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Density and Viscosity of Saturated Solutions of Lithium Potassium Sulfate + Water + Methanol at 298.15 K

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The solubility of lithium potassium sulfate double salt in water and in aqueous methanol has been determined at a temperature of 298.15 K, in the methanol mass concentration range 0−0.4 kg of methanol/kg of water. An equation is given for the solubility as a function of the composition of potassium sulfate in solution. The densities and viscosities of the saturated solutions are also reported. Equations are given for both properties as a function of the solubility.

Introduction

In comparison with other conventional procedures, several advantages have been recognized in the crystallization of salts from aqueous solutions by use of some organic compounds miscible with water (*1−3*). Equilibrium studies on sulfate salts + water + alcohol (*4−6*) show a decrease in the solubility of sulfate salts by a salting-out effect produced by addition of alcohol and suggest applications in differential crystallization processes (*7, 8*).

Lithium potassium sulfate is an interesting electrooptic material, with an electrooptic effect more than 3 times that of quartz (*9, 10*). At 298.15 K the solubility diagram of the system Li_2SO_4 + K_2SO_4 + H_2O shows a region for the double salt $LiKSO_4$ as a solid phase (*11−13*). Hence, it is possible to crystallize $LiKSO_4$ from a diluted aqueous solution by water evaporation at ambient temperature, but the process must be controlled because this salt is not congruently soluble in water. The procedure might be improved by adding alcohol as cosolvent. In a previous work (*14*), the solubility of $LiKSO_4$ in water and in aqueous ethanol at 298.15 K together with the density and viscosity results of the saturated solutions was reported. In this study, we present the solubility, density, and viscosity for the same salt but in aqueous methanol, as an alternative precipitant. These properties may be useful in controlling the salt precipitation process.

Experimental Section

Panreac PRS grade lithium sulfate monohydrate (99+%) and potassium sulfate (99+%) were preliminarily dried at 60 °C. Panreac pa methanol (99.5+%) and distilled water passed through a Millipore ultrapure cartridge kit were used. All reagents were utilized without further purification.

The experimental procedure was according to the following scheme: For the aqueous system, several solutions were prepared by dissolving in water a known mass of Li_2SO_4 (or K_2SO_4, depending on the composition required) and then adding a known amount of the other salt to give a final composition of the other salt greater than the expected equilibrium value. For the salt + methanol + water systems we prepared a series of H_2O + Li_2SO_4 + K_2SO_4 solutions of compositions near saturation. Different masses of methanol were added to known masses of these solutions. The accuracy of the compositions was $\pm 10^{-5}$ kg.

In all cases, supersaturated solutions resulted, which were magnetically stirred for more than 72 h in closed flasks to equilibrate. All flasks were thermostated at 298.15 K in a bath controlled to ±0.05 K, the temperature being measured by a digital thermometer (Yokogawa 7563) with a precision of ±0.01 K (which had previously been calibrated against a quartz thermometer, Hewlett-Packard 2804 A, with ±0.001 K precision). The solutions were then allowed to settle at constant temperature for 1 h, and samples of the clear liquid were collected by means of a Masterflex peristaltic pump, filtered through a Gelman Versapor 0.22 μm filter fitted to the pump, and discharged directly into the densimeter or viscometer. Possible solvent evaporation was eliminated by this procedure. Samples of the solid phase were also filtered and characterized by X-ray diffraction.

Total concentrations of the solutions were determined by evaporating a known mass of solution (between 15 and 30 g) to the anhydrous salt at 473.15 K. All the masses were measured on an analytical balance with a precision of $\pm 10^{-7}$ kg. A constant mass of anhydrous salt was considered only when successive measurements of a sample differed by less than 10^{-6} kg. On the basis of repeated determinations, the determined concentration was reproducible to ±0.1% (relative mean standard deviation). The concentration of potassium was determined spectrophotometrically by emission at 766.5 nm using a Philips flame spectrophotometer (PU 9400). The calibration line was obtained from aqueous solutions of K_2SO_4 prepared by mass at concentrations ranging from 0 to 0.01 kg of K_2SO_4/100 kg of solution. At these dilutions, no significant influence of the initial methanol and Li_2SO_4 concentrations on the spectrophotometric readings was observed. Five measurements of concentration of each sample were made, and the reproducibility was ±0.5%. On the basis of standard solution measurements, an accuracy of $\pm 2 \times 10^{-2}$ kg of K_2SO_4/100 kg of solution was established. The procedure to determine the concentration of the solutions was checked with a gravimetric standard analysis of sulfates (*15*).

