J. Chem. Eng. Data **1995,** *40,* 987−991

Density, Viscosity, and Electrical Conductivity of Aqueous Solutions of Lithium Sulfate

Angel Cartón,* Francisco Sobrón, Silvia Bolado, and José I. Gerbolés

Department of Chemical Engineering, University of Valladolid, Valladolid 47011, Spain

The density, viscosity, and electrical conductivity of aqueous lithium sulfate solutions has been determined over the concentration range 0.4−3.2 *m*. This range covered both undersaturated and supersaturated solutions. Apparent molal volumes of electrolyte are given along with equations for the properties as a function of temperature and composition.

Introduction

The density, viscosity, and electrical conductivity of electrolyte solutions are useful in determining the nature of solute−solute interactions (Horvath, 1985). In addition, they are useful in chemical engineering for material balance calculations and design of crystallizers. The knowledge of these properties, particularly near saturation and in the metastable region, is useful in crystallization processes.

Lithium sulfate and double salts of the type $LiASO_4$ (A = K, Na, Rb, ...) might be used as ionic conductors and in ferroelectrics and optoelectronics (Abello *et al.*, 1985; Singh and Deshpande, 1984; Fujimoto *et al.*, 1985). Within a general framework of the study of macroscopic (Cartón *et al.*, 1994a,b, 1995a,b) and microscopic (Martinez *et al.*, 1995; Rull *et al.*, 1994) properties of aqueous solutions of these salts, we are interested in the precise determination of physical and transport properties, especially at high solute concentration (concentration range in which the study of interactions occurring in solution is useful to understand the crystallization process). Recently, we reported (Cartón *et al.*, 1994a, 1995b) the densities, viscosities, and electrical conductivities of saturated solutions of lithium sulfate. The present paper contains results on the same properties but in the range 0.4−3.2 $mol{\cdot}kg^{-1}$ solvent and at temperatures ranging from 278.15 to 338.15 K. Several supersaturated solutions are measured within this wide concentration range, depending on the solution temperature.

Experimental Section

Lithium sulfate has inverted solubility (Cartón *et al.*, 1994a), so the experiments were conducted as follows: The density, viscosity, and conductivity of a sample of known composition was measured at the lowest temperature, and the measurements were repeated after the temperature was increased by fixed amounts. For the more concentrated solutions the temperature increase was carried out until the limit of the supersaturated region was detected. The limit of the metastable zone was determined from the first appearance of crystals in the viscometer.

PRS grade lithium sulfate monohydrate (Panreac) without further purification and distilled water, degassed and passed through a Millipore ultrapure cartridge kit, were used. Prior to the determination of the density, viscosity, and conductivity, all samples were filtered under pressure through a Gelman VERSAPOR 0.22 μm filter at adequate temperature to prevent any precipitation.

All the solutions were prepared by mass using an analytical balance with a precision of $\pm 10^{-4}$ g. The compositions were checked by evaporating at 493.15 K a known mass of solution; a constant mass of anhydrous salt was considered only when succesive measurements of a sample differed by less than 10^{-3} g. On the basis of repeated determinations, the reproducibility of the gravimetric method was $\pm 10^{-4}$ g of Li_2SO_4/g of solution.

The temperature was measured by a digital thermometer (Yokogawa 7563) with a precision of ±0.01 K (which had previously been calibrated with ±0.005 K accuracy against a quartz thermometer, Hewlett-Packard 2804 A). A cascade water bath apparatus was used to regulate the temperature. This system permits stability within ±0.02 K as checked by the Yokogawa 7563 thermometer.

Densities were measured with an Anton Paar DMA 602 vibrating tube densimeter operating under static conditions. The oscillation period (about 3−4 ms) was measured with a Philips PM 6669 frequency meter. This was counted with 8 digits which were integrated and renewed every 4 s and was obtained from an average of 100 measurements, maintaining an overall stable indication of $\tau = \pm 5$ ns. All measuring operations and calculations were computer controlled, and for each sample three measurements were made. Before each series of measurements the instrument was calibrated with ultrapure and degassed water and with vacuum. The reproducibility in the determination of the density is better than $\pm 10^{-2}$ $kg{\cdot}m^{-3}$. The accuracy was $\pm 2 \times 10^{-2}$ $kg{\cdot}m^{-3}$, estimated from comparison of NaCl solutions using the density data of Lo Surdo *et al.* (1982).

