Viscosity, Conductivity, and Refractive Index of Saturated Solutions of Lithium Sulfate + Water + Methanol

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

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

The viscosity, electrical conductivity, and refractive index of saturated solutions of lithium sulfate in water and water + methanol have been determined over the temperature range 283.15−313.15 K and in the mass fraction of methanol range 0−0.9. Equations are given for these properties as a function of temperature and the mass fraction of methanol.

Introduction

Methanol is an organic compound frequently used as a cosolvent in processes of crystallization by salting-out (*1*−*3*). The addition of the alcohol to an aqueous solution of a salt usually decreases the salt solubility and induces its precipitation. Together with other known advantages (*4*), the technique is attractive in salt systems where the temperature has little effect on the solubility. Such a salt is lithium sulfate, which is an ionic conductor material with technological applications (*5*−*7*).

In a previous paper (*8*) we reported the solubility and density for solutions of lithium sulfate in aqueous methanol. The viscosities, electrical conductivities, and refractive indices for the saturated solutions, in the same temperature and methanol concentration ranges, are given in this paper. These properties may be of engineering utility to control a possible lithium sulfate precipitation process using methanol. Moreover, there are no comparable data in the literature.

Experimental Section

PRS grade lithium sulfate monohydrate from Panreac (99+%), pa methanol from Panreac (99.5+%), and distilled water passed through a Millipore ultrapure cartridge kit were used without further purification. The saturation at a particular temperature was achieved by equilibrating crystals and solution in 150 mL closed glass vessels, all fitted with a magnetic stirrer. The cell was immersed in a thermostatic water bath controlled to ±0.05 K. Known masses of methanol and water together with an excess of salt were charged to the solubility cell and agitated for at least 48 h at the equilibrium temperature, 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). At the end of this time, the agitator was switched off and the solutions were 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 viscometer, conductimeter, or refractometer. 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.

Solution concentrations were determined, in duplicate, by evaporating a known mass of a saturated solution (between 15 and 35 g) in a thermostated furnace at 350 K. After solidification, the temperature was increased to 493.15 K and maintained over 24 h. All the masses were measured on an analytical balance with a precision of $\pm10^{-7}$ 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 reproducibility of the solution composition was $\pm10^{-4}$ kg of Li_2SO_4/kg of solution.

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.

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 of 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 (*9*). The exact compositions of the glycerol + water samples were checked by comparing the experimental density measurements with those found in ref 9. 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. Typical time scales were 70−300 s for measurements with ball A and 35−130 s when using sphere B. The results given in Table 3 are the average of at least five determinations for each solution, the measurements of flow time being reproducible to within ±0.1%. The densities, needed for viscosity calculations, were taken from ref 8. The viscosities of the samples were measured with a reproducibility better than ±0.5%. On the basis of the comparison with reliable data from the literature (*9*−*11*), as shown in Table 1, the accuracy of the viscosity was better than ±1%.

Electrical conductivities were measured by a Crison microCM 2100 conductimeter with replatinized platinum electrodes. The electrical conductivities at 298.15 K of potassium chloride solutions in the composition range 0.001−1.0 N (*12*) were used for fitting the constant cell as a function of conductance. In order to verify the accuracy of the electrical conductivity measurements, the apparatus was used to measure several KBr aqueous solutions in the temperature range 293.15−318.15 K, with their electrical conductivities being taken from the literature (*13*). The resulting accuracy was ±0.5%. At least five measurements

0021-9568/95/1740-0980$09.00/0

Table 1. Viscosity η of Pure Liquids and of the System Methanol + Water as a Function of Methanol Mass Fraction, w

