In the concentrated acid solutions, however, the solubility of gypsum has been shown to decrease with increasing the acidity. This is explained by the salting-out effect, which increases the mean activity coefficients, as shown in Figure 6. The maximum solubility observed for gypsum at a certain acidity (Figure 1), is in fact a combined influence of the common-ion effect and salting-out effect.

Application of Solubility Data to Leaching. Figure 5 gives an example for the concentrations of Ca^{2+} and SO_4^{2-} in a solution saturated with gypsum precipitate. The results simulate the regeneration of HNO_3 by increasingly adding H_2SO_4, as represented in reaction 2. As seen, the addition of H_2SO_4 decreases $[Ca^{2+}]$ in solution but it increases $[SO_4^{2-}]$ as well as the solubility of gypsum. The maximum solubility of gypsum is when $[Ca]/[SO_4] = 1$, which represents the complete regeneration of HNO_3. At this condition, the corresponding concentration of SO_4^{2-} is ca. 0.19 M for a solution containing 5 M NO_3^-. If such a solution is used directly for leaching (reaction 1), gypsum will precipitate as the equilibrium concentration is expected to be approximately 0.01 M when the solution contains 1 M H_3PO_4 and 2 M $Ca(NO_3)_2$. Under these conditions, the use of 1 L of regenerated nitric acid solution may introduce ca. 5.6 g of sulfur into the leached ore.

In order to avoid the precipitation of gypsum during the use of regenerated nitric acid, a partial regeneration of the acid is recommended. In this way a certain amount (a steady-state concentration) of calcium nitrate will be maintained in the solution, thus reducing the solubility of gypsum.

The above method seems to be the simplest method to overcome problems with introducing sulfur to the leached ore. Other options are (1) selective separation of nitric acid, e.g., by solvent extraction with minimum or no coextraction of sulfates, and (2) evaporation of the completely regenerated nitric acid. This will produce concentrated nitric acid solution with very little sulfate present.

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Received for review April 26, 1988. Accepted October 11, 1988. This work is financially supported by the Swedish National Board of Technical Development (STU).

Solubility and Density Isotherms for Potassium Sulfate–Water–2-Propanol

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The solubility of potassium sulfate in water and in aqueous 2-propanol has been determined over the temperature range 20–50 °C, and the densities of the resulting saturated solutions have been measured. In all cases, the presence of 2-propanol significantly reduces both the solubility and density of potassium sulfate in aqueous solution. The solubility data may conveniently be expressed by a relationship of the form ln (w_{eq}) = A + Bx + Cx^2 with an accuracy of +2%, where w_{eq} is the equilibrium saturation concentration of potassium sulfate, expressed as kilograms of potassium sulfate per kilogram of water, and x is the concentration of 2-propanol expressed as kilograms of 2-propanol per kilogram of water.

Introduction

The drowning-out precipitation of soluble inorganic salts from aqueous solution by the addition of an organic second solvent has a number of advantages. These generally lie in the possibility of carrying out the operation at ambient temperature and obtaining crystals of high purity. The technique is attracting the increasing attention of technologists in the chemical and pharmaceutical industries (*1*, *2*).

Recent complementary investigations of the continuous drowning-out precipitation of potassium sulfate have clearly shown that it is possible to retrieve a crystal product which is close to that obtained by cooling crystallization (*3*). The aim of the present work was to provide accurate solubility and density data for solutions of potassium sulfate in water and aqueous 2-propanol mixtures as an aid toward the assessment of the potential of drowning-out precipitation using alcohol as a separation technique.

Experimental Section

The solubility of the system potassium sulfate–water–2-propanol has been determined by equilibrating crystals and solution in an agitated solubility cell (*1*). The apparatus used for the solubility measurements was a 150-mL glass vessel closed by a ground glass stopper and fitted with a magnetic stirrer. The cell was immersed in a thermostatic water bath controlled to ±0.05 °C. The procedure was as follows. Volumetric quantities of saturated aqueous potassium sulfate solution and 2-propanol were charged to the solubility cell and agitated for a minimum of 1 h at a temperature at least 5 °C lower than the saturation temperature. The temperature of the water bath was then increased to that corresponding to the

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0021-9568/89/1734-0124$01.50/0