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 in the temperature range 278.15−313.15 K was used as the fluid for calibration for sphere A, and several glycerol + water solutions prepared at 293.15 K were used as the standard for sphere B calibration. In both cases, their viscosities were taken from the literature (Weast, 1980). The exact compositions of the glycerol + water samples were checked by comparing the experimental density measurements with those found in Weast (1980). Condensation or evaporation was prevented by sealing the solutions into the central cylinder. All solutions were maintained at the desired temperature by circulating water from the constant-temperature bath through the outer jacket of the viscosimeter. The flow times were determined with an estimated precision of ±0.1 s using a digital stopwatch. The results given in Table 1 are the average of at least five determinations for each solution, measurements of flow time being reproducible within ±0.1%. The viscosities of the samples were measured with a reproducibility better than ±0.5%. On the basis of comparison with reliable data

0021-9568/95/1740-0987$09.00/0

Table 1. Density ϱ, Viscosity η, Electrical Conductivity κ, and Apparent Molal Volume Φ_v of Aqueous Lithium Sulfate Solutions (from 0.4 to 3.2 mol·kg^{-1}) at Different Temperatures

T/K	ϱ/(kg·m^{-3})	$10^3\eta$/(Pa·s^{-1})	κ/(S·m^{-1})	$10^6\Phi_v$/(m^3·mol^{-1})	T/K	ϱ/(kg·m^{-3})	$10^3\eta$/(Pa·s^{-1})	κ/(S·m^{-1})	$10^6\Phi_v$/(m^3·mol^{-1})
m = 0.4057 mol·kg^{-1}									
283.15	1037.18	1.65	2.85	16.91	303.15	1032.20	0.99	4.50	18.85
293.15	1035.09	1.26	3.67	18.23	313.15	1028.62	0.80	5.35	18.98
298.15	1033.72	1.12	4.08	18.66					
m = 0.7952 mol·kg^{-1}									
283.15	1071.19	2.00	4.38	18.92	303.15	1065.59	1.22	6.88	20.50
293.15	1068.70	1.55	5.60	20.00	313.15	1061.89	0.99	8.22	20.61
298.15	1067.20	1.38	6.24	20.34					
m = 1.1924 mol·kg^{-1}									
283.15	1103.09	2.48	5.22	21.04	303.15	1097.05	1.51	8.33	22.36
293.15	1100.32	1.89	6.68	21.95	313.15	1093.27	1.21	9.94	22.44
298.15	1098.74	1.69	7.47	22.21					
m = 1.5788 mol·kg^{-1}									
283.15	1132.37	3.07	5.62	22.86	303.15	1126.05	1.82	9.01	23.96
293.15	1129.42	2.31	7.25	23.62	313.15	1122.31	1.49	10.84	23.96
298.15	1127.79	2.05	8.14	23.84					
m = 1.9562 mol·kg^{-1}									
283.15	1160.00	3.83	5.72	24.11	303.15	1153.55	2.21	9.31	25.03
293.15	1156.94	2.82	7.47	24.76	313.15	1150.11	1.76	11.24	24.86
298.15	1155.28	2.49	8.36	24.94					
m = 2.6030 mol·kg^{-1}									
283.15	1202.86	5.53	5.34	26.49	303.15	1196.32	3.06	8.98	27.18
293.15	1199.70	4.02	7.16	27.00	313.15	1192.81	2.42	11.12	27.06
298.15	1198.09	3.49	8.05	27.11					
m = 2.9853 mol·kg^{-1}									
278.15	1229.08	8.48	4.17	27.00	324.15	1213.12	2.33	12.91	27.56
283.15	1227.65	7.02	5.02	27.34	325.15	1212.62	2.29	13.12	27.56
288.15	1226.13	5.96	5.80	27.58	326.15	1212.39	2.25	13.34	27.47
293.15	1224.68	5.05	6.79	27.71	327.15	1211.92	2.21	13.52	27.44
298.15	1223.05	4.36	7.76	27.81	328.15	1211.67	2.16	13.74	27.36
303.15	1221.34	3.81	8.61	27.84	331.15	1210.05	2.04	14.35	27.34
308.15	1219.51	3.33	9.57	27.84	333.15	1209.13	1.96	14.79	27.26
313.15	1217.67	2.96	10.65	27.78	336.15	1207.96	1.86	15.40	27.08
318.15	1215.59	2.65	11.70	27.72	338.15	1206.97	1.81	15.82	27.00
323.15	1213.36	2.37	12.72	27.65					
m = 3.0660 mol·kg^{-1}									
278.15	1234.54	8.88	4.15	27.08	311.15	1223.98	3.25	10.19	27.83
283.15	1233.09	7.35	4.88	27.41	313.15	1223.23	3.10	10.55	27.80
288.15	1231.65	6.20	5.70	27.62	316.15	1221.94	2.89	11.16	27.78
293.15	1230.23	5.28	6.72	27.74	318.15	1221.31	2.77	11.57	27.69
298.15	1228.70	4.57	7.59	27.80	320.15	1220.47	2.66	11.97	27.66
303.15	1226.98	3.99	8.56	27.84	323.15	1219.11	2.52	12.57	27.61
308.15	1225.13	3.49	9.58	27.85					
m = 3.1248 mol·kg^{-1}									
278.15	1238.10	9.21	4.13	27.24	305.15	1229.66	3.89	8.87	28.04
283.15	1237.05	7.63	4.84	27.45	308.15	1228.58	3.57	9.37	28.02
288.15	1235.29	6.40	5.63	27.76	310.15	1227.82	3.39	9.74	28.01
293.15	1233.66	5.47	6.61	27.93	312.15	1227.07	3.24	10.13	27.99
298.15	1232.11	4.71	7.57	27.99	313.15	1226.71	3.17	10.34	27.97
300.15	1231.40	4.47	7.94	28.03	314.15	1226.30	3.11	10.54	27.96
303.15	1230.40	4.11	8.49	28.03					
m = 3.1992 mol·kg^{-1}									
278.15	1242.26	9.65	4.10	27.53	298.15	1236.80	4.95	7.48	28.12
283.15	1241.27	8.02	4.79	27.72	300.15	1235.96	4.70	7.88	28.18
288.15	1239.96	6.71	5.59	27.89	303.15	1234.95	4.30	8.41	28.19
293.15	1238.32	5.71	6.54	28.06	305.15	1233.28	4.10	8.82	28.18

