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Solubility and Density Isotherms for Magnesium Sulfate Heptahydrate–Water–Ethanol

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Solubility data for use in the assessment of the drowning-out precipitation of magnesium sulfate heptahydrate in aqueous ethanol over the temperature range 15–35 °C and the densities of the resulting saturated solutions are reported. In all cases, the presence of ethanol significantly reduces both the solubility and density of magnesium sulfate heptahydrate in aqueous solution. The solubility data may conveniently be expressed by a relationship of the form ln $w_{eq} = A + Bx + Cx^2 + Dx^3$ with an accuracy ∓2% where w_{eq} is the equilibrium saturation concentration of magnesium sulfate heptahydrate, expressed as kg of magnesium sulfate (hydrate)/100 kg of free water, and x is the concentration of ethanol expressed as kg ethanol/kg of free water.

Introduction

Drowning-out precipitation of soluble inorganic salts from aqueous solution by the addition of an organic second solvent is attracting the increasing attention of technologists in chemical and pharmaceutical industries (*1–9*). The technique has a number of advantages over simple cooling. These generally lie in the possibility of carrying out the operation at ambient temperature and obtaining crystals of high purity. Recent complementary investigations of the continuous drowning-out precipitation of potassium sulfate (*10*) and potash alum (*11*) have clearly shown that, by application of suitable control, it is possible to retrieve a crystal product which is close to that obtained by simple cooling crystallization.

Assessment of such precipitation processes requires accurate solubility data. These can conveniently be determined with the aid of a sensitive densitometer that relates solution concentration to density measurements (*12*, *13*). The aim of the present work was thus to determine accurate solubility and density data for solutions of magnesium sulfate heptahydrate in water and aqueous ethanol mixtures, respectively, as an aid toward the assessment of the potential of drowning-out precipitation using organic solutions as a separation technique.

Experimental Section

The solubility of magnesium sulfate heptahydrate in water and in aqueous ethanol was determined via density measurements made over the temperature range 15–35 °C as follows. Saturated solutions were made by approaching equilibrium from undersaturated states. The apparatus used is described in detail elsewhere (*14*, *15*). Briefly, it consists of a 150-mL glass vessel closed by a ground-glass stopper and fitted with a magnetic stirrer. The cell is immersed in a thermostatic water bath controlled to ±0.5 K. Volumetric quantities of twice-distilled water and AnalaR grade ethanol (minimum assay 99.5%) are charged to the solubility cell. Then, the mass (in excess of saturation) of AnalaR grade magnesium sulfate ($MgSO_4 \cdot 7H_2O$, AnalaR grade; BDH Chemical Ltd.) is added to the solubility cell and agitated for a minimum of 1 h at a temperature at least 2

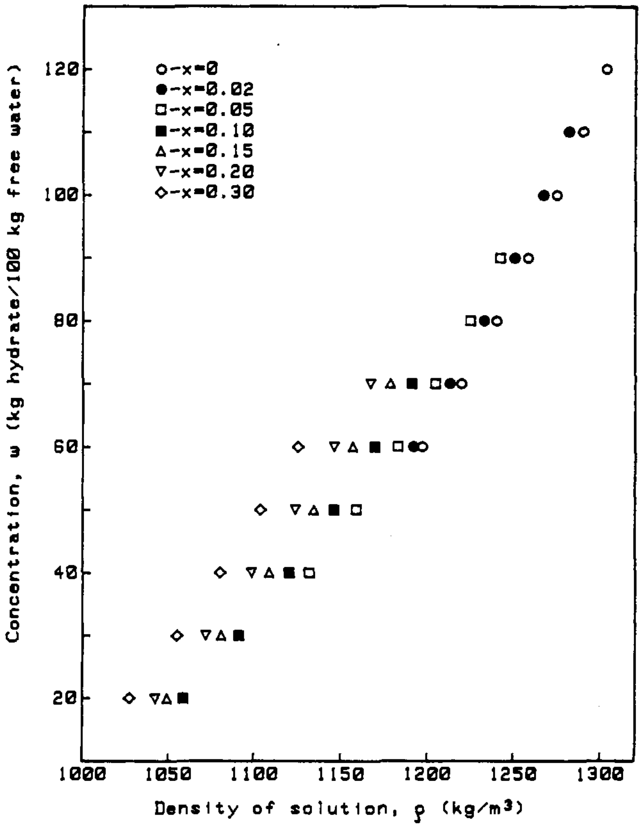

Figure 1. Densities of aqueous solutions and aqueous ethanol solutions of magnesium sulfate at 25 °C.