Table I. Solubility and Density of Potassium Sulfate-Water-2-Propanol Measured at 20, 30, 40, and 50 °C

concn of 2-prOH, kg of 2-prOH/ 100 kg of H_2O	solubility of K_2SO_4, kg of K_2SO_4/ 100 kg of H_2O	ρ, kg/m³
	20 °C	
0	11.19	1081.16
1.62	9.72	1066.61
3.23	8.59	1054.95
4.85	7.54	1044.26
6.46	6.67	1035.17
8.08	5.94	1027.36
11.31	4.70	1014.18
16.20	3.39	998.12
21.00	2.53	988.54
26.01	1.97	980.36
31.02	1.58	971.12
36.35	1.30	964.61
	30 °C	
0	12.99	1090.12
1.63	11.43	1077.14
4.07	9.64	1059.36
6.51	8.08	1043.24
9.77	6.56	1026.07
11.40	5.93	1018.06
13.02	5.36	1011.84
16.28	4.43	1000.87
19.54	3.70	990.36
22.79	3.20	983.04
26.05	2.78	973.15
29.30	2.44	966.47
32.56	2.15	962.15
40.70	1.72	954.78
	40 °C	
0	14.79	1097.56
1.64	13.14	1081.87
4.10	11.15	1062.36
6.57	9.53	1046.19
8.21	8.05	1031.63
9.86	7.78	1028.30
14.79	5.95	1008.22
19.71	4.67	992.67
24.64	3.81	980.49
28.75	3.29	971.90
32.86	2.86	963.90
41.07	2.26	950.30
49.29	1.78	937.64
	50 °C	
0	16.52	1103.74
1.66	14.82	1087.56
3.32	13.37	1073.90
4.97	12.06	1061.07
6.63	10.88	1049.96
8.29	9.95	1040.18
11.61	8.33	1023.21
16.58	6.55	1002.96
20.73	5.55	990.24
26.53	4.52	975.20
31.51	3.85	963.85
36.48	3.35	954.28
41.46	2.90	945.81

Table II. Coefficients for the Model Equation (1)

temp, °C	coeff for model eq 1		
	A	*B*	*C*
20	-2.1856	-8.5826	7.2787
30	-2.0424	-7.6613	6.6314
40	-1.9317	-6.6221	4.9364
50	-1.8134	-6.2880	5.2445

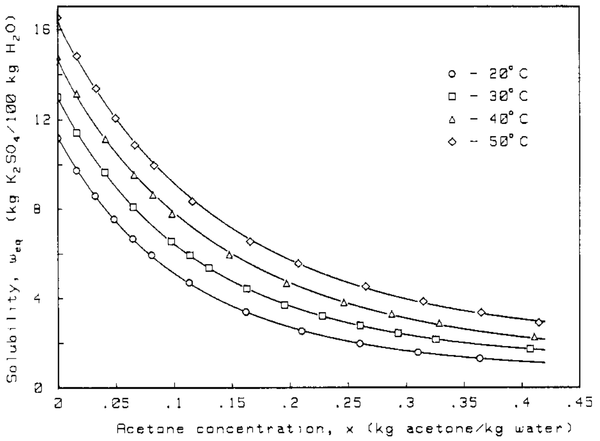

Figure 1. Solubility of potassium sulfate in aqueous 2-propanol at 20, 30, 40, and 50 °C.

saturation temperature of aqueous potassium sulfate solution. The contents of the solubility cell were then agitated for at least 24 h at constant temperature. At the end of this time, the agitator was switched off, and 1 h later samples of clear solution were withdrawn and both the concentration of potassium sulfate in solution and its density were measured.

The solvents used were analytical-grade (BDH Chemical Ltd.) 2-propanol with a minimum assay of 99.5% and twice-distilled water. Commercial pure-grade potassium sulfate was dissolved in hot twice-distilled water, filtered through a no. 3 sintered-glass filter, and recrystallized by cooling.

Solution concentration measurements were made by evaporating a sample to dryness giving an estimated accuracy of $\pm 10^{-7}$ kg of K_2SO_4/kg of solution. The densities of the various saturated solutions produced in the solubility cell were subsequently determined by use of a Digital Density Meter (PAAR DMA 60), which gives a claimed precision up to 10^{-6} g cm^{-3}.

Solubilities and densities of potassium sulfate in water and in aqueous mixtures of 2-propanol were determined at four temperatures, viz., 20, 30, 40, and 50 °C.

Potassium sulfate solubility data in water and in aqueous 2-propanol mixtures are presented in Figure 1 and Table I. The densities of potassium sulfate-water solutions and potassium sulfate-water-2-propanol mixtures at 20, 30, 40, and 50 °C are also shown in Table I. In all cases, both the solubility of potassium sulfate and the density of its saturated aqueous 2-propanol solution are significantly reduced by the presence of 2-propanol.

The experimental solubility data are well correlated by an expression of the form

$$\ln (w_{eq}) = A + Bx + Cx^2 \qquad (1)$$

where w_{eq} is the equilibrium concentration of potassium sulfate (kg of K_2SO_4/kg of H_2O), x is the prevailing concentration of 2-propanol in solution (kg of 2-propanol/kg of H_2O), and A, B, and C are coefficients for the model equation (1). Values of A, B, and C determined are listed in Table II.

