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Liquid-Liquid Equilibria for Saturated Aqueous Solutions of Sodium Sulfate in Contact with 1-Propanol, 2-Propanol or Tertiary Butanol

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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 t-butanol. 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.

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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 Lynn and coworkers. 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 di-isopropyl-amine (DIPA) with sodium chloride (*1*), and N,N-diethyl-methyl-amine (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 tertiary butanol.

Experimental Section

Chemicals. Solvents used were Fisher Scientific 2-propanol (spectranalyzed), Aldrich 1-propanol (99+ %), and Mallinckrodt t-butanol (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. For the determination of the lower consolute temperature, the solvent-water ratio was chosen according to the data obtained for the two-phase region at low temperatures. If the mixture's composition was between the organic-phase and the aqueous-phase composition of those temperatures, a transition to the one-phase region could be expected by further decreasing the temperature. In addition to data for the saturated system, it was of interest to measure the liquid-phase compositions for systems subsaturated with respect to sodium sulfate. For 2-propanol, an experiment with a known

salt concentration in the aqueous solution was made at 35°C. At this temperature, the solubility of sodium sulfate in water reaches a very high value of 32.9 weight percent. To examine the solubility of sodium sulfate in the one-phase region, mixtures were prepared containing different solvent-water ratios saturated with salt. The analytical techniques were those applied for the organic phase in the two-phase region.

Analytical Methods. Gas chromatography was used to measure the relative amount of water and solvent in the organic phase and the amount of solvent and an internal standard in the aqueous phase. A water-compatible column had to be found, since water was present in the samples to be analyzed. A 30 m x 0.53 mm I.D. x 3.0-μm J & W Scientific DB-624 column was used for the separation. Helium was the carrier gas and the capillary make-up gas for the thermal-conductivity (TCD) detector. The gas in the cylinders had a manufacturer-guaranteed purity of 99.995%. Oxygen was removed from the carrier gas with an Alltech oxygen trap. A Molecular Sieve 5 A chemical filter installed in the carrier-gas flow line served as further protection against contamination of the column packing.

A Hewlett Packard 5890 A gas chromatograph was used for the analysis. The 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 make-up 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. In contrast to other detector systems, a thermal-conductivity detector enables detection of water. The detector temperature was set at 180°C.

The detected signal was analyzed quantitatively with a Hewlett Packard 3392 A integrator. From the area percent measured by the integrator, the weight percent ratio of solvent and water in the organic phase was determined with the calibration factor CF_{org} in equation (1).

$$CF_{org} = \left(\frac{weight\ water\ (g)}{weight\ solvent\ (g)}\right) * \left(\frac{area\ solvent}{area\ water}\right) \qquad (1)$$

All injections were made with a Hamilton 1-Microliter 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 were averaged. The weight ratio of solvent and water was determined from equation (1) after CF_{org} was known by calibration.

Since the solvent concentration in the aqueous phase is very low, a comparison of the water peak and the solvent peak does not give satisfactorily exact results.

Ethylene glycol was chosen as the internal standard for the aqueous phase. Below 32.4°C, the sodium sulfate precipitates as decahydrate ($Na_2SO_4 \cdot 10\ H_2O$). Therefore, solid salt in the sample makes an analysis of the water peak questionable. Although the high concentration of water in the aqueous-phase samples is preferable to the low solvent concentration for comparison with an internal standard, it was decided to ignore the water peak and to analyze the solvent peak. A quantity of ethylene glycol close to that expected for the solvent was added to the samples before the chromatographic analysis. Equation (2) defines the calibration factor CF_{aq} used for comparing the solvent peak to the ethylene-glycol (*e.g.*) peak in the aqueous-phase analysis.

$$CF_{aq} = \left(\frac{weight\ solvent\ (g)}{weight\ e.g.\ (g)}\right) * \left(\frac{area\ e.g.}{area\ solvent}\right) \qquad (2)$$

The injection amount was 1µl 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.