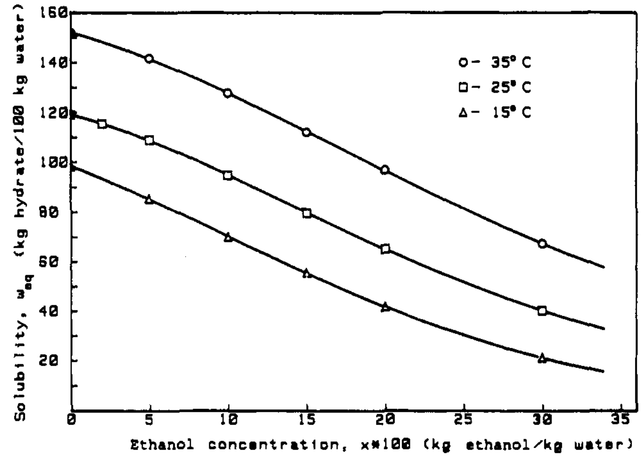

Figure 2. Solubilities of magnesium sulfate heptahydrate in aqueous ethanol at 15, 25, and 35 °C.

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Table I. Densities (kg m^{-3}) of Under- and Supersaturated Magnesium Sulfate–Water and Magnesium Sulfate–Water–Ethanol Solutions at Temperatures (θ) of 15, 25, and 35 °C[a]

ethanol concn	density at various solute concns												
	20	30	40	50	60	70	80	90	100	110	120	130	140
						θ = 15 °C							
0			1148.83	1176.05	1200.77	1222.66	1242.40	1260.42					
0.05		1105.69	1135.33	1162.02	1186.21	1207.91	1227.83						
0.10	1062.193	1094.36	1123.34	1149.44	1172.95	1194.52							
0.15	1053.747	1084.48	1112.53	1137.94	1161.05	1182.05							
0.20	1046.041	1075.83	1103.00	1127.60									
0.30	1032.047	1059.80	1085.26	1108.51									
						θ = 25 °C							
0					1196.99	1219.52	1239.93	1258.33	1274.86	1290.05	1303.15		
0.02					1192.00	1212.79	1232.66	1250.31	1266.91	1281.91			
0.05			1131.85	1158.82	1182.99	1204.47	1224.67	1241.90					
0.10	1058.973	1091.21	1120.21	1145.98	1169.50	1190.79							
0.15	1049.452	1080.80	1108.77	1134.20	1156.91	1178.40							
0.20	1042.380	1071.90	1098.66	1123.76	1146.21	1167.05							
0.30	1027.331	1055.03	1080.35	1103.92	1125.36								
						θ = 35 °C							
0								1252.12	1268.84	1284.21	1298.62	1310.13	1322.26
0.05							1219.71	1237.98	1253.89	1269.68	1283.85	1296.23	
0.10						1186.22	1206.29	1224.20	1240.98	1255.62	1270.60		
0.15					1153.04	1173.79	1192.07	1210.50	1226.70	1242.07			
0.20				1118.73	1140.90	1161.57	1180.52	1198.05	1214.41				
0.30			1074.16	1097.16	1118.68	1154.86							

[a] Units: ethanol concentration, kg of ethanol/kg of free water; solute concentration, kg of hydrate/100 kg of free water.

Table II. Solubilities and Densities of Magnesium Sulfate–Aqueous Ethanol Measured at Temperatures (θ) of 15, 25, and 35 °C[a]

ethanol concn	solubility of magnesium sulfate	density of satd soln
	θ = 25 °C	
0	98.32	1274.15
0.05	85.38	1237.82
0.10	70.02	1194.55
0.15	55.58	1151.12
0.20	41.76	1107.41
0.30	21.05	1035.08
	θ = 25 °C	
0	119.14	1302.14
0.02	110.50	1282.62
0.05	108.98	1271.31
0.10	94.73	1236.55
0.15	79.71	1197.57
0.20	65.27	1157.43
0.30	40.28	1081.13
	θ = 35 °C	
0	151.83	1335.45
0.05	141.73	1309.62
0.10	127.78	1281.55
0.15	112.04	1245.08
0.20	96.85	1209.37
0.30	67.44	1144.17

[a] Units: ethanol concentration, kg of ethanol/kg of free water; solubility, kg of hydrate/100 kg of free water; density, kg/m^3.

Table III. Coefficients of the Model Equation (1)

θ,[a] °C	A	B	C	D
15	4.5888	−2.3841	−10.0526	2.8913
25	4.7814	−1.4036	−9.5510	7.2403
35	5.0236	−1.1111	−6.6625	4.4792

[a] θ = temperature.

K lower than the saturation temperature. The contents of solubility cell are then agitated for at least 10 h at constant temperature. At the end of this time, the agitator is switched off, and, 1 h later, samples of clear solution are withdrawn and their densities measured.