We found lithium potassium sulfate as the solid phase in all systems, except for the solids corresponding to eutectic solutions which were a mixture of $LiKSO_4$ and lithium or potassium sulfate.

The temperature for all the next measurements was regulated through a cascade water bath apparatus. This system permits stability within ±0.02 K as checked by the cited Yokogawa 7563 thermometer.

Densities were measured with an Anton Paar DMA 602 vibrating tube densimeter operating under static conditions. The temperature of the sample was kept constant

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Table 1. Solubility *s*, Density *ϱ*, and Viscosity *η* of Lithium Potassium Sulfate for Various Methanol Mass Compositions *w* in 1 kg of Water at 298.15 K

w/(kg of CH_3OH/kg of H_2O)	s_K/(kg of K_2SO_4/100 kg of soln)	s/(kg of salt/100 kg of soln)	ϱ/(kg·m^{-3})	$10^3\eta$/(Pa·s)
0.00	2.30	27.58	1250.37	4.90
	2.46	26.88	1242.94	4.61
	2.48	27.11	1246.43	4.70
	3.13	25.44	1229.28	3.99
	3.91	23.88	1213.08	3.38
	4.93	22.47	1196.46	2.79
	6.54	21.40	1187.07	2.44
	7.82	21.07	1182.76	2.25
	9.62	20.92	1180.17	2.18
	10.21	20.94	1181.95	2.23
0.10	1.37	21.63	1178.68	4.28
	1.60	19.86	1161.31	3.91
	2.33	16.60	1128.91	2.93
	3.43	14.30	1103.87	2.19
	4.78	13.25	1092.98	1.91
	5.47	13.16	1091.63	1.85
0.20	0.80	17.38	1121.73	3.69
	0.83	17.22	1119.99	3.69
	1.07	14.30	1093.48	2.98
	1.65	10.67	1059.76	2.26
	2.26	9.03	1042.06	1.93
	2.96	8.38	1036.83	1.83
	3.12	8.04	1036.20	1.77
0.30	0.50	13.79	1077.43	3.28
	0.52	13.60	1076.62	3.21
	0.55	12.50	1068.24	3.13
	0.85	8.77	1034.22	2.34
	1.26	6.59	1012.88	1.99
	1.65	5.52	1004.34	1.83
	1.76	5.28	1003.04	1.82
0.40	0.34	10.74	1044.71	3.04
	0.34	10.62	1043.35	2.93
	0.31	10.75	1043.11	2.93
	0.45	7.71	1015.67	2.39
	0.67	5.42	994.27	2.04
	0.95	4.34	985.00	1.87
	1.10	3.60	980.48	1.79

with the cascade bath. For each sample three runs were developed. Before each series of measurements the instrument was calibrated with ultrapure and degassed water and vacuum. The reproducibility in the determination of the density is better than ±10^{-2} kg·m^{-3}. The measured accuracy was ±2 × 10^{-2} kg·m^{-3}, obtained from the known concentrations of NaCl solutions using the density data of Lo Surdo et al. (*16*).

Viscosities were measured with a Hoppler-type BH falling sphere viscometer, using two different sphere diameters: one (A) for solutions of viscosity <2.5 mPa·s and the other (B) for those of higher viscosities. Pure water at temperatures ranging from 278.15 to 313.15 K was used as the fluid for calibration for sphere A, taking its viscosity from ref 17. As the standard for sphere B calibration several glycerol + water samples were used at 293.15 K, their viscosities being taken from ref 17 and their compositions being checked by comparison of the experimental density measurements with the values in ref 17. All solutions were maintained at 298.15 K, measured by a Yokogawa 7563 thermometer, by circulating water from the constant-temperature bath through the outer jacket of the viscometer. The flow times were determined with an estimated precision of ±0.1 s using a digital stopwatch. Typical time scales were 22−370 s for measurements with ball A and 45−80 s when using the second sphere. The results for the viscosity, given in Table 1, are the average of at least five determinations, and the measurements of flow time were reproducible within ±0.1%. The measured viscosities were reproducible to ±0.5%. On the basis of comparison with reliable data from the literature, the accuracy of the viscosity was better than ±1%.