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 sodium chloride NaCl (i.e. 1 g of sodium Na^+) were dissolved in water and diluted to one liter. 0.5 and 1 ml of this concentrated stock solution were aspirated to prepare two standards containing 0.5 and 1 mg sodium per liter solution. To improve dilution accuracy, a Gilson 1000-µl micropipette was used to aspirate the concentrated stock solution for the standards. 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 manual for the spectrophotometer gives a linear range of Beer's law up to a concentration of 1 mg sodium per liter solution. Analyzing the two standards and comparing the respective signals indicated a slight deviation of linearity at 1 mg sodium per liter solution. To insure applicability of Beer's law, the samples were diluted close to a concentration of 0.5 mg sodium per liter solution.

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

1 mg of sodium Na^+ is equivalent to 3.0893 mg sodium sulfate (Na_2SO_4) per liter solution. Equation (3) 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 salt amount.

$$salt\,(weight\,fraction) = \frac{\left(\frac{3.0893}{2} * \frac{AS\ sample}{AS\ \ 0.5\text{-}mg/l}\right)(mg) * 10^{-3}}{weight\ sample\ (g)} \qquad (3)$$

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 relatively high when the solvent concentration is low, the relative error associated with this method is less than one percent.

Results

Tables I-III show the ternary equilibrium data at salt saturation for 1-propanol, 2-propanol, and t-butanol between the lower consolute temperature and 80°C. Figure 1 shows a plot of the coexistence curves for the three solvents. In all cases, the solvent capacity for water above 32°C remains relatively constant. The lower consolute temperatures of all three solvents are close to ambient.

Table IV gives a comparison of equilibrium data measured at different salt-saturation levels at 35°C for 2-propanol. Although the salt concentration in the aqueous phase remained as high as 21 weight percent (compared to 29 weight percent at saturation), the water concentration in the solvent increased from 33.3 to 50 weight percent, indicating that phase separation is strongly dependent on salt concentration. All three solvents are completely miscible with water in the absence of salt.

It was also of interest to investigate salt solubility in the one-phase region at different solvent-water ratios. Table V summarizes data at different ratios of 2-propanol and water in the one-phase region at 20 and 25°C. The mixtures were saturated with sodium sulfate. 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 concentration of solvent decreases salt solubility considerably. Salt solubility in the one-phase region also decreases at the lower temperature. Tables VI and VII give data at different ratios of solvent and water in the one-phase region at 20°C for 1-propanol and t-butanol. Figure 3 presents the data at 20°C. 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 investigated alcohols' capacity for water remains practically constant.

For the solvents studied here, an extractive-crystallization process cannot operate with solvent regeneration by phase-splitting at a different temperature. For these solvents, solvent regeneration must be achieved by solvent stripping which requires some energy of vaporization. The experimental data and subsequent analysis suggest that, for extractive crystallization, it is preferable to choose a solvent which is partially immiscible with water in the absence of salt.

Literature Cited

(1) Weingaertner, D.A.; Lynn, S.; Hanson, D.N. *Ind. Eng. Chem. Res.*; **1991**, *30*, 490.

(2) Ting, A.M.; Lynn, S.; Prausnitz, J.M. *J. Chem. Eng. Data* ; in press 1992.

(3) Bartholomé, E. (ed.) et al. *Ullmanns Encyklopaedie der technischen Chemie* ; Fourth Edition, Vol. 17, p. 212, Verlag Chemie: Weinheim/Bergstr., 1975.

