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Liquid–Liquid Equilibria for Saturated Aqueous Solutions of Sodium Sulfate + 1-Propanol, 2-Propanol, or 2-Methylpropan-2-ol

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Liquid–liquid equilibria were determined for ternary systems containing sodium sulfate, water, and a polar organic solvent. Three solvents were studied: 1-propanol, 2-propanol, and 2-methylpropan-2-ol (*tert*-butyl alcohol). In the salt-saturated two-phase region, data were obtained in the temperature range between the lower consolute temperature and 80 °C. In the one-phase region, the solubility of sodium sulfate was measured at 20 and 25 °C at different solvent/water ratios.

Introduction

Salts are generally recovered from aqueous solutions by crystallization. If the solubility of the salt in aqueous solution varies appreciably with temperature, it is sufficient to heat or cool a saturated solution to precipitate the solid salt. If the solubility of the salt is relatively constant with temperature, salt can be precipitated by evaporating water. However, evaporation of water has a high energy cost. An economically promising process alternative is provided by extractive crystallization: evaporation of water is avoided by using a second solvent that is able to extract water.

Extractive crystallization has been discussed by Weingaertner et al. (*1*) and Ting et al. (*2*). Previously published papers give data for ternary systems containing water and different solvents and salts: 1-butanol and 1-propanol with sodium carbonate, 2-propanol and diisopropylamine (DIPA) with sodium chloride (*1*), and *N*,*N*-diethylmethylamine (DEMA) with sodium chloride and sodium sulfate (*2*).

The experimental work presented here was conducted to determine suitability of different solvents for extractive crystallization of sodium sulfate. Experimental results are given for 2-propanol, 1-propanol, and 2-methylpropan-2-ol (*tert*-butyl alcohol).

Experimental Section

Chemicals. Solvents used were Fisher Scientific 2-propanol (spectranalyzed), Aldrich 1-propanol (99+ %), and Mallinckrodt *tert*-butyl alcohol (analytical reagent). Ethylene glycol was supplied by Fisher Scientific. Baker analyzed anhydrous sodium sulfate served as the electrolyte. Distilled water was deionized with a Barnstead Nanopure ultrapure water system.

Apparatus and Procedure. The experimental apparatus and procedures are the same as those previously described for the saturated DEMA + water + sodium chloride system (*2*). Liquid–liquid equilibrium compositions were determined for systems saturated with sodium sulfate. To determine the lower consolute temperature, a mixture of organic solvent, water, and salt with an overall solvent/water ratio intermediate between the two liquid phases was cooled to a temperature where only a single liquid phase remained in contact with solid sodium sulfate. In addition to liquid–liquid equilibria for systems saturated with salt, two other types of phase equilibria were measured. Below the lower consolute temperature, solubility of sodium sulfate at 20 and 25 °C and various organic solvent/water ratios was measured for all three solvents. The analytical techniques were those applied for the organic phase in the two-phase region. In addition, liquid–liquid equilibria were measured for 2-propanol and water at 35 °C with less sodium sulfate than would dissolve at saturation. At 35 °C, the solubility of sodium sulfate in pure water reaches a relatively high value of 32.9 wt % (*3*).

Analytical Methods. Gas chromatography was used to measure the relative amounts of water and solvent in the organic phase and the amount of solvent and an internal standard in the aqueous phase. Compatibility with water was a major reason for selecting a 30-m × 0.53-mm-i.d. × 3.0-μm J & W Scientific DB-624 column for the separation. Helium was the carrier gas and the capillary makeup gas for the thermal-conductivity (TCD) detector. The gas in the cylinders had a manufacturer-guaranteed purity of 99.995%. An Alltech oxygen trap and a Molecular Sieve 5 A chemical filter installed in the carrier-gas flow line served as further protection against contamination of the column.

A Hewlett-Packard 5890 A gas chromatograph was used for analysis. Samples were injected in a split capillary inlet. The injector temperature was 190 °C. The initial head pressure was set at 14 kPa. A total carrier flow of 100 mL/min produced a column flow rate of approximately 4 mL/min. The septum purge flow rate was 5 mL/min. The capillary makeup gas flow rate and the reference gas flow rate were 6 and 25 mL/min, respectively. A constant oven temperature of 120 °C proved adequate for separating the components. A thermal-conductivity detector was selected to allow detection of water. The detector temperature was set at 180 °C.

