J. Chem. Eng. Data **2002,** *47,* 1193−1196

Solubilities, Densities, Viscosities, Electrical Conductivities, and Refractive Indices of Saturated Solutions of Potassium Sulfate in Water + 1-Propanol at 298.15, 308.15, and 318.15 K

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The solubilities, densities, refractive indices, electrical conductivities, and viscosities were determined for saturated solutions of potassium sulfate in aqueous solutions of 1-propanol over the temperature range of 298.15−318.15 K. Different mass fractions of propanol/solution were studied in a range from 0 to 0.6. Equations are given for these properties as a function of temperature and mass fraction of propanol. Knowledge of the properties evaluated and solubility data are useful in the study of the crystallization of potassium sulfate from aqueous solutions by means of the addition of 1-propanol.

Introduction

World production of potassium salts is nearly 5.5×10^6 tons/year, with 90% of this production destined toward agricultural use. Potassium sulfate is a source of potassium and soluble sulfur, both of which are essential plant nutrients. This material is also used in the manufacture of glass, medicines, and foods and in the polymerization of natural and synthetic rubber. The various uses cited have promoted numerous studies on its crystallization from aqueous solutions.[1]

One alternative to traditional methods of crystallization by cooling and evaporation has been the use of a third component, which changes the phase equilibrium within the solution and promotes crystallization of the salt.

Addition of organic solvents such as alcohol to an aqueous solution normally decreases the solubility of a salt. On this basis, selective crystallization may be achieved, termed “salting out”. This process has certain advantages over other methods of crystallization because ambient temperature may be employed, producing crystals of high purity.[2] In this case, the important variables to be considered include the miscibility of the solvent with the original solution, the limiting solubility of the solute in the second solvent, economic considerations in separating the organic solvent from the water, and the physical properties of the system.

We report in this paper the solubilities, densities, viscosities, electrical conductivities, and refractive indices for saturated solutions of potassium sulfate in aqueous 1-propanol mixtures at different temperatures. These properties are useful in the study of the crystallization process for the salting out of K_2SO_4, using 1-propanol as the second solvent.

The majority of solubility data on potassium sulfate in the literature concern aqueous solutions.[1,3−5] Mydlarz et al.[6] presented data on the solubility and density of K_2SO_4 in water + 2-propanol between 20 and 30 °C. They found that the presence of 2-propanol significantly reduced the solubilities and densities of the aqueous solutions of potassium sulfate.

Mydlarz and Jones[7] gave data on the solubilities of K_2SO_4 in aqueous solutions of acetone, ethanol, and methanol between 15 and 35 °C, as well as density values for the saturated solutions. The results of both of the cited studies were obtained at low alcohol concentrations.

Experimental Section

Reagents included anhydrous potassium sulfate (+99%; Merck), grade absolute 1-propanol (+99.5%, Merck), and ultrapure water (conductivity = 0.05 μS/cm^3) obtained by passing distilled water through a Millipore ultrapure cartridge kit. All reagents were used in the commercially obtained form.

Different alcohol/water proportions were employed, in mass fractions ranging from 0 to 0.6; 48 solutions were prepared over this range. Measurements on each solution were made in triplicate.

A rotary, thermostatically controlled water bath was used to obtain phase equilibria, with a holder containing eight 90 mL glass jars. The system worked within a range of 293.15−363.15 K, with a precision of 0.1 K.

Known masses of 1-propanol, water, and potassium sulfate, with the latter being in excess to ensure the saturation of the solutions, were measured on a Mettler Toledo Co. model AX204 analytical balance with a precision of 0.07 mg.

The samples were agitated for 48 h in order to reach equilibrium at the desired temperature. Following the agitation step, samples were allowed to decant for a further 24 h. The clear liquid was collected from the flasks using Versapore membrane filters having a nominal pore size of 0.45 μm.

Salt concentrations were determined by evaporation of known masses of filtered saturated solutions at 423 K.

The density of each sample was determined using a Mettler Toledo model DE50 vibrating tube densimeter, operated in the static mode, having a precision of 5×10^{-2} kg·m^{-3}. Three runs were made for each sample, with the reproducibility being better than $\pm 1 \times 10^{-1}$ kg·m^{-3}.

Refractive indices for the sodium D line were measured on a Mettler Toledo RE40 refractometer with a resolution of 1×10^{-4} unit. The measurements were repeated at least three times without appreciable variation. The average of these readings was used to calculate the refractive index.

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10.1021/je020024g CCC: $22.00
Published on Web 07/30/2002

Ultrapure degassed water and air were used as references for calibration of both densimeter and refractometer in the temperature range 298.15−318.15 K.

Measurements of electrical conductivity were carried out using an Orion model 170 conductimeter with a precision of ≤0.5% of the value measured and calibrated using a standard KCl solution. The reproducibility was ±0.7%.

The kinematic viscosities of the saturated solutions were measured with an automatic Schott-Gerate AVS 310 laser viscosimeter, which measured the transit time of the liquid meniscus through a capillary, with a precision of ±0.1 s. A calibrated Micro-Oswald viscosimeter, type 51710, was immersed in a transparent Schott-Gerate