For the sake of comparison, potassium sulfate solubility data in pure aqueous solutions obtained in this work are presented in Table III together with other data available in literature (*1*, *4*-*6*). The solubility of potassium sulfate in pure aqueous solutions obtained in the present study is very close to that re-

Table III. Solubility and Density of Potassium Sulfate Aqueous Solution at 10, 20, 30, 40, and 50 °C

temp, °C	solubility, kg of K_2SO_4/kg of H_2O				density, kg/m³			
	ref *1*	ref *4*	ref *6*	this study	ref *1*	ref *4*	ref *5*	this study
10	0.092		0.0924					
20	0.109	0.1106	0.1105	0.1119	1080	1082		1081.16
30	0.130	0.1303	0.1291	0.1300	1090		1086.64	1090.12
40	0.148	0.1494	0.1478	0.1479	1100			1097.56
50		0.1670	0.1661	0.1652	1105			1103.74

ported while a more significant difference is observed in the case of density. The latter is likely to be due to using a more accurate instrument here than in previous work.

Glossary

A, B, C	coefficients (eq 1)
w_{eq}	solubility, kg of K_2SO_4/kg of H_2O
x	concentration of 2-propanol, kg of 2-propanol/kg of H_2O
ρ	density of saturated solution, kg/m^3

Registry No. K_2SO_4, 7778-80-5; 2-propanol, 67-63-0.

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Received for review December 8, 1987. Accepted August 15, 1988.

Isobaric Vapor–Liquid Equilibria for 6-Methyl-5-hepten-2-one + Bis(3-methyl-2-butenyl) Ether, Bis(3-methyl-2-butenyl) Ether + 3,3-Dimethyl-2-propen-1-ol, 3,3-Dimethyl-2-propen-1-ol + 6-Methyl-5-hepten-2-one, and 6-Methyl-5-hepten-2-one + 6-Methyl-3-isopropenyl-5-hepten-2-one Binary Systems

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Isobaric vapor–liquid equilibria (VLE) data and UNIQUAC parameters of four binary systems, 6-methyl-5-hepten-2-one + bis(3-methyl-2-butenyl) ether, bis(3-methyl-2-butenyl) ether + 3,3-dimethyl-2-propen-1-ol, 3,3-dimethyl-2-propen-1-ol + 6-methyl-5-hepten-2-one, and 6-methyl-5-hepten-2-one + 6-methyl-3-isopropenyl-5-hepten-2-one at 50, 100, and 150 mmHg are presented. The vapor pressure data and Antoine constants for pure components are also reported.

Introduction

6-Methyl-5-hepten-2-one is an important organic intermediate for synthesizing vitamins A, E, and K_1 as well as some kinds of perfumes and fine chemicals. For the design and operation of separation processes for manufacturing 6-methyl-5-hepten-2-one with high purity, it is necessary to obtain precise VLE data at low pressures for various combinations of components concerning these processes. In this work, the isobaric p–t–x data for 6-methyl-5-hepten-2-one + bis(3-methyl-2-butenyl) ether, bis(3-methyl-2-butenyl) ether + 3,3-dimethyl-2-propen-1-ol, 3,3-dimethyl-2-propen-1-ol + 6-methyl-5-hepten-2-one, and 6-methyl-5-hepten-2-one + 6-methyl-3-isopropenyl-5-hepten-2-one binary systems at low pressures and vapor pressures of corresponding pure components were presented. The vapor compositions were calculated by a direct method based on the Gibbs–Duhem equation developed previously (*1*). The experimental data sets were also correlated with UNIQUAC model (*2*) for practical purposes.

Experimental Section

All chemicals prepared from other laboratories using the methods provided by literature (*3*) were further purified by rectification in an Auto Annular Still (Perkin-Elmer Model 251) under vacuum with approximately 100 theoretical plates. The purity of all chemicals as tested by gas chromatography was greater than 99.9 wt %. Vapor–liquid equilibria and vapor pressures were measured by an Eckert ebulliometer (*4*) connected with a constant-pressure control unit (sensitivity ±0.02 mmHg) and charged with liquid mixture of known amount and composition. After the steady state was established, the pressure readings were taken from a mercury manometer by a cathetometer (accuracy ±0.02 mm) and corrected for standard density and gravitation acceleration. The temperatures were measured by using a calibrated mercury thermometer (accuracy ±0.01 °C). The equilibrium composition of liquid

0021-9568/89/1734-0126$01.50/0