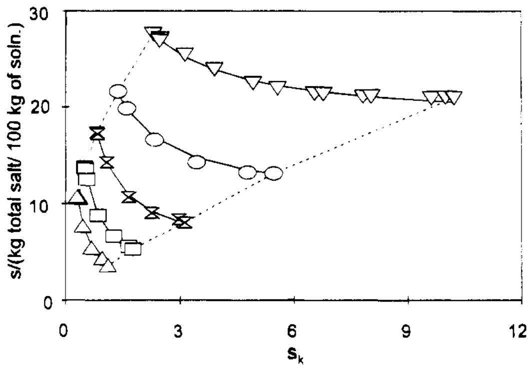

Figure 1. Solubility *s* of lithium potassium sulfate in *w* methanol + (1 − *w*) water at 298.15 K, as a function of the concentration of potassium sulfate s_K: ▽, $w = 0$; ○, $w = 0.1$; hourglass, $w = 0.2$; □, $w = 0.3$; △, $w = 0.4$.

Table 2. Coefficients of the Model Eqs 1−3

a_0	a_1	$10^{-1}a_2$	b_0	b_1	b_2
18.45	−93.37	12.34	21.11	−64.96	50.48

$10^{-1}a'_0$	a'_1	a'_2	b'_0	$10b'_1$	$10^2b'_2$
96.55	−37.66	−11.44	10.35	−40.77	32.10

$10^4a''_0$	$10^3a''_1$	$10^2a''_2$	$10^2a''_3$	$10^2a''_4$	$10^5b''_0$	$10^4b''_1$	$10^4b''_2$
−62.77	62.56	−23.07	45.24	−37.78	40.48	−13.49	19.14

Results

The solubility, density, and viscosity of the saturated solutions, limited to the $LiKSO_4$ region, for the system lithium sulfate + potassium sulfate + water + methanol at 298.15 K are given in Table 1.

The solubility results may be correlated as total salt (lithium sulfate + potassium sulfate) concentration, *s*, as a function of the concentration of potassium sulfate in solution, s_K, according to the equation

$$s/(\text{kg of total salt}/100\text{ kg of soln}) = A(w) + \frac{B(w)}{s_K/(\text{kg of }K_2SO_4/100\text{ kg of soln})} \tag{1}$$

with

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

$$B(w) = b_0 + b_1w + b_2w^2$$

where *w* stands for the methanol concentration expressed as kg of CH_3OH/kg of H_2O. The a_i and b_i coefficient values are presented in Table 2. The mean relative standard deviation between all experimental and calculated solubility values is 1.8%. The maximum relative deviation is about 4.5%.

Figure 1 illustrates the decrease in the solubility of lithium potassium sulfate with addition of methanol. Experimental results are plotted as points, and the solid lines correspond to the fitting through eq 1. For each curve, the end points correspond to the eutectic compositions which separate three crystallization fields based on $Li_2SO_4·H_2O$, $LiKSO_4$, and K_2SO_4. The region delimited between both eutectics establishes the double salt field, so the solid phase equilibrated with the saturated solutions in that area was $LiKSO_4$.

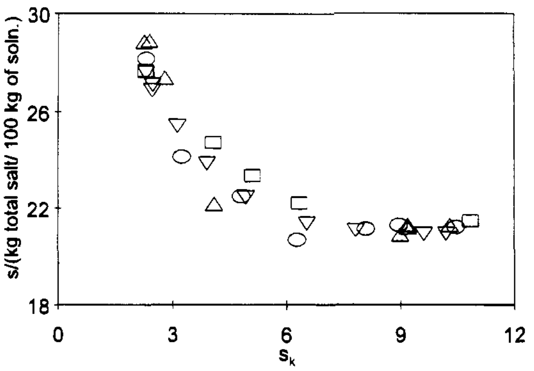

Figure 2. Comparison between the present experimental results on aqueous lithium potassium sulfate solubility and the literature: ▽, this study; □, ref 11; △, ref 12; ○, ref 13.

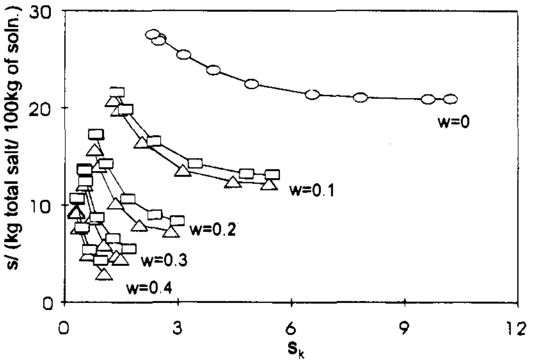

Figure 3. Solubility of lithium potassium sulfate in w alcohol + $(1 - w)$ water at 298.15 K: □, methanol; △, ethanol.

For the purpose of comparison, we have plotted in Figure 2 the experimental $LiKSO_4$ solubility results for the aqueous system and those taken from the literature (*11–13*). In general, there is a good concordance between the results. No references have been found for the solubility of this salt in the presence of methanol. A comparison between the solubility results with those obtained using water + ethanol as the solvent (*14*) is found in Figure 3.

The density results may be correlated as the density of the saturated solution, ϱ, as a function of the total salt concentration, s, according to the equation

$$\varrho/(\mathrm{kg{\cdot}m^{-3}}) = A'(w) + B'(w)[s/(\text{kg of total salt/100 kg of soln})] \quad (2)$$

with

$$A'(w) = a'_0 + a'_1 w + a'_2 w^2$$

$$B'(w) = b'_0 + b'_1 w + b'_2 w^2$$

The a'_i and b'_i coefficient values are presented in Table 2. The mean relative standard deviation between all experimental and calculated density values is 0.09%. The maximum relative deviation is about 0.2%. We can see as solid lines in Figure 4 the fitting resulting from eq 2.

The viscosity results may be correlated as the viscosity of the saturated solution, η, as a function of the total salt concentration, s, according to the equation

$$\eta/(\mathrm{Pa{\cdot}s}) = A''(w) + B''(w)[s/(\text{kg of total salt/100 kg of soln})] \quad (3)$$

with

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

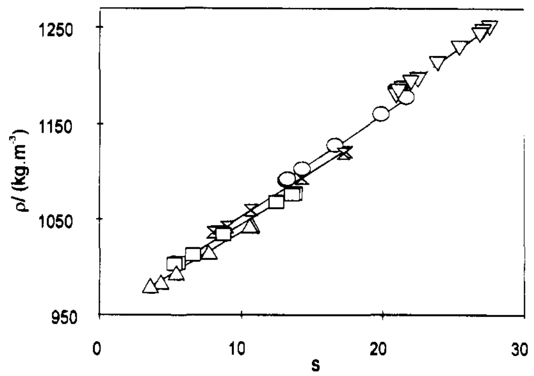

Figure 4. Density ϱ versus the solubility s of lithium potassium sulfate for various methanol mass compositions w in 1 kg of water at 298.15 K: ▽, $w = 0$; ○, $w = 0.1$; hourglass, $w = 0.2$; □, $w = 0.3$; △, $w = 0.4$.

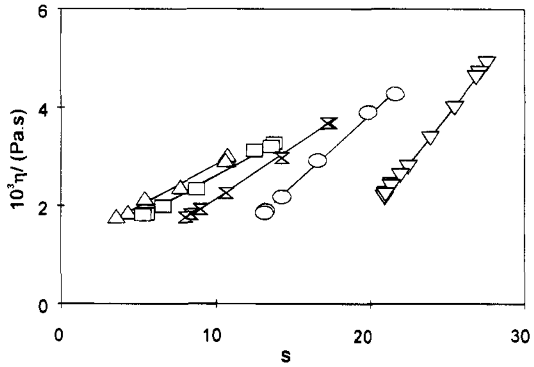

Figure 5. Viscosity η versus the solubility s of lithium potassium sulfate for various methanol mass compositions w in 1 kg of water at 298.15 K: ▽, $w = 0$; ○, $w = 0.1$; hourglass, $w = 0.2$; □, $w = 0.3$; △, $w = 0.4$.

$$B''(w) = b''_0 + b''_1 w + b''_2 w^2$$

The a''_i and b''_i coefficient values are also presented in Table 2. The mean relative standard deviation between all experimental and calculated viscosity values is 1.1%. The maximum relative deviation is about 3%. We can see as solid lines in Figure 5 the fitting resulting from eq 3.

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Registry Numbers Supplied by Author. Li_2SO_4, 10377-48-7; K_2SO_4, 7778-80-5; $LiKSO_4$, 14520-76-4; methanol, 67-56-1.

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