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

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The solubility of lithium potassium sulfate double salt in water and in aqueous ethanol has been determined at a temperature of 298.15 K, in the ethanol mass concentration range of 0–0.4 kg of ethanol/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

At 298.15 K the solubility diagram of the system $Li_2SO_4$ + $K_2SO_4$ + $H_2O$ shows a field for the double salt $LiKSO_4$ as a solid phase (*1–3*). 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 ethanol as cosolvent, leading to a decrease in the solubility of the salt by a salting out effect and an increase in the yield of crystals. The applicability of alcohols for differential crystallization processes has been suggested by some researchers (*4–6*).

Lithium potassium sulfate is an interesting electrooptic material, having an electrooptic effect more than 3 times that of quartz (*7, 8*). Some results of the solubility of $LiKSO_4$ in water may be found in the literature (*1–3*), but there is a lack of published values on the solubility of this salt in the presence of ethanol. Therefore, we have measured the solubility of $LiKSO_4$ in water and in aqueous ethanol at 298.15 K. In addition, we report density and viscosity results for the saturated solutions. 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. Merck pa ethanol absolute and distilled water passed through a Millipore ultrapure cartridge kit were used. All reagents were used 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 an amount of the other salt to give a final composition of the other salt greater than the expected equilibrium value. For the salt + ethanol + water systems we prepared a series of $H_2O$ + $Li_2SO_4$ + $K_2SO_4$ solutions of compositions near saturation. Different masses of ethanol 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. The clear liquor was collected from the flasks by means of a Masterflex peristaltic pump and then 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. On the other hand, all sampling equipment was adequately thermostated in order to avoid salt precipitation when transporting the solutions to the different apparatus. Samples of the solid phase were also filtered and characterized by X-ray diffraction.

Total concentrations of the solutions were determined, in duplicate, by evaporating at 473.15 K a known mass of solution (between 15 and 30 g) to the anhydrous salt. 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 ethanol and $Li_2SO_4$ concentration on the spectrophotometric readings was observed. Five measurements of concentration of each saturated solution 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 (*9*).

After characterization by X-ray diffraction, the solid phase found in all systems was lithium potassium sulfate, except for the solids corresponding to eutectic solutions which were a mixture of $LiKSO_4$ and lithium or potassium sulfates.

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.

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**Table 1. Solubility $s$ and Density $\varrho$ of Potassium Sulfate Aqueous–Alcoholic Solutions for Various Alcohol Mass Compositions $w$ in 1 kg of Water at 298.15 K**

| $w$ | $s$/(kg/100 kg of soln) |  | $\varrho$/(kg·m$^{-3}$) |  |
|---|---|---|---|---|
|  | this study | ref 11 | this study | ref 11 |
|  |  | Methanol |  |  |
| 0.0952 | 5.52 | 5.51 | 1025.72 | 1025.58 |
| 0.1904 | 3.04 | 3.04 | 994.12 | 994.16 |
| 0.3173 | 1.55 | 1.53 | 970.01 | 969.76 |
| 0.3966 | 1.06 | 1.07 | 959.48 | 959.27 |
|  |  | Ethanol |  |  |
| 0.0949 |  | 5.16 |  | 1023.13 |
| 0.0961 | 5.18 |  | 1022.91 |  |
| 0.1898 |  | 2.67 |  | 992.54 |
| 0.1901 | 2.68 |  | 992.56 |  |
| 0.2373 | 1.98 | 1.98 | 982.78 | 982.68 |
| 0.3955 | 0.86 | 0.85 | 960.03 | 959.72 |

Densities were measured with an Anton Paar DMA 602 vibrating tube densimeter operating under static conditions. The temperature of the sample was kept constant with the cascade bath. Before each series of measurements the instrument was calibrated with ultrapure and degassed water and vacuum. For each saturated sample three runs were developed. The reproducibility in the determination of the density is better than $\pm 10^{-2}$ kg·m$^{-3}$. The measured accuracy was $\pm 2 \times 10^{-2}$ kg·m$^{-3}$, obtained from the known concentrations of NaCl solutions using the density data of Lo Surdo et al. (*10*). In order to establish the confidence of the experimental procedure of density measurements, a comparison of the results with those from ref 11 is given in Table 1 for saturated solutions of $K_2SO_4$ in water + ethanol and water + methanol.

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 of the sphere (A), taking its viscosity from ref 12. As the standard for sphere B calibration several glycerol + water samples were prepared at 293.15 K, their viscosities also being taken from ref 12 and their exact compositions being checked by comparison of the experimental density measurements with the reported values found in the literature (*12*). 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 270–370 s for measurements with ball A and 45–80 s when using the second sphere. The results for the viscosity, given in Table 2, 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%.