solvent	T/K	$10^3\eta$/(Pa·s) this study	$10^3\eta$/(Pa·s) literature
methanol	298.15	0.55	0.547 (*9*), 0.5513 (*10*)
ethanol	303.15	1.00	1.003 (*9*), 0.987 (*10*)
1-propanol	288.15	2.50	2.52 (*9*), 2.492 (*10*)
1-butanol	293.15	2.95	2.948 (*9*)
isobutyl alcohol	288.15	4.67	4.703 (*9*), 4.6556 (*10*)
isoamyl alcohol	283.15	6.17	6.20 (*9*)
1-heptanol	288.15	8.45	8.53 (*9*)
methanol + water			
$w = 0.10$	293.15	1.34	1.329 (*9*)
	313.15	0.79	0.7972 (*11*)
$w = 0.30$	293.15	1.78	1.795 (*9*)
	313.15	1.02	1.0337 (*11*)
$w = 0.50$	293.15	1.75	1.761 (*9*)
	313.15	1.04	1.0477 (*11*)
$w = 0.70$	293.15	1.38	1.368 (*9*)
	313.15	0.87	0.8773 (*11*)
$w = 0.90$	293.15	0.85	0.861 (*9*)
	313.15	0.60	0.6125 (*11*)

Table 2. Refractive Index n(D) at 293.15 K of the System Methanol + Water as a Function of Methanol Mass Fraction, w

w	n(D) this study	n(D) ref 9	w	n(D) this study	n(D) ref 9
0.10	1.3350	1.3354	0.70	1.3415	1.3411
0.30	1.3400	1.3407	0.90	1.3345	1.3348
0.50	1.3425	1.3431			

of each sample were made. The reproducibility was better than ±0.5%.

Refractive indices have been measured on an Abbe-type refractometer capable of measuring with a precision of 0.0005 unit. The procedure was repeated at least three times without appreciable variation in the measured refractive index. The accuracy established by determining the refractive index of pure water at the temperatures used in this work (*10*) was ±0.02%. The measured refractive indices of several methanol + water solutions, shown in Table 2, were used as the second standard.

The viscosity η, electrical conductivity κ, and refractive index n(D,T) of the saturated solutions for lithium sulfate + water + methanol determined in the range 283.15–313.15 K are given in Table 3 and plotted, respectively, in Figures 1–3.

The viscosities, electrical conductivities, and refractive indices of the saturated solutions of lithium sulfate are, for all temperatures, lower in the mixed solvent than in the aqueous solutions and decrease when the mass fraction of methanol, w, increases. For high w values, a regular trend to reach those values for pure methanol is observed for all properties.

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

$$\ln[\eta/(\text{Pa·s})] = A(w) + B(w)/(T/\text{K}) \qquad (1)$$

with

$$A(w) = a_0 + a_1w + a_2w^2 + a_3w^3 + a_4w^4$$

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

The a_i and b_i coefficient values, for methanol compositions from 0 to 0.90 mass fraction, are presented in Table 4. 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 experimental and calculated viscosity values is 1.3%. The maximum relative deviation is about 2.7%.