Table I. 1-Propanol/Water/$Na_2SO_{4(sat)}$ Equilibrium Data

	organic phase composition (wt%)			aqueous phase composition (wt%)		
Temp.(°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/$Na_2SO_{4(sat)}$ Equilibrium Data

	organic phase composition (wt%)			aqueous phase composition (wt%)		
Temp.(°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. t-Butanol/Water/$Na_2SO_{4(sat)}$ Equilibrium Data

	organic phase composition (wt%)			aqueous phase composition (wt%)		
Temp.(°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

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

	organic phase composition (wt%)			aqueous phase composition (wt%)		
Temp.(°C)	Na_2SO_4	2-PrOH	water	Na_2SO_4	2-PrOH	water
$35_{(subsat)}$	1.1	48.9	50.0	21.0	4.1	74.9
$35_{(sat)}$	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

	(wt%)		
Temp.(°C)	Na_2SO_4	2-PrOH	water
20	16.0	0.0	84.0*
20	2.3	22.2	75.5
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*
25	3.8	23.2	73.0
25	0.765	45.8	53.4
25	0.155	62.3	37.5
25	0.017	81.7	18.3

* solubility of Na_2SO_4 in pure water (*3*)

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

	(wt%)		
Temp.(°C)	Na_2SO_4	1-PrOH	water
20	16.0	0.0	84.0*
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

* solubility of Na_2SO_4 in pure water (*3*)

Table VII. Salt Solubility at Different Ratios of t-Butanol and Water in the One-Phase Region

	(wt%)		
Temp.(°C)	Na_2SO_4	t-BuOH	water
20	16.0	0.0	84.0*
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

* solubility of Na_2SO_4 in pure water (*3*)

