Composition and Density of Saturated Solutions of Lithium Sulfate + Water + Methanol

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The solubility of lithium sulfate in water and in aqueous methanol has been determined over the temperature range 283.15–313.15 K and in the range 0–0.9 mass fraction methanol. The densities of the saturated solutions are also reported. Equations are given for the solubility and the density of the saturated solutions as a function of the mass fraction of methanol and temperature.

Introduction

The precipitation of inorganic salts from aqueous solutions by addition of alcohols as cosolvents has several advantages over other standard crystallization techniques (*1–3*). High yield and purity of the product, operation at ambient temperature, and fitness for systems where the temperature has little effect on the solubility are some of them.

Aqueous lithium sulfate has a nearly zero temperature coefficient of solubility and may be purified by salting out with alcohols. As fundamental knowledge to practice this precipitation process, we reported in a previous work (*4*) the solubility and density of saturated solutions of lithium sulfate in water and aqueous ethanol mixtures. In this study, we report the solubility and density for the same salt but in aqueous methanol, as an alternative precipitant.

Experimental Section

Equilibrium experiments were carried out by agitation, for more than 48 h, of known masses of methanol and water together with an excess of salt. Closed flasks fitted with a magnetic stirrer were immersed in a thermostated water bath controlled to ±0.05 K. At the finish of each run, after sedimentation of the dispersed solids, samples of clear liquid filtered at the experimental temperature through a (GELMAN VERSAPOR) 0.22-μm filter were withdrawn and their solubility and density measured.

PRS grade lithium sulfate monohydrate (PANREAC), p.a. methanol (PANREAC), and distilled water passed through a (MILLIPORE) ultrapure cartridge kit were always used. Both salt and methanol were used without further purification.

Solution concentrations were determined by evaporation to dryness to anhydrous salt of a known mass of a saturated solution; the reproductibility is estimated to be about ±0.1%. Densities of the solutions at each temperature were measured by a vibrating-tube densimeter (Paar DMA602) with an accuracy of $\pm 1.5 \times 10^{-6}$ g/cm^3.

The solubility and density of the saturated solutions for lithium sulfate + water + methanol determined in the range 283.15–313.15 K are given in Table 1. The solubility and density data at 298.15 K are also presented in Figure 1.

There is an appreciable reduction of the solubility of lithium sulfate by the addition of methanol. The effect of the temperature on the solubility, in both water and aqueous methanol solutions, is almost insignificant.

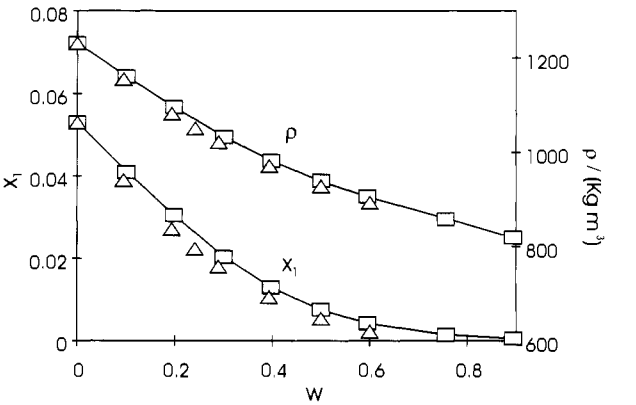

Figure 1. Solubility x_1 and density ϱ of lithium sulfate in w alcohol + $(1 - w)$ water at 298.15 K: □, methanol; △, ethanol.

The solubility results, expressed as the mole fraction of lithium sulfate, may be correlated, both with composition and temperature, according to the equation

$$\ln x_1 = A(w) + B(w)/(T/K) \quad (1)$$

with

$$A(w) = a_0 + a_1 w + a_2 w^2 + a_3 w^3 + a_4 w^4$$

$$B(w) = b_0 + b_1 w + b_2 w^2 + b_3 w^3 + b_4 w^4$$

The coefficient values are presented in Table 2. The mean relative standard deviation between all experimental and calculated solubility values is 1.13%. The maximum relative deviation is about 6.7%.Taking into account the low s values at high w compositions, the calculated solubility values can be considered in close agreement with the experimental ones. The fitting for $T = 298.15$ K is shown in Figure 1.

