CO_3/Water/t-Butanol

Sample No.	Aqueous-phase compositions (weight %)			Organic-phase compositions (weight %)		
	Na_2CO_3	Water	t-Butanol	Na_2CO_3	Water	t-Butanol
1	29.21	70.64	0.15	0.005	16.68	83.31
2	26.68	73.06	0.26	0.006	18.88	81.11
3	24.16	75.21	0.63	0.01	21.42	78.57
4	21.89	77.31	0.80	0.02	23.51	76.47
5	19.43	79.40	1.17	0.02	25.49	74.49
6	16.25	81.58	2.17	0.03	28.83	71.14
7	13.23	83.16	3.61	0.05	32.67	67.28
8	11.73	83.86	4.41	0.06	34.55	65.39
9	8.70	85.82	5.48	0.09	36.67	63.24
10	8.54	84.87	6.59	0.44	37.59	61.97

Table 20

Equilibrium Data: Na₂SO₃/Na₂SO₄/Acetone/Water at 35°C with a Salt Ratio of

$Na_2SO_3/Na_2SO_4/Acetone/Water$ at 35°C with a Salt Ratio of

25 mol% Sulfite to 75 mol% Sulfate

Sample Number	Aqueous-phase compositions (weight %)				Organic-phase compositions (weight %)			
	$Na_2SO_3+Na_2SO_4$	Water	Acetone	Mole Ratio $[SO_3^{-2}]/[SO_4^{-2}]$ (Aqueous)	$Na_2SO_3+Na_2SO_4$	Water	Acetone	Mole Ratio $[SO_3^{-2}]/[SO_4^{-2}]$ (Organic)
1	29.10	69.83	1.07	0.245	0.35	43.10	56.55	0.261
2	27.78	70.97	1.25	0.235	0.72	50.12	49.16	0.250
3	25.86	72.50	1.64	0.229	1.26	57.21	41.53	0.255
4	23.53	73.65	2.82	0.254	2.29	64.61	33.10	0.242

50 mol% Sulfite to 50 mol% Sulfate

Sample Number	$Na_2SO_3+Na_2SO_4$	Water	Acetone	Mole Ratio (Aqueous)	$Na_2SO_3+Na_2SO_4$	Water	Acetone	Mole Ratio (Organic)
1	26.21	72.30	1.49	0.492	0.45	49.07	50.48	0.511
2	23.81	74.15	2.04	0.482	0.88	55.48	43.64	0.515
3	21.35	75.99	2.66	0.482	2.01	60.04	37.95	0.482
4	18.69	77.49	3.82	0.497	2.99	64.11	32.90	0.491

75 mol% Sulfite to 25 mol% Sulfate

Sample Number	$Na_2SO_3+Na_2SO_4$	Water	Acetone	Mole Ratio (Aqueous)	$Na_2SO_3+Na_2SO_4$	Water	Acetone	Mole Ratio (Organic)
1	26.21	72.30	1.49	0.740	0.45	49.07	50.48	0.725
2	23.81	74.15	2.04	0.749	0.88	55.48	43.64	0.735
3	21.35	75.99	2.66	0.727	2.01	60.04	37.95	0.736
4	18.69	77.49	3.82	0.756	2.99	64.11	32.90	0.742

Table 21
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

Sample Number	Aqueous-phase compositions (weight %)				Organic-phase compositions (weight %)			
	$Na_2SO_3+Na_2SO_4$	Water	Propanol	Mole Ratio $[SO_3^{-2}]/[SO_4^{-2}]$ (Aqueous)	$Na_2SO_3+Na_2SO_4$	Water	Propanol	Mole Ratio $[SO_3^{-2}]/[SO_4^{-2}]$ (Organic)
1	32.14	67.20	0.66	0.223	0.11	25.43	74.46	0.257
2	27.79	71.04	1.18	0.242	0.24	31.43	68.33	0.248
3	25.62	72.93	1.45	0.249	0.38	35.78	63.84	0.243
4	23.97	74.36	1.67	0.252	0.41	38.95	60.63	0.268
5	21.77	75.97	2.26	0.268	0.81	45.15	54.04	0.257
6	20.98	76.21	2.81	0.262	0.89	46.50	52.61	0.241
50 mol% Sulfite to 50 mol% Sulfate								
1	28.94	69.97	1.10	0.486	0.13	27.85	72.02	0.493
2	25.79	72.83	1.38	0.501	0.24	33.51	66.25	0.522
3	22.86	75.29	1.86	0.491	0.45	39.59	59.96	0.515
4	21.50	76.10	2.40	0.505	0.65	42.73	56.62	0.475
5	20.16	76.80	3.05	0.498	0.87	46.03	53.10	0.489
75 mol% Sulfite to 25 mol% Sulfate								
1	32.14	67.20	0.66	0.771	0.11	25.43	74.46	0.753
2	27.79	71.04	1.18	0.781	0.24	31.43	68.33	0.759
3	25.62	72.93	1.45	0.749	0.38	35.78	63.84	0.768
4	23.97	74.36	1.67	0.747	0.41	38.95	60.63	0.757
5	21.77	75.97	2.26	0.761	0.81	45.15	54.04	0.752
6	20.98	76.21	2.81	0.764	0.89	46.50	52.61	0.741

Table 22

Separation Factors for $Na_2SO_3/Na_2SO_4/Acetone/Water$ at 35 °C

Separation Factor $\equiv ([SO_3^{-2}]/[SO_4^{-2}])_{Org.}/([SO_3^{-2}]/[SO_4^{-2}])_{Aq.}$

Sample Number	Overall Composition: $(SO_3^{-2}/SO_4^{-2})_{Total}$		
	0.25	0.50	0.75
1	1.06	1.04	0.98
2	1.06	1.07	0.98
3	1.11	0.94	1.01
4	0.95	0.99	0.98

Table 23

Separation Factors for $Na_2SO_3/Na_2SO_4/2\text{-Propanol}/Water$ at 35 °C

Separation Factor $\equiv ([SO_3^{-2}]/[SO_4^{-2}])_{Org.}/([SO_3^{-2}]/[SO_4^{-2}])_{Aq.}$

Sample Number	Overall Composition: $(SO_3^{-2}/SO_4^{-2})_{Total}$		
	0.25	0.50	0.75
1	1.15	1.04	0.98
2	1.02	1.04	0.97
3	0.98	1.05	1.02
4	1.06	1.06	1.01
5	0.96	0.98	0.99

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