from the literature, the accuracy of the viscosity was better than ±1%.

Conductivities were measured with a Crison microCM 2100 conductimeter. The conductivities at 298.15 K of potassium chloride solutions in the composition range 0.001–1.0 M (Diaz Peña and Roig, 1976) were used for calibration. In order to verify the accuracy of the conductivity, measurements were made on several KBr aqueous solutions in the temperature range 293.15–318.15 K, with their conductivities being taken from the literature (Isono, 1984). The resulting accuracy was better than ±0.5%. At least five measurements of each sample were made. The reproducibility was ±0.02 S·m^{-1}.

Results

The measured densities, viscosities, and conductivities of aqueous lithium sulfate solutions for salt concentrations ranging from 0.4 to 3.2 m are given in Table 1.

The densities are plotted as a function of the temperature for various constant molalities in Figure 1. Arrows in the figure indicate saturation. The densities calculated from eq 2 are shown as lines. A comparison between our density values and those found in the literature (Washburn, 1928; Söhnel and Novotny, 1985) are shown in Figure 1. Agreement is within ±0.04%.

Table 2. Coefficients of Equations 2, 3, and 4

a_{ij}	$i = 2$	$i = 3$	$i = 4$	$i = 5$
$j = 0$	-20.56208×10^{-4}	38.12222×10^{-4}	-24.25201×10^{-4}	52.33744×10^{-5}
$j = 1$	14.21999×10^{-6}	-26.13685×10^{-6}	16.60074×10^{-6}	-35.82487×10^{-7}
$j = 2$	-24.47397×10^{-9}	44.55566×10^{-9}	-28.22544×10^{-9}	60.85246×10^{-10}
b_{ij}	$i = 1$	$i = 2$	$i = 3$	$i = 4$
$j = 0$	-21.945	18.216	-51.782×10^{-2}	-63.374×10^{-2}
$j = 1$	15.468×10^{-2}	-12.701×10^{-2}	67.472×10^{-4}	40.948×10^{-4}
$j = 2$	-26.571×10^{-5}	22.316×10^{-5}	-17.308×10^{-6}	-63.527×10^{-7}
c_{ij}	$i = 0$	$i = 1$	$i = 2$	$i = 3$
$j = 0$	-92.576×10^{-3}	13.502×10^{-2}	-50.263×10^{-3}	19.965×10^{-4}
$j = 1$	37.072×10^{-5}	-67.879×10^{-5}	25.278×10^{-5}	82.189×10^{-8}
$j = 2$	-60.115×10^{-10}	59.725×10^{-8}	-23.807×10^{-8}	-23.625×10^{-9}