The detected signal was integrated with a Hewlett-Packard 3392 A integrator. From the area percent measured by the integrator, the weight ratio of solvent to water in the organic phase was determined with the calibration factor CF in eq 1.

$$\mathrm{CF} = \left(\frac{\mathrm{mass(water)/g}}{\mathrm{mass(solvent)/g}}\right)\left(\frac{\mathrm{area(solvent)}}{\mathrm{area(water)}}\right) \quad (1)$$

All injections were made with a Hamilton 1-μL syringe 7001-N. The injection amount for the organic-phase samples and calibration standards was 0.2 μL. The number of injections was five for the sample analysis. The area percents

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Table I. 1-Propanol + Water + Na_2SO_4(satd) Equilibrium Data

temp	organic-phase composition (wt %)			aqueous-phase composition (wt %)		
(°C)	Na_2SO_4	1-PrOH	water	Na_2SO_4	1-PrOH	water
23.5	0.865	52.2	46.9	8.1	14.5	77.4
25	0.41	61.2	38.3	12.4	6.7	80.9
26	0.29	64.8	34.9	15.7	4.6	79.7
27	0.205	67.4	32.4	17.9	3.15	78.95
29	0.105	72.3	27.6	22.2	1.7	76.1
31	0.054	76.9	23.1	27.2	0.85	71.95
35	0.048	78.8	21.2	29.7	0.63	69.67
40	0.055	78.4	21.6	29.5	0.67	69.83
50	0.059	77.4	22.6	29.6	0.77	69.63
60	0.076	75.9	24.0	28.5	0.98	70.52
70	0.110	74.5	25.4	27.5	1.2	71.3
80	0.125	73.2	26.7	26.9	1.35	71.75

Table II. 2-Propanol + Water + Na_2SO_4(satd) Equilibrium Data

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

Table III. 2-Methylpropan-2-ol + Water + Na_2SO_4(satd) Equilibrium Data

temp	organic-phase composition (wt %)			aqueous-phase composition (wt %)		
(°C)	Na_2SO_4	*t*-BuOH	water	Na_2SO_4	*t*-BuOH	water
23	0.88	49.2	49.9	4.6	18	77.4
24	0.37	57.0	42.6	8.2	14	77.8
25	0.20	62.9	36.9	13.6	6.0	80.4
26	0.13	66.1	33.8	16.2	3.8	80.0
28	0.07	72.1	27.8	21.5	1.6	76.9
30	0.04	76.8	23.2	27.1	0.83	72.07
32	0.035	79.9	20.1	30.9	0.34	68.76
35	0.025	80.5	19.5	31.5	0.26	68.24
40	0.04	80.5	19.5	30.8	0.27	68.93
50	0.02	80.4	19.6	30.0	0.34	69.66
60	0.02	80.3	19.7	28.9	0.40	70.7
70	0.02	80.1	19.9	28.7	0.49	70.81
80	0.02	79.8	20.2	28.0	0.54	71.46

were averaged. The mass ratio of solvent and water was determined from eq 1 after CF was determined by calibration.

Since the solvent concentration in the aqueous phase is very low, water and solvent peak sizes are very different; direct comparison of the water and solvent peaks does not give satisfactory results. Ethylene glycol was used as an internal standard for the aqueous phase: A known quantity of ethylene glycol, close to the expected amount of solvent in the aqueous phase, was added to the aqueous samples before the chromatographic analysis. The amount of solvent in the aqueous phase was determined by comparing the peak areas for the solvent and ethylene glycol; peak areas were converted to mass ratios using eq 1 with the calibration factor CF set by analyzing known aqueous solutions of solvent and ethylene glycol.

The injection amount was 1 μL for the aqueous-phase samples. This higher injection amount was chosen to compensate for the small peaks of the solvent and the internal standard. The amount of water in the aqueous phase was calculated by difference from the analytically determined amounts of solvent and salt.

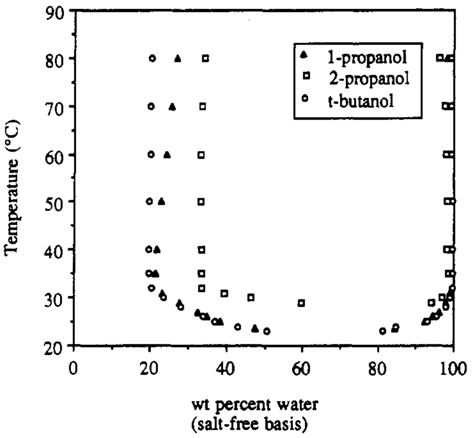

Figure 1. Coexisting liquid phases for 1-propanol, 2-propanol, and 2-methylpropan-2-ol (*tert*-butyl alcohol) and water saturated with Na_2SO_4.

