

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

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The solubilities of lithium sulfate in water and in aqueous ethanol have been determined over the temperature range 283.15–323.15 K and at 0–0.6 mass fraction of ethanol. 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 temperature and mass fraction of ethanol.

Introduction

The utilization of organic solvents such as alcohols in crystallization processes is an interesting method to crystallize inorganic salts and proteins (1–3). The addition of a nonsolvent (an organic compound in which the salt is insoluble) to an aqueous salt solution usually decreases the salt solubility, so selective precipitation may occur by a salting-out process. The technique permits operation at ambient temperature and is especially attractive in salt systems where the temperature has little effect on the solubility.

Lithium sulfate has technological interest as an ionic conductor material for laser technology. Aqueous lithium sulfate solutions, as other salts of lithium, have inverted solubility and a nearly zero temperature coefficient of solubility. This work considers the possibility of purification by salting out with alcohols.

We report in this study the solubility and density for solutions of lithium sulfate in water and aqueous ethanol mixtures. Solubility is required to determine the proper conditions of operation in a crystallizer and is useful for a microscopic interpretation of the solution structures.

Experimental Section

The saturation of aqueous and ternary solutions was achieved by stirring for more than 48 h, in closed glass vessels, known masses of ethanol and water together with an excess of salt. All flasks fitted with a magnetic stirrer were thermostated in a bath controlled to ± 0.05 K. At the finish of each run, the agitator was switched off and the equilibrium mixture was allowed to stand for more than 1 h at constant temperature to enable any dispersed solid to settle down. Samples of clear solution filtered at the experimental temperature through a 0.22- μm filter were taken in order to determine both solubility and density.

PRS grade lithium sulfate monohydrate (PANREAC), p.a. ethanol absolute (MERCK), and distilled water passed through a (MILLIPORE) ultrapure cartridge kit were used.

Solution concentrations were determined by evaporation to dryness to an anhydrous salt of a known mass of a saturated solution; the reproducibility is estimated to be about $\pm 0.1\%$. 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/cm³.

The solubility and density of the saturated solutions for lithium sulfate + water + ethanol determined in the range 283.15–323.15 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 ethanol. The effect of the

Table 1. Solubility s and Density ρ of Lithium Sulfate for Various Mass Fractions w in $(1-w)$ Water + w Ethanol at 282.75, 292.95, 298.15, 303.05, 312.85, and 323.15 K

w	s (kg/100 kg of soln)	ρ (kg m ⁻³)	w	s (kg/100 kg of soln)	ρ (kg m ⁻³)
$T = 282.75$ K					
0.0000	26.03	1239.40	0.3934	4.93	980.02
0.0949	19.68	1162.89	0.5004	2.34	938.99
0.1934	13.57	1089.92	0.6005	0.96	906.28
0.2922	8.54	1029.34			
$T = 292.95$ K					
0.0000	25.61	1234.86	0.3929	5.16	974.51
0.0953	19.35	1156.67	0.5006	2.44	931.34
0.1936	13.54	1084.52	0.6012	0.99	898.86
0.2921	8.81	1024.57			
$T = 298.15$ K					
0.0000	25.48	1231.28	0.2906	8.92	1022.23
0.0952	19.21	1155.34	0.3941	5.14	971.89
0.1936	13.49	1082.61	0.5001	2.53	928.61
0.2412	11.10	1051.15	0.6005	1.02	894.27
$T = 303.05$ K					
0.0000	25.32	1229.16	0.2926	8.88	1019.25
0.0951	18.92	1148.74	0.3939	5.34	969.64
0.1933	13.45	1078.42	0.5006	2.58	923.81
0.2418	11.07	1047.62	0.6003	1.02	890.22
$T = 312.85$ K					
0.0000	24.99	1221.43	0.2926	8.87	1011.92
0.0951	18.79	1142.04	0.3935	5.24	960.76
0.1933	13.33	1071.54	0.4998	2.58	915.88
0.2423	10.99	1040.35	0.6015	1.00	881.29
$T = 323.15$ K					
0.0000	24.79	1216.37	0.2926	8.76	1003.91
0.0955	18.67	1134.77	0.3932	5.22	952.64
0.1932	13.18	1064.37	0.4996	2.58	907.80
0.2421	10.89	1033.38	0.6013	1.00	872.50

temperature on the solubility in both water and aqueous ethanol solutions is almost insignificant.