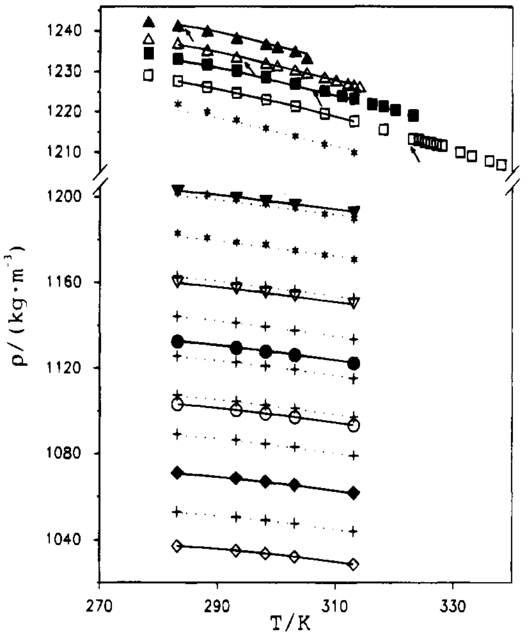

Figure 1. Temperature dependence of the solution density ϱ for aqueous lithium sulfate: this study {◇, $m = 0.4057$; ◆, $m = 0.7952$; ○, $m = 1.1924$; ●, $m = 1.5788$; ▽, $m = 1.9562$; ▼, $m = 2.6030$; □, $m = 2.9853$; ■, $m = 3.0660$; △, $m = 3.1248$; ▲, $m = 3.1992$}; +, Washburn (1928) {m = 0.5806, 1.0107, 1.2404, 1.4807, 1.7326, 1.9967}; *, Söhnel and Novotny (1985) {m = 2.2740, 2.5656, 2.8724}.

The apparent molal volume of lithium sulfate was calculated at each concentration from the equation

$$\Phi_v = (M_2/\varrho) - (\varrho - \varrho_0)/m\varrho\varrho_0 \qquad (1)$$

where ϱ is the solution density, ϱ_0 is the density of pure water at the same temperature, M_2 is the solute molecular weight, and m is the molality. The results are listed in Table 1. Uncertainties in Φ_v are related to uncertainty in both the molality and the density measurements. At 0.40 mol·kg^{-1} the uncertainty in Φ_v is $\pm 4 \times 10^{-8}$ m^3·mol^{-1}, and at high molalities the values of Φ_v are reliable to $\pm 1.5 \times 10^{-8}$ m^3·mol^{-1}. The densities of water at different temperatures were taken from the literature (Marsh, 1987; Handa and Benson, 1979).

The calculated apparent molal volumes, Φ_v, may be correlated with both composition and temperature according to the equation

$$\Phi_v(T,m)/(\mathrm{m^3{\cdot}mol^{-1}}) = \Phi_v{}^0 + S_v m^{1/2} + \sum_{i=2}^{5}[\sum_{j=0}^{2} a_{ij}(T/\mathrm{K})^j](m/(\mathrm{mol{\cdot}kg^{-1}}))^{i/2} \qquad (2)$$

The a_{ij} coefficient values for the complete molality range and temperatures ranging from 283.15 to 313.15 K are presented in Table 2. Values of the partial molal volumes at infinite dilution, $\Phi_v{}^0$, have been calculated by fitting the data given by Millero (1971) through the following equation: $\Phi_v{}^0(T)/(\mathrm{m^3{\cdot}mol^{-1}}) = 10.63236 \times 10^{-4} - 10.92715 \times 10^{-6}(T/\mathrm{K}) + 37.5158 \times 10^{-9}(T/\mathrm{K})^2 - 42.56 \times 10^{-12}(T/\mathrm{K})^3$. Values of the Debye–Hückel theoretical limiting law slope, S_v, have been calculated by using the following equation given by Millero (1971) for 2:1 electrolytes: $S_v(T)/(\mathrm{m^3{\cdot}kg^{1/2}{\cdot}mol^{-3/2}}) = 5.196 \times 10^{-6}(1.444 + 1.6799 \times 10^{-2}((T/\mathrm{K}) - 273.15) - 8.4055 \times 10^{-6}((T/\mathrm{K}) - 273.15)^2 + 5.5153 \times 10^{-7}((T/\mathrm{K}) - 273.15)^3)$. The mean relative standard deviation between experimental and calculated Φ_v values is 0.38%. The maximum relative deviation is about 1.4%. The fitting is shown in Figure 2 together with a comparison of the Φ_v results with those calculated from the densities taken from Washburn (1928) and Söhnel and Novotny (1985).