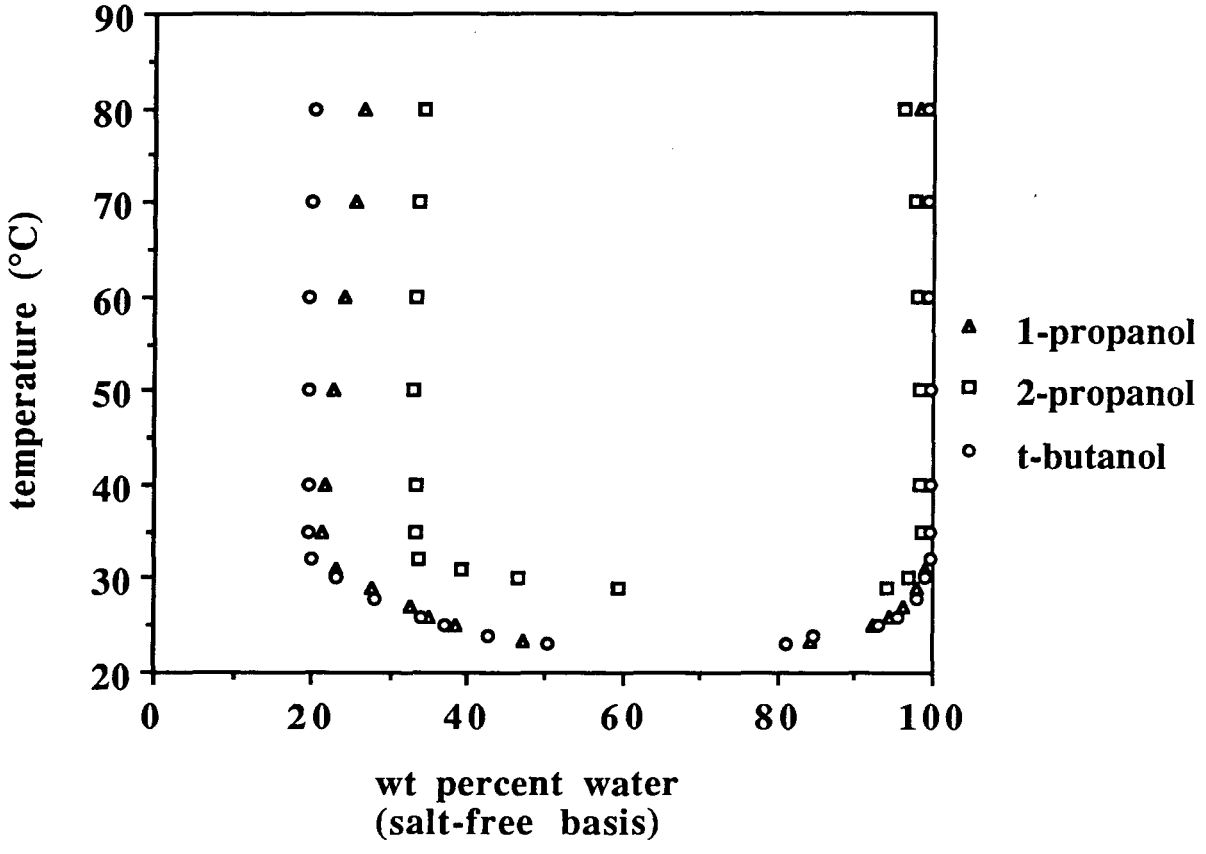


Fig. 1. Coexistence Curves for 1-Propanol, 2-Propanol, and t-Butanol with Water on a Sodium-Sulfate-Free Basis