Table 3. Solubility s, Viscosity η, Electrical Conductivity κ, and Refractive Index n(D,T) of Lithium Sulfate Saturated Solutions 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)	$10^3\eta$/(Pa·s)	κ/(S·m^{-1})	n(D,T)
		T = 283.15 K		
0.0000	25.98	8.06	4.86	1.3790
0.1009	20.70	7.07	3.72	1.3730
0.1992	15.29	5.96	2.71	1.3665
0.2975	10.44	4.86	1.877	1.3600
0.3960	6.57	3.93	1.225	1.3555
0.4997	3.63	3.11	0.743	1.3520
0.6006	1.98	2.48	0.451	1.3495
0.7505	0.74	1.77	0.1967	1.3455
0.8950	0.28	1.12	0.0982	1.3395
		T = 293.15 K		
0.0000	25.60	5.52	6.52	1.3780
0.0950	20.70	4.85	5.16	1.3715
0.2012	14.95	4.05	3.68	1.3640
0.2991	10.19	3.34	2.50	1.3580
0.3963	6.35	2.76	1.598	1.3530
0.4990	3.58	2.26	0.937	1.3495
0.6016	1.80	1.90	0.541	1.3465
0.7488	0.65	1.35	0.217	1.3420
0.9017	0.23	0.92	0.0947	1.3355
		T = 298.15 K		
0.0000	25.48	4.67	7.55	1.3770
0.1007	19.97	4.10	5.79	1.3705
0.1979	14.94	3.45	4.26	1.3635
0.3009	9.93	2.82	2.84	1.3570
0.3981	6.23	2.34	1.803	1.3520
0.4998	3.50	1.93	1.045	1.3480
0.5949	1.90	1.65	0.609	1.3450
0.7561	0.58	1.19	0.222	1.3400
0.8944	0.21	0.84	0.0992	1.3340
		T = 303.15 K		
0.000	25.31	4.01	8.53	1.3760
0.0988	20.18	3.49	6.60	1.3695
0.1983	14.84	2.93	4.80	1.3625
0.3045	9.76	2.41	3.15	1.3555
0.4003	6.12	2.03	1.996	1.3510
0.5050	3.36	1.68	1.136	1.3465
0.5999	1.81	1.42	0.664	1.3430
0.7459	0.67	1.09	0.254	1.3385
0.9027	0.19	0.75	0.0977	1.3320
		T = 313.15 K		
0.0000	24.97	3.10	10.62	1.3735
0.0981	19.88	2.67	8.55	1.3675
0.1979	14.58	2.21	6.06	1.3605
0.3024	9.63	1.83	3.97	1.3535
0.3947	6.17	1.55	2.55	1.3485
0.4963	3.46	1.34	1.458	1.3445
0.5988	1.75	1.15	0.769	1.3405
0.7493	0.55	0.88	0.272	1.3350
0.9043	0.18	0.63	0.1010	1.3285

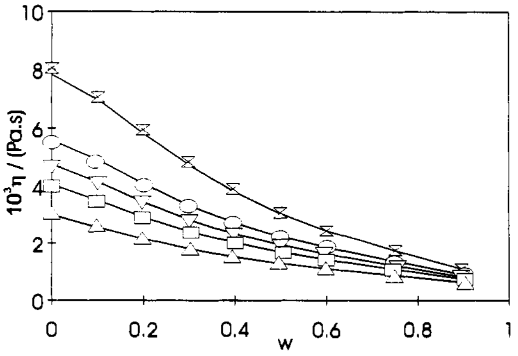

Figure 1. Viscosity η of saturated solutions of lithium sulfate in w methanol + $(1 - w)$ water at different temperatures: hourglass, 283.15 K; ○, 293.15 K; ▽, 298.15 K; □, 303.15 K; △, 313.15 K.

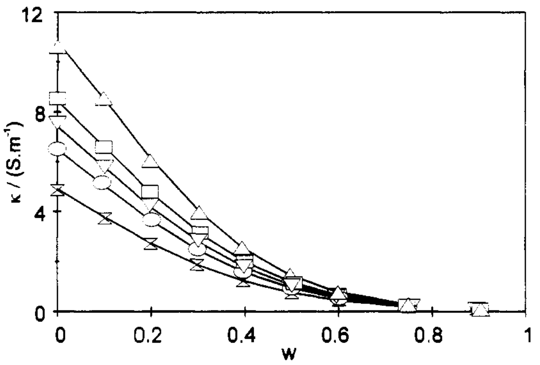

Figure 2. Electrical conductivity κ of saturated solutions of lithium sulfate in w methanol + $(1 - w)$ water at different temperatures: hourglass, 283.15 K; ○, 293.15 K; ▽, 298.15 K; □, 303.15 K; △, 313.15 K.

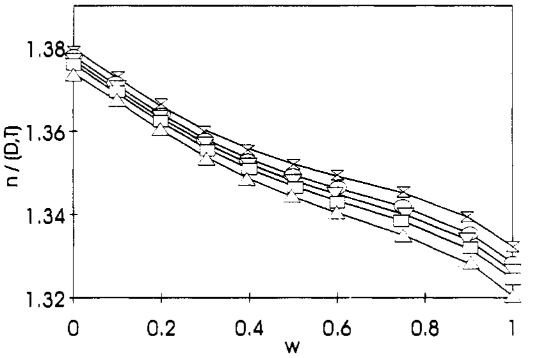

Figure 3. Refractive index n(D,T) of saturated solutions of lithium sulfate in w methanol + $(1 - w)$ water at different temperatures: hourglass, 283.15 K; ○, 293.15 K; ▽, 298.15 K; □, 303.15 K; △, 313.15 K.