The solubility results are compared in Figure 1 with those obtained using water + ethanol as solvent (*4*). For similar alcohol composition and temperature the salting out effect of both cosolvents on the salt solubility is rather close. Moreover, the resulting equilibrated solid phases were always the hydrated form of the salt, even in the experiments at high alcohol concentration. The only difference that we have verified by some preliminary experiments is a slow dehydration of the lithium sulfate monohydrate working with absolute methanol but not with absolute ethanol.

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Table 1. Solubility s (x_1) and Density ϱ of Lithium Sulfate for Various Mass Fractions w in (1 − w) Water + w Methanol at 283.15, 293.15, 298.15, 303.15, and 313.15 K

w	s/(kg/100 kg of soln)	x_1	ϱ/(kg m^{-3})	w	s/(kg/100 kg of soln)	x_1	ϱ/(kg m^{-3})	w	s/(kg/100 kg of soln)	x_1	ϱ/(kg m^{-3})
					T = 283.15 K						
0.0000	25.98	0.054 36	1239.38	0.2975	10.44	0.021 48	1044.75	0.6006	1.98	0.004 47	917.04
0.1009	20.70	0.042 81	1173.24	0.3960	6.57	0.013 73	995.11	0.7505	0.74	0.001 82	872.89
0.1992	15.29	0.031 37	1105.73	0.4997	3.63	0.007 84	951.44	0.8950	0.28	0.000 76	832.31
					T = 293.15 K						
0.0000	25.60	0.053 35	1234.63	0.2991	10.19	0.020 94	1038.10	0.6016	1.80	0.004 07	908.70
0.0950	20.70	0.042 70	1170.25	0.3963	6.35	0.013 26	987.28	0.7488	0.65	0.001 59	864.69
0.2012	14.95	0.030 60	1098.03	0.4990	3.58	0.007 72	944.49	0.9017	0.23	0.000 63	821.53
					T = 298.15 K						
0.0000	25.48	0.053 02	1231.28	0.3009	9.93	0.020 38	1033.00	0.5949	1.90	0.004 27	907.13
0.1007	19.97	0.041 00	1161.23	0.3981	6.23	0.013 00	982.95	0.7561	0.58	0.001 43	858.48
0.1979	14.94	0.030 54	1096.50	0.4998	3.50	0.007 56	940.34	0.8944	0.21	0.000 58	819.41
					T = 303.15 K						
0.0000	25.31	0.052 58	1228.96	0.3045	9.76	0.020 02	1027.82	0.5999	1.81	0.004 08	901.45
0.0988	20.18	0.041 48	1161.61	0.4003	6.12	0.012 79	978.58	0.7459	0.67	0.001 64	857.19
0.1983	14.84	0.030 30	1093.12	0.5050	3.36	0.007 27	934.53	0.9027	0.19	0.000 53	812.47
					T = 313.15 K						
0.0000	24.97	0.051 69	1221.26	0.3024	9.63	0.019 71	1021.13	0.5988	1.75	0.003 93	893.18
0.0981	19.88	0.040 73	1154.33	0.3947	6.17	0.012 85	973.51	0.7493	0.55	0.001 34	848.42
0.1979	14.58	0.029 70	1085.63	0.4963	3.46	0.007 45	930.02	0.9043	0.18	0.000 49	802.64

Table 2. Coefficients of Model Eq 1

a_0	a_1	a_2	a_3	a_4
−3.373	−7.168	28.635	−64.410	33.736
$b_0 \times 10^1$	$b_1 \times 10^3$	$b_2 \times 10^3$	$b_3 \times 10^4$	$b_4 \times 10^3$
12.995	1.482	−9.238	1.810	−9.121