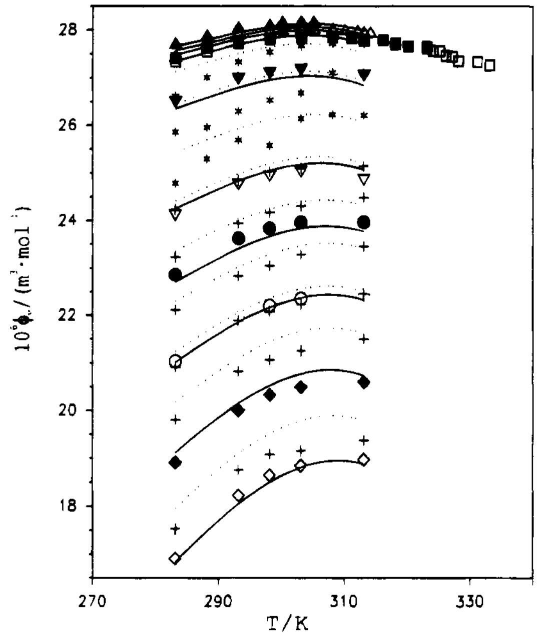

Figure 2. Temperature dependence of the solute molal volume Φ_v for aqueous lithium sulfate at the same molalities used in Figure 1.

The viscosity results may be fitted with both composition and temperature according to the equation

$$\frac{\eta(T,c)}{\eta_0(T)} = 1 + \sum_{i=1}^{4}[\sum_{j=0}^{2} b_{ij}(T/\mathrm{K})^j](m/(\mathrm{mol{\cdot}kg^{-1}}))^i \qquad (3)$$

η_0 being the viscosity of pure water (Weast, 1980). The matrix b_{ij} coefficients for the molality range and temperatures from 283.15 to 313.15 K are given in Table 2. The mean relative standard deviation between all experimental

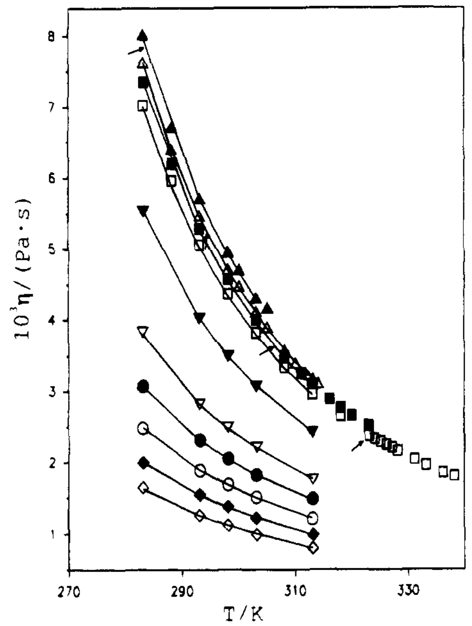

Figure 3. Temperature dependence of the solution viscosity η for aqueous lithium sulfate at the same molalities used in Figure 1 for this study.