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

$$s/(\text{kg}/100 \text{ kg of soln}) = A(w)e^{B(w)/(T/K)} \quad (1)$$

with

$$A(w) = a_0 + a_1w + a_2w^2 + a_3w^3$$

$$B(w) = b_0 + b_1w + b_2w^2 + b_3w^3 + b_4w^4$$

The coefficient values, for ethanol compositions from 0 to 0.5 mass fraction, are presented in Table 2. The mean relative standard deviation between experimental and calculated

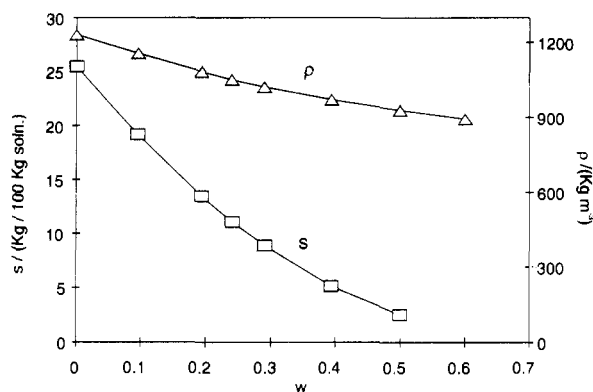


Figure 1. Solubility s and density ρ of lithium sulfate in w ethanol + $(1-w)$ water at 298.15 K.

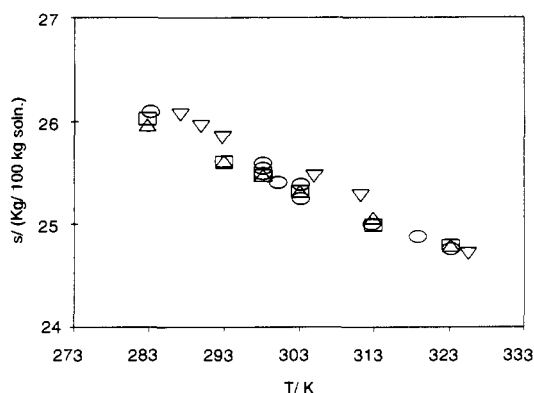


Figure 2. Solubility of lithium sulfate in aqueous solutions as a function of the temperature: \square , this study; Δ , ref 4; ∇ , ref 5; \circ , ref 6.

Table 2. Coefficients of Model Equation 1

a_0	a_1	$a_2 \times 10^2$	$a_3 \times 10^2$	
17.505 53	-69.377 40	2.393 00	-3.058 68	
$b_0 \times 10^2$	$b_1 \times 10^2$	$b_2 \times 10^3$	$b_3 \times 10^3$	$b_4 \times 10^4$
1.118 06	3.582 02	-2.226 90	-7.643 67	1.683 39

solubility values is 0.82%. The maximum relative deviation is about 3.2%. As an example we can see in Figure 1 the fitting for $T = 298.15$ K.

The solubility results can be compared with those from the literature. For aqueous systems, being slightly lower, they show acceptable agreement with the data given by refs 4–6 as we can see in Figure 2; the concordance with the results of ref 4 is almost total. The discrepancy with those of the other cited references is probably due to using a material of

Table 3. Coefficients of Model Equation 2

$a'_0 \times 10^3$	$a'_1 \times 10$	$a'_2 \times 10^3$	$a'_3 \times 10^4$	$a'_4 \times 10^4$
1.408 13	-9.325 38	-5.619 87	1.597 87	-1.262 53
$b'_0 \times 10^{-1}$	b'_1	$b'_2 \times 10$	$b'_3 \times 10$	$b'_4 \times 10$
-5.934 41	-2.597 61	2.016 39	-5.163 59	4.018 23

different purity, in agreement with a b_0 value lower than the one which would have been expected.

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

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

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 0.06%. The maximum relative deviation is about 0.27%. We can also see in Figure 1 the fitting for $T = 298.15$ K.

Nomenclature

s	solubility, kg of $\text{Li}_2\text{SO}_4/100$ kg of solution
w	mass fraction of ethanol
ρ	density of solution, kg/m^3
T	temperature, K
a_i, b_i	coefficients of eq 1
a'_i, b'_i	coefficients of eq 2

Registry Numbers Supplied by Author. Li_2SO_4 , 10377-48-7; ethanol, 64-17-5.

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