A Perkin-Elmer 2280 atomic absorption spectrophotometer was used for measuring the salt concentration in the organic phase. A Perkin-Elmer Intensitron sodium lamp served to detect the sodium amount in the sample. The fuel–oxidant combination for the flame was acetylene and air.

For the standards, 2.542 g of NaCl (i.e., 1 g of sodium, Na^+) was dissolved in water and diluted to 1 L. A Gilson 1000-μL micropipet was used to aspirate 0.5 and 1 mL of this concentrated stock solution to prepare standards containing 0.5 and 1 mg of sodium/L of solution. Class A 1-liter volumetric flasks were employed for all dilutions. To minimize contamination, all glassware was cleaned with sulfuric acid and rinsed with deionized water.

For sodium, the Perkin-Elmer spectrophotometer manual gives a linear range from 0 to 1 mg of sodium/L of solution. Analyzing the two standards and comparing the respective signals indicated a slight deviation from linearity at 1 mg of sodium/L of solution. To insure applicability of Beer's law, the samples were diluted to yield a concentration of 0.5 mg of sodium/L of solution.

The diluted standards and samples were stored in plastic bottles; about 0.1 wt % potassium ion (K^+) as KCl was added to each to prevent ionization interference of the sodium. It was verified that 2-propanol had no influence on the atomic absorption analysis by adding 1 g of 2-propanol (an approximation to the expected sample matrix) to a 1 mg of Na^+/L of standard and comparing the absorbance signal to that of the propanol-free standard. There is no matrix interference of the solvents in this concentration range.

A 1-mg sample of sodium, Na^+, is equivalent to 3.0893 mg of Na_2SO_4/L of solution. Equation 2 gives the relation used to determine the amount of salt in a sample by comparing its absorbance signal AS to that of a standard with a known amount of salt.

$$\text{weight fraction(salt)} = \frac{\left[\left(\dfrac{3.0893}{2}\,\dfrac{\text{AS(sample)}}{\text{AS(0.5 mg/L)}}\right)\Big/\text{mg}\right] \times 10^{-3}}{\text{weight(sample)/g}} \tag{2}$$

The amount of salt in the aqueous phase was determined gravimetrically after drying one sample in a Blue M laboratory oven at 75 °C. Since the solubility of the salt in the aqueous phase is high, the weight of the residue can easily be determined. The relative error associated with this method is less than 1%.

Table IV. Effect of Salt Content on Mutual Solubilities of Water and 2-Propanol

temp (°C)	organic-phase composition (wt %)			aqueous-phase composition (wt %)		
	Na_2SO_4	2-PrOH	water	Na_2SO_4	2-PrOH	water
35(subsatd)	1.1	48.9	50.0	21.0	4.1	74.9
35(satd)	0.15	66.6	33.3	29.0	1.1	69.9

Table V. Salt Solubility at Different Ratios of 2-Propanol and Water in the One-Phase Region

temp (°C)	Na_2SO_4 (wt %)	2-PrOH (wt %)	water (wt %)
20	16.0	0.0	84.0[a]
20	15.6	0.0	84.4
20	8.2	6.6	85.2
20	4.0	10.8	85.2
20	2.3	22.2	75.5
20	1.5	22.8	75.7
20	0.68	30.0	69.3
20	0.76	40.3	58.9
20	0.11	60.7	39.2
20	0.014	79.9	20.1
25	21.8	0.0	78.2[a]
25	20.6	0.0	79.4
25	14.6	4.2	81.2
25	9.6	9.2	81.2
25	7.7	14.1	78.2
25	3.8	23.2	73.0
25	2.4	20.8	76.8
25	1.52	28.4	70.1
25	0.765	45.8	53.4
25	0.155	62.3	37.5
25	0.017	81.7	18.3

[a] Solubility of Na_2SO_4 in pure water (*3*).

Results

Tables I–III give the ternary equilibrium data at salt saturation for 1-propanol, 2-propanol, and 2-methylpropan-2-ol between the lower consolute temperature and 80 °C. Figure 1 shows coexisting liquid-phase compositions at saturation for each of the three solvents with water. In all cases, the amount of water in the organic phase (on a salt-free basis) remains relatively constant about 32 °C. The lower consolute temperatures of all three solvents are close to ambient.