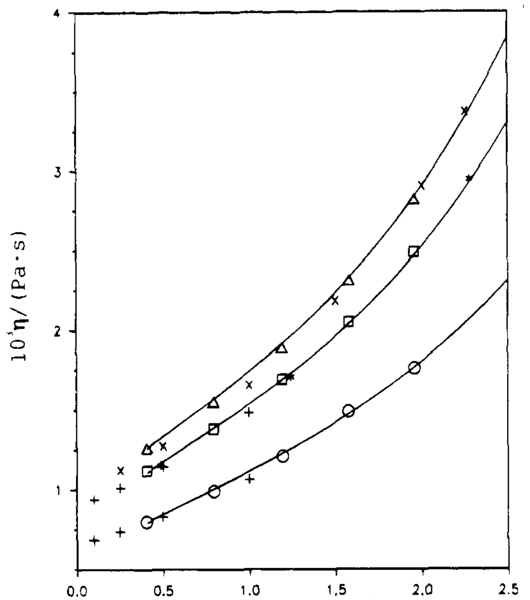

Figure 4. Viscosity η of aqueous lithium sulfate solutions as a function of the molality: this study {△, T = 293.15 K; □, T = 298.15 K; ○, T = 313.15 K}; ×, Erich Pietsch (1960); *, Puchkov and Sargaev (1974); +, Washburn (1929a).

and calculated relative viscosity values is 0.37%. The maximum relative deviation is about 1.1%. The viscosity results are plotted against temperature in Figure 3. The measured viscosities at three different temperatures are compared in Figure 4 with those found in the literature (Erich Pietsch, 1960; Puchkov and Sargaev, 1974; Washburn, 1929a).

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

$$\Lambda(T,c)/(\mathrm{S\cdot m^2\cdot mol^{-1}}) = \sum_{i=0}^{3}\Big[\sum_{j=0}^{2} c_{ij}(T/\mathrm{K})^j\Big](c/(\mathrm{mol\cdot dm^{-3}}))^{i/2} \qquad (4)$$

Λ being the molar conductance and c the molarity. The c_{ij} coefficient values for the molality range and temperatures from 283.15 to 313.15 K are given in Table 2. The mean relative standard deviation between experimental and calculated molar conductance values is 0.38%. The maximum relative deviation is about 1.5%. Experimental electrical conductivity results and the fitting resulting from eq 4 are plotted against the solute concentration in Figure 5. For the purpose of comparison, the conductivity values taken from the literature (Washburn, 1929b) are also shown in Figure 5, the dashed line corresponding to the fitting through eq 4.

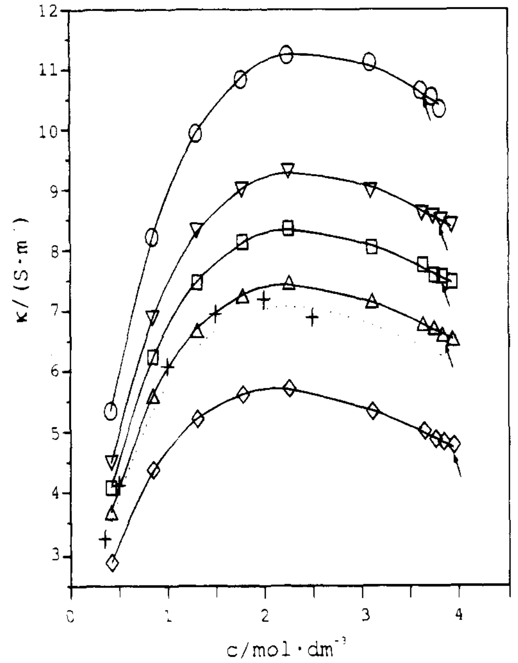

Figure 5. Electrical conductivity κ of aqueous lithium sulfate solutions as a function of the molarity: this study {◇, T = 283.15 K; △, T = 293.15 K; □, T = 298.15 K; ▽, T = 303.15 K; ○, T = 313.15 K}; +, Washburn (1929b).

Acknowledgment

We thank Pedro A. Fuertes Olivera for English translation.

Registry Number Supplied by Authors. Li_2SO_4, 10377-48-7.

Literature Cited

Abello, L.; Chhor, K.; Pommier, C. Thermodynamic Studies on the Successive Phase Transitions in $LiKSO_4$ Crystals at Low Temperatures. *J. Chem. Thermodyn.* **1985**, *17*, 1023–1034.

Cartón, A.; Sobrón, F.; Bolado, S.; Tabarés, J. Composition and Density of Saturated Solutions of Lithium Sulfate + Water + Ethanol. *J. Chem. Eng. Data* **1994a**, *39*, 61–62.

Cartón, A.; Sobrón, F.; Bolado, S.; Tabarés, J. Composition and Density of Saturated Solutions of Lithium Sulfate + Water + Methanol. *J. Chem. Eng. Data* **1994b**, *39*, 733–734.