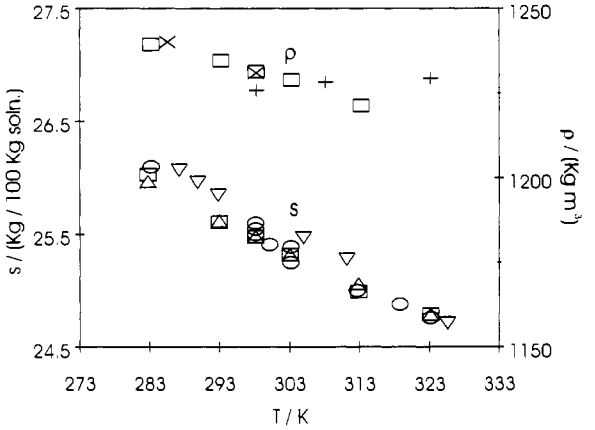

Figure 2. Solubility s and density ϱ of lithium sulfate in aqueous solutions as a function of the temperature: □, this study; △, ref 5; ▽, ref 6; ○, ref 7; +, ref 8; ×, ref 9.

For the aqueous systems, the solubility results are in acceptable agreement with those taken from the literature (*5*−*7*), as shown in Figure 2.

The density results may be correlated, both with composition and temperature, according to the equation

$$\varrho/(\text{kg m}^{-3}) = A'(w) + B'(w)(T/\text{K}) \qquad (2)$$

with

$$A'(w) = a'_0 + a'_1 w + a'_2 w^2 + a'_3 w^3 + a'_4 w^4$$

$$B'(w) = b'_0 + b'_1 w + b'_2 w^2 + b'_3 w^3 + b'_4 w^4$$

The coefficient values are presented in Table 3. The mean relative standard deviation between all experimental and calculated density values is 0.08%. The maximum relative deviation is about 0.25%. The fitting for T = 298.15 K is also shown in Figure 1.

Table 3. Coefficients of Model Eq 2

$a'_0 \times 10^3$	$a'_1 \times 10^2$	$a'_2 \times 10^3$	$a'_3 \times 10^3$	$a'_4 \times 10^3$
1.412 44	−4.251 10	−1.063 20	2.621 25	−1.528 40
$b'_0 \times 10^{-1}$	$b'_1 \times 10^{-1}$	b'_2	b'_3	b'_4
−6.067 38	−8.858 59	3.083 82	−5.307 70	2.902 69

A comparison between the density results with those obtained using water + ethanol as solvent (*4*) can also be seen in Figure 1. For the aqueous system at different temperatures, the density results are compared with the literature (*8*, *9*) in Figure 2.

Registry Numbers Supplied by Author. Li_2SO_4, 10377-48-7; methanol, 67-56-1.

Literature Cited

(1) Lozano, J. A. F. *Ind. Eng. Chem. Process Des. Dev.* **1976**, *15* (3), 445.
(2) Jones, A. G.; Mydlarz, J. *Chem. Eng. Res. Des.* **1989**, *67*, 238.
(3) Fleischmann, W.; Mersmann, A. In *Industrial Crystallization 84*; Jancic, S., de Jong, E. J., Eds.; Elsevier Science Publishers: Amsterdam, 1984; p 165.
(4) Cartón, A.; Sobrón, F.; Bolado, S.; Tabarés, J. *J. Chem. Eng. Data* **1994**, *39*, 61.
(5) Broul, M.; Nyvlt, J.; Söhnel, O. *Solubility in Inorganic Two-Component Systems*, 1st ed.; Academia: Prague, 1981; p 244.
(6) Stephen, H., Stephen, T., Eds. *Solubilities of Inorganic and Organic Compounds*; Pergamon Press: Oxford–New York–Toronto–Sydney–Paris–Frankfurt, 1963; Vol. I, Binary Systems, Part I, p 101.
(7) Silcock, H., Ed. *Solubilities of Inorganic Compounds;* Pergamon Press: Oxford, 1979; Vol.3, Part 1, pp 701–703, 714–716.
(8) Zdanovskii, A. B.; Solov'eva, E. F. *Salt System Solubility Handbook*; Khimia: Leningrad, 1973; Vol. I-1, pp 87–90.
(9) *Gmelins Handbuch der Anorganischen Chemie*; Verlag Chimie: Heidelberg, 1960; Vol. 20, p 481.

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