Table IV gives liquid–liquid equilibrium compositions for 2-propanol + water + Na_2SO_4 at 35 °C with different amounts of salt. Comparing the case saturated with respect to salt (29 wt % salt in the aqueous phase) with the case with 21 wt % salt in the aqueous phase, we see that the water content of the organic phase increases from 33.3 to 50 wt %. For these solvents, the degree of phase separation is strongly dependent on salt concentration; all three solvents are completely miscible with water in the absence of salt.

In the one-liquid-phase region, Na_2SO_4 solubility was measured at different solvent/water ratios. Table V gives salt solubility at different ratios of 2-propanol to water at 20 and 25 °C. Figure 2 shows solubility of sodium sulfate in mixtures of 2-propanol and water; also shown are literature data (*3*) for the solubility of sodium sulfate in solvent-free water. Figure 2 shows that a small amount of 2-propanol decreases salt solubility considerably. Salt solubility in the one-phase region decreases with temperature. Tables VI and VII give salt solubility data at 20 °C for various ratios of 1-propanol and 2-methylpropan-2-ol to water. Figure 3 presents salt solubility at 20 °C for mixtures of each of the three solvents with water. For all solvents, salt solubility becomes very small at high solvent/water ratios.

Conclusions

Above the transition temperature of the decahydrate to the anhydrous sodium sulfate (32.4 °C), the capacity of each of these solvents to extract water from saturated sodium sulfate solution remains practically constant.

Table VI. Salt Solubility at Different Ratios of 1-Propanol and Water in the One-Phase Region

temp (°C)	Na_2SO_4 (wt %)	1-PrOH (wt %)	water (wt %)
20	16.0	0.0	84.0[a]
20	3.6	19.9	76.5
20	1.3	39.9	58.8
20	0.31	59.5	40.2
20	0.018	80.3	19.7

[a] Solubility of Na_2SO_4 in pure water (*3*).

Table VII. Salt Solubility at Different Ratios of 2-Methylpropan-2-ol and Water in the One-Phase Region

temp (°C)	Na_2SO_4 (wt %)	*t*-BuOH (wt %)	water (wt %)
20	16.0	0.0	84.0[a]
20	2.8	22.6	74.6
20	0.95	41.5	57.5
20	0.16	60.6	39.2
20	0.02	79.6	20.4

[a] Solubility of Na_2SO_4 in pure water (*3*).

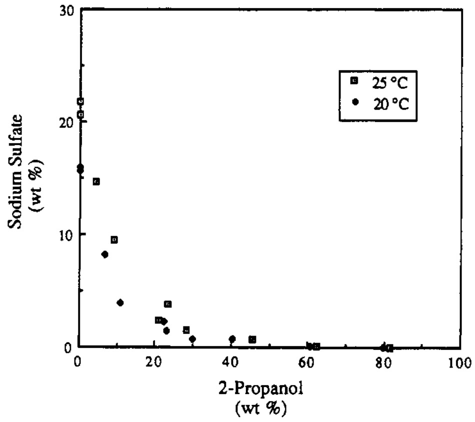

Figure 2. Solubility of Na_2SO_4 in mixtures of 2-propanol and water in the one-phase region.

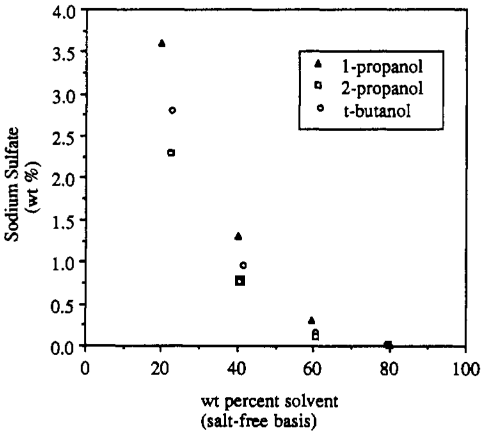

Figure 3. Solubility of Na_2SO_4 in water + alcohol mixtures at 20 °C.

Extractive crystallization is most economic when the wet organic solvent can be regenerated by changing the temperature and decanting an aqueous phase. It will be difficult to regenerate these solvents by decantation, as indicated by the data with 2-propanol for less than the saturation amount of salt, and by the miscibility of the solvents with water in the absence of salt. The experimental data and subsequent analysis suggest that it is preferable to choose an extractant which is partially immiscible with water in the absence of salt.

Acknowledgment

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