Cartón, A.; Sobrón, F.; Bolado, S. Density and Viscosity of Saturated Solutions of Lithium Potassium Sulfate + Water + Ethanol at 298.15 K. *J. Chem. Eng. Data* **1995a**, in press.

Cartón, A.; Sobrón, F.; Bolado, S.; Gerbolés J. I. Viscosity, conductivity and refractive index of saturated solutions of Lithium Sulfate + Water + Methanol. *J. Chem. Eng. Data* **1995b**, in press.

Diaz Peña, M.; Roig Muntaner, A. *Quimica Fisica*, 2nd ed.; Alhambra: Madrid, 1976.

Erich Pietsch, E. H., Ed. *Gmelins Handbuch der Anorganischen Chemie*; Verlag Chimie: Heidelberg, 1960; Vol. 20, p 481.

Fujimoto, S.; Yasuda, N.; Hibino, H. Temperature Dependence of the Electro-optic Coefficient in $LiKSO_4$. *J. Phys. D: Appl. Phys.* **1985**, *18*, L135–L137.

Handa, Y. P.; Benson, G. C. Volume Changes on Mixing Two Liquids: A Review of the Experimental Techniques and the Literature Data. *Fluid Phase Equilib.* **1979**, *3*, 185–249.

Horvath, A. L. *Handbook of Aqueous Electrolyte Solutions*, 1st ed.; Ellis Horwood Limited: Chichester, 1985.

Isono, T. Density, Viscosity, and Electrolytic Conductivity of Concentrated Aqueous Electrolyte Solutions at Several Temperatures. Alkaline-Earth Chlorides, $LaCl_3$, Na_2SO_4, $NaNO_3$, NaBr, KNO_3, KBr, and $Cd(NO_3)_2$. *J. Chem. Eng. Data* **1984**, *29*, 45–52.

Lo Surdo, A.; Alzola, E. M.; Millero, F. J. The (p, V, T) Properties of Concentrated Aqueous Electrolytes. I. Densities and Apparent Molar Volumes of NaCl, Na_2SO_4, $MgCl_2$, and $MgSO_4$ Solutions from 0.1 $mol{\cdot}kg^{-1}$ to Saturation and from 273.15 to 323.15 K. *J. Chem. Thermodyn.* **1982**, *14*, 649–662.

Marsh, K. N., Ed. *Recommended Reference Materials for the Realization of Physicochemical Properties*; Blackwell Scientific Publications: Oxford, 1987.

Martinez, A.; Sobrón, F.; Rull, F.; Prieto, A. C.; Edwards, H. G. M. Mass Diffusion Transport Studies of Lithium Sulphate in Aqueous Solutions Using Raman Spectroscopy. *Appl. Spectrosc.* **1995**, in press.

Millero, F. J. The Molal Volumes of Electrolytes. *Chem. Rev.* **1971**, *29* (2), 147–176.

Puchkov, L. V.; Sargaev, P. M. Viscosity of Solutions of Lithium, Sodium and Potassium Sulfate in the Temperature Range up to 275 °C. *Zh. Prikl. Khim. (Leningrad)* **1974**, *47* (1), 96.

Rull, F.; Prieto, M.; Sobrón, F. Crystal Growth of Li Salts From Aqueous Solutions and Gels Studied by Raman Spectroscopy. *J. Phys. IV* **1994**, C2, *4*, 47–51.

Singh, K.; Deshpande, V. K.; Electrical Conductivity of Binary Sulphates of Lithium Sulphate. *Solid State Ionics* **1984**, *13*, 157–164.

Söhnel, O.; Novotny, P. *Densities of Aqueous Solutions of Inorganic Substances. Physical Sciences Data 22*; Elsevier Science Publishing Co.: New York, 1985.

Washburn, E. W. *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; McGraw-Hill Book Co.: New York, 1928; Vol. III, p 78.

Washburn, E. W. *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; McGraw-Hill Book Co.: New York, 1929a; Vol. V, pp 12–19.

Washburn, E. W. *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; McGraw-Hill Book Co.: New York, 1929b; Vol. VI, pp 239–254.

Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 61st ed.; CRC Press: Boca Raton, FL, 1980.

Received for review October 31, 1994. Accepted March 28, 1995.[⊗] This study was supported by the Spanish Ministry of Education under Project MAT90-0775-C03-02.

JE940231J

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1995.