Table 4. Coefficients of the Model Eq 1

a_0	a_1	a_2	a_3	a_4
−14.79	−7.33	23.92	−23.01	9.54
$10^{-2}b_0$	$10^{-2}b_1$	$10^{-2}b_2$	$10^{-2}b_3$	$10^{-2}b_4$
28.15	18.77	−82.89	88.93	−40.48

Solid lines in Figure 1 show the fitting resulting from eq 1.

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

$$\ln[\kappa/(\mathrm{S{\cdot}m^{-1}})] = A'(w) + B'(w)/(T/\mathrm{K}) \qquad (2)$$

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, for methanol compositions from 0 to 0.75 mass fraction, are presented in Table 5. The mean relative standard deviation between experimental and calculated electrical conductivity values is 0.9%. The maximum relative deviation is about 2.2%. The fitting using eq 2 can be seen in Figure 2.

Table 5. Coefficients of the Model Eq 2

a'_0	a'_1	a'_2	a'_3
9.81	1.48	−17.04	1.04

$10^{-2}b'_0$	$10^{-2}b'_1$	$10^{-2}b'_2$
−23.26	−10.64	38.40

Table 6. Coefficients of the Model Eq 3

a''_0	$10^2a''_1$	$10^2a''_2$	$10^4a''_3$	$10^3a''_4$
1.433	−9.532	19.439	−38.579	−87.594
$10^5b''_0$	$10^6b''_1$	$10^5b''_2$	$10^5b''_3$	
−18.688	77.861	−68.017	40.767	

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

$$n(\mathrm{D,T}) = A''(w) + B''(w)(T/\mathrm{K}) \qquad (3)$$

with

$$A''(w) = a''_0 + a''_1w + a''_2w^2 + a''_3w^3 + a''_4w^4$$

$$B''(w) = b''_0 + b''_1w + b''_2w^2 + b''_3w^3$$

For the whole methanol mass fraction range, the a''_i and b''_i coefficient values are given in Table 6. The mean relative standard deviation between experimental and calculated refractive index values is 0.02%. The maximum relative deviation is about 0.08%. The fitting by the model eq 3 is shown in Figure 3.

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) Hoppe, H. *Chem. Proc. Eng.* **1968**, *49*, 61.
(3) Okada, S.; Zhang, D.; Yazawa, A. Presented at the 1st Int. Congr. Hydrometall., Beijing, October, 1988; p 430.
(4) Mullin, J. W. *Crystallization*, 3rd ed.; Butterworth-Heinemann: Oxford, 1993; p 301.
(5) Lunden, A.; Mellander, B. E.; Bengtzelius, A.; Ljungmark, H.; Tärneberg, R. *Solid State Ionics* **1986**, *18–19*, 514.
(6) Guzhva, V. G.; Kokodii, N. G.; Kuz'michev, V. M. *Radiotekhnika (Kharkov)* **1972**, *23*, 143.
(7) Lukaszewick, T.; Dorosz, J. PL Patent 156,846, 1992.
(8) Cartón, A.; Sobrón, F.; Bolado, S.; Tabarés, J. *J. Chem. Eng. Data* **1994**, *39*, 1994.
(9) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 61st ed.; CRC Press: Boca Raton, FL, 1980.
(10) Riddick, A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.
(11) Fleischmann, W.; Mersmann, A. *J. Chem. Eng. Data* **1984**, *29*, 452.
(12) Diaz Peña, M.; Roig Muntaner, A. *Quimica Fisica*, 2nd ed.; Alhambra: Madrid, 1976; p 1214.
(13) Isono, T. *J. Chem. Eng. Data* **1984**, *29*, 45.

Received for review February 6, 1995. Accepted March 7, 1995.[⊗] This study was supported by the Spanish Ministry of Education under Project MAT90-0775-C03-02.

JE950035S

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