The densities of the various solutions were subsequently determined with a digital density meter (PAAR DMA 60), which gives a claimed precision of up to 10^{-7} g cm^{-3}. The densities of magnesium sulfate–water solutions and magnesium sulfate–water–ethanol mixtures at temperatures of 15, 25, and 35 °C are shown in Table I. The densities at 25 °C are also presented in Figure 1. It is apparent from Figure 1 and Table I that solution densities of magnesium sulfate in water and aqueous ethanol solutions, respectively, are nonlinear functions of solute concentration. At each concentration of ethanol in solution, the density data of under- and oversaturated solutions were correlated with concentration by a polynomial equation (not shown) and the solubility was calculated.

Magnesium sulfate solubility data in water and in aqueous ethanol mixtures are presented in Table II and in Figure 2. In all cases, the solubility of magnesium sulfate heptahydrate is significantly reduced by the presence of ethanol. The experimental solubility data are well correlated by an expression of the form

$$\ln w_{\mathrm{eq}} = A + Bx + Cx^2 + Dx^3 \qquad (1)$$

where w_{eq} is the equilibrium concentration of magnesium sulfate (kg of hydrate/100 kg of free water), x is the prevailing concentration of ethanol in solution (kg of ethanol/kg of free water), and A, B, C, and D are coefficients. Determined values of A, B, C, and D are also presented in Table III.

Finally, for the purpose of comparison, both the solubility and density data of magnesium sulfate in pure aqueous solutions obtained in this work are presented in Table IV together with those data available in the literature (*16–19*). The solubility data of magnesium sulfate in pure aqueous solutions obtained in the present study are mostly within the range of those previously reported while solution densities are also generally comparable, albeit slightly lower.

Nomenclature

A, B, C, D, coefficients (eq 1)

w, magnesium sulfate concentration, kg of hydrate/kg of free water

Table IV. Solubilities and Densities of Magnesium Sulfate Aqueous Solution at Temperatures (θ) of 10, 15, 20, 25, 30, 35, and 40 °C[a]

	solubility					density	
θ, °C	this study	ref 16	ref 17	ref 18	ref 19	this study	ref 16
10		93.56	80.07	91.58	82.00		1260
15	98.32	104.52*	92.17	101.00*	93.02*	1274.12	1275.8*
20		115.73	105.53	111.47	106.65		1290.0
25	119.14	130.08*	120.22	124.66*	120.66	1302.14	1307.8*
30		145.9	136.29	139.32	134.43		1330.0
35	151.83	160.76*	153.76	154.20*	150.04	1335.45	1340.0*
40		178.02	172.60	170.97	170.84		1350.0

[a] Units: solubility, kg of hydrate/100 kg of free water; density, kg/m^3. Values marked with an asterisk are interpolated data.

w_{eq}, solubility, kg of hydrate/100 kg of free water

x, ethanol concentration, kg of ethanol/kg of free water

ρ, density of solution, kg/m^3

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Transference Numbers of Lithium Chloride and Tetraalkylammonium Halides in 1-Butanol at Various Temperatures

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Transference numbers of lithium chloride and some tetraalkylammonium halides have been measured in 1-butanol at 298.15, 308.15, and 318.15 K up to concentrations of 11.84 × 10^{-2} mol dm^{-3}. The transference numbers of the ions show much less variation with concentration and are in accordance with the Debye–Hückel limiting law. Transference numbers of the ions at infinite dilution have been evaluated from the linear plots of the transference number versus the square root of the concentration. Variation of limiting transference numbers of the ions with temperature agrees with the theoretical predictions. Relative solvation numbers of the ions evaluated at all the temperatures by the method suggested by Carman show some anomalies. Solvation numbers of the ions have been evaluated at 298.15 K by combining the present transference number data with reported conductance data. The solvation numbers of the ions reveal that the anions in 1-butanol are heavily solvated as compared to the cations of comparable sizes. This is in line with the protic nature of this solvent.

Conductance data of some electrolytes in 1-butanol have been reported in the literature (*1–4*). However, limiting equivalent ionic conductances have been evaluated on the basis of the Walden product of large ions and the Kohlrausch law of independent ion migration. Recently, we reported (*5*) the transference numbers of tetrabutylammonium bromide in this solvent only at one temperature (298.15 K). In this paper, transference number measurements by Hittorf's method of some electrolytes at 298.15, 308.15, and 318.15 K are reported. The data at various temperatures have been used to evaluate relative solvation numbers of the ions by using Carman's equation (*6*), and the data at 298.15 K have been used to evaluate solvation numbers of the ions in this solvent.

Experimental Section

1-Butanol was purified essentially by the method reported earlier (*5, 7*). Freshly distilled solvent was used in each experiment, and the purity (greater than 99.9 mol %) of the solvent was checked by its conductivity and density measurements.

All the electrolytes (BDH AnalaR or Reidal Pure, with stated purity levels of 99 mol % or better) used in these studies were recrystallized from conductivity water and dried under reduced pressure at an elevated temperature (373.15 K) before use.

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