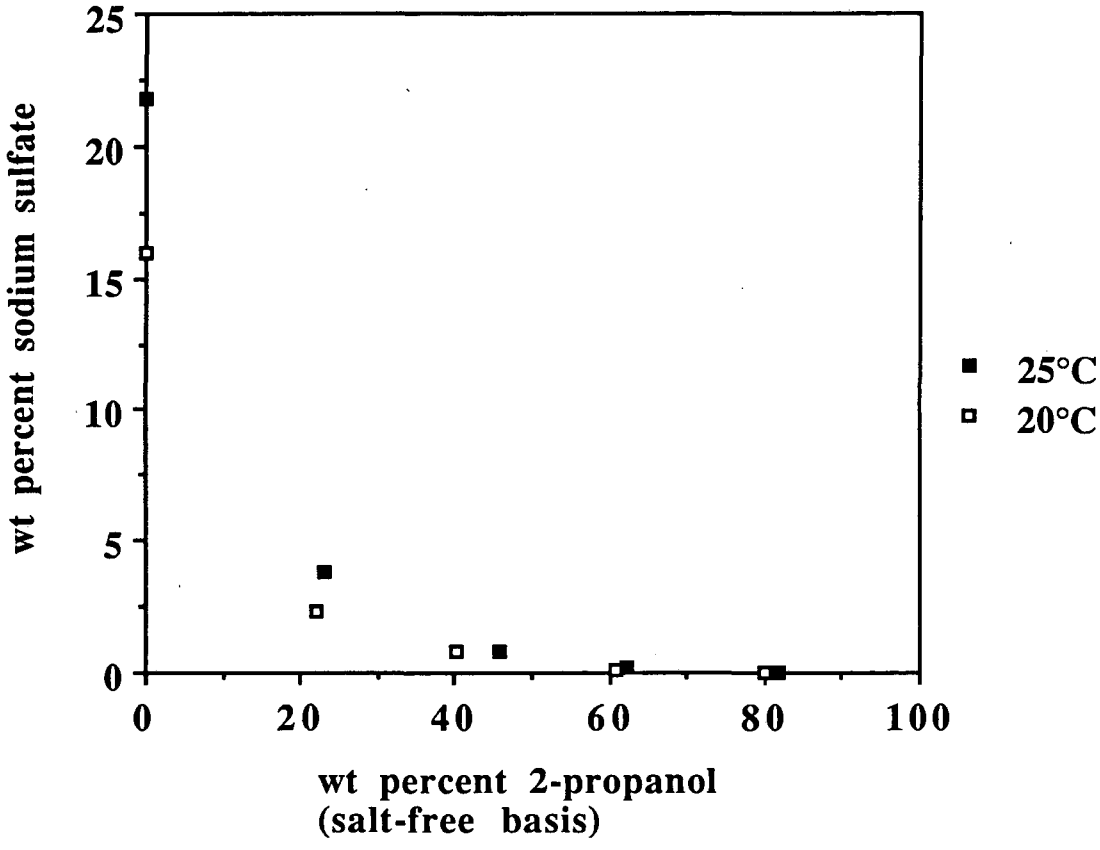
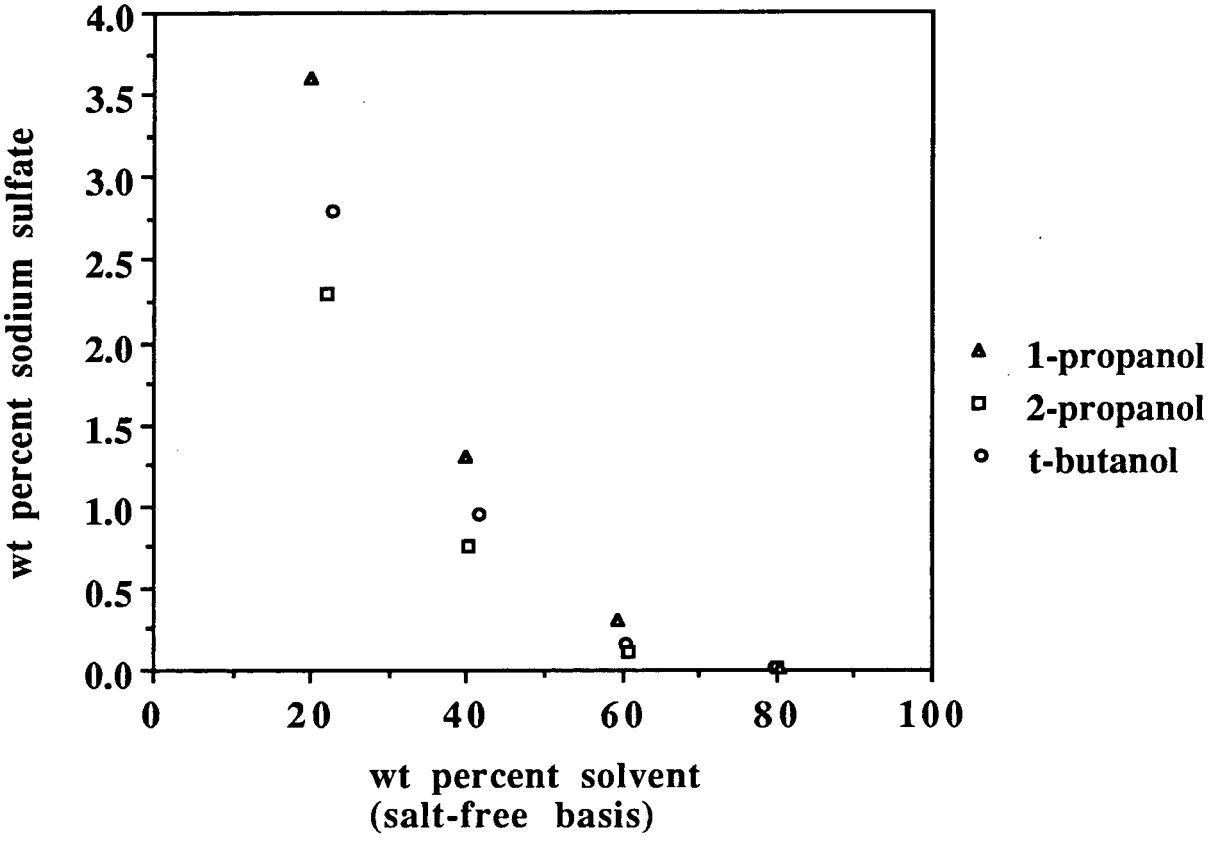


Fig. 2. Salt Solubility at Different Concentrations of 2-Propanol in Water in the One-Phase Region



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