## Results

The solubility, density, and viscosity of the saturated solutions, limited to the $LiKSO_4$ region, for the system lithium sulfate + potassium sulfate + water + ethanol at 298.15 K are given in Table 2.

**Table 2. Solubility $s$, Density $\varrho$, and Viscosity $\eta$ of Lithium Potassium Sulfate for Various Ethanol Mass compositions $w$ in 1 kg of Water at 298.15 K**

| composition of saturated solutions |  |  |  |  |
|---|---|---|---|---|
| $w$/(kg of $C_2H_5OH$/kg of $H_2O$) | $s_K$/(kg of $K_2SO_4$/100 kg of soln) | $s$/(kg of salt/100 kg of soln) | $\varrho$/(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 | 1.28 | 20.80 | 1169.28 | 4.31 |
|  | 1.43 | 19.82 | 1158.69 | 3.95 |
|  | 2.03 | 16.55 | 1126.79 | 3.08 |
|  | 3.11 | 13.60 | 1097.97 | 2.27 |
|  | 4.43 | 12.45 | 1085.34 | 2.01 |
|  | 5.39 | 12.23 | 1084.57 | 1.93 |
| 0.20 | 0.78 | 15.75 | 1105.88 | 3.80 |
|  | 0.88 | 14.02 | 1091.54 | 3.46 |
|  | 1.34 | 10.22 | 1056.04 | 2.69 |
|  | 1.96 | 7.95 | 1034.86 | 2.30 |
|  | 2.63 | 7.29 | 1029.99 | 2.14 |
| 0.30 | 0.51 | 12.12 | 1061.68 | 3.60 |
|  | 0.72 | 8.61 | 1031.80 | 2.98 |
|  | 1.03 | 5.94 | 1009.91 | 2.55 |
|  | 1.36 | 4.79 | 1000.22 | 2.33 |
|  | 1.47 | 4.46 | 997.17 | 2.27 |
| 0.40 | 0.30 | 9.45 | 1028.28 | 3.58 |
|  | 0.31 | 9.23 | 1026.20 | 3.54 |
|  | 0.37 | 7.64 | 1012.96 | 3.17 |
|  | 0.62 | 4.90 | 991.09 | 2.69 |
|  | 1.04 | 2.93 | 976.00 | 2.37 |

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

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

with

$$A(w) = a_0 + a_1 w + a_2 w^2$$

$$B(w) = b_0 + b_1 w + b_2 w^2$$

where $w$ stands for the ethanol concentration expressed as kg of $C_2H_5OH$/kg of $H_2O$. The $a_i$ and $b_i$ coefficient values are presented in Table 3. The coefficients of the empirical equation of two independent variables have been exclusively determined in order to minimize the mean quadratic deviation of the fitting to the experimental values. The mean relative standard deviation between all experimental and calculated solubility values is 1.9%. The maximum relative deviation is about 5%.

Figure 1 illustrates the decrease in the solubility of lithium potassium sulfate with addition of ethanol. 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 $Li_2SO_4 \cdot H_2O$, $LiKSO_4$, 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 $LiKSO_4$.

For the purpose of comparison, we have plotted in Figure 2 the experimental solubility results for the aqueous system and those taken from the literature. In general, there is a good concordance between the results. In order to give a

**Table 3. Coefficients of the Model Eqs 1–3**

| $a_0$ | $10^{-1}a_1$ | $10^{-1}a_2$ | $b_0$ | $b_1$ | $b_2$ |
|---|---|---|---|---|---|
| 18.45 | −10.65 | 15.37 | 20.87 | −65.36 | 50.14 |
| $10^{-1}a'_0$ | $a'_1$ | $10^{-1}a'_2$ | $b'_0$ | $b'_1$ | $b'_2$ |
| 96.08 | 41.99 | −15.46 | 10.54 | −7.69 | 2.73 |

| $10^4a''_0$ | $10^3a''_1$ | $10^2a''_2$ | $10^2a''_3$ | $10^5b''_0$ | $10^4b''_1$ | $10^4b''_2$ |
|---|---|---|---|---|---|---|
| −61.64 | 62.89 | −17.50 | 16.94 | 39.97 | −14.89 | 23.49 |

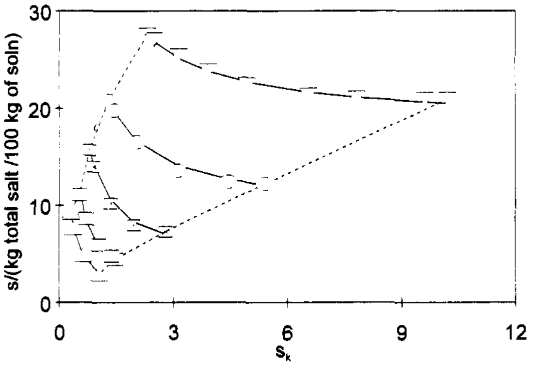

**Figure 1.** Solubility $s$ of lithium potassium sulfate in $w$ ethanol + $(1 - w)$ water at 298.15 K, as a function of the concentration of potassium sulfate $s_K$: ▽, $w = 0$; ○, $w = 0.1$; hourglass, $w = 0.2$; □, $w = 0.3$; △, $w = 0.4$.

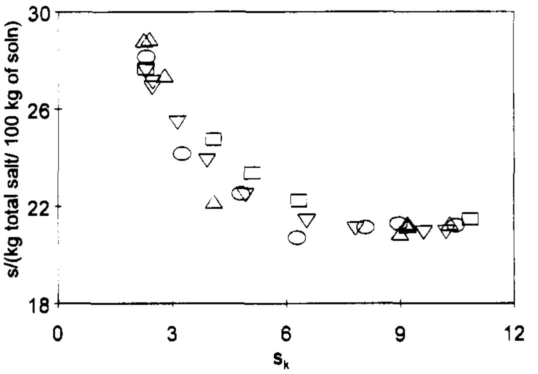

**Figure 2.** Comparison between the present experimental results on aqueous lithium potassium sulfate solubility and the literature: ▽, this study; △, ref 1; □, ref 2; ○, ref 3.

more detailed checking of the solubilities, we have determined the solubility of $K_2SO_4$ in water + methanol and in water + ethanol. The solubility results along with a comparison with those found in the literature (*11*) are given in Table 1.

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

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

with

$$A'(w) = a'_0 + a'_1w + a'_2w^2$$

$$B'(w) = b'_0 + b'_1w + b'_2w^2$$

The $a'_i$ and $b'_i$ 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 0.17%. We can see as solid lines in Figure 3 the fitting resulting from eq 2.

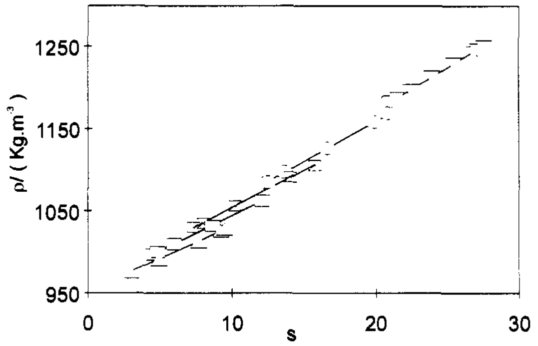

**Figure 3.** Density $\varrho$ versus the solubility $s$ of lithium potassium sulfate for various ethanol mass compositions $w$ in 1 kg of water at 298.15 K: ▽, $w = 0$; ○, $w = 0.1$; hourglass, $w = 0.2$; □, $w = 0.3$; △, $w = 0.4$.

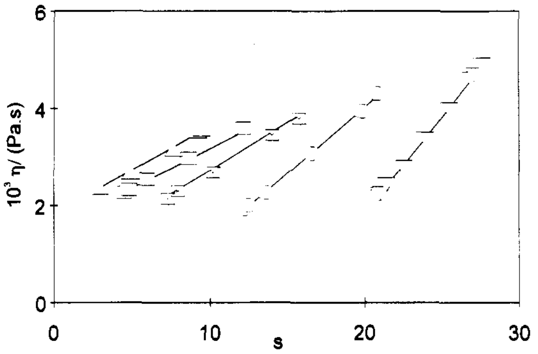

**Figure 4.** Viscosity $\eta$ versus the solubility $s$ of lithium potassium sulfate for various ethanol mass compositions $w$ in 1 kg of water at 298.15 K: ▽, $w = 0$; ○, $w = 0.1$; hourglass, $w = 0.2$; □, $w = 0.3$; △, $w = 0.4$.

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

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

with

$$A''(w) = a''_0 + a''_1w + a''_2w^2 + a''_3w^3$$

$$B''(w) = b''_0 + b''_1w + b''_2w^2$$

The $a''_i$ and $b''_i$ coefficient values are also presented in Table 3. The mean relative standard deviation between all experimental and calculated viscosity values is 1.2%. The maximum relative deviation is about 3%. We can see as solid lines in Figure 4 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; ethanol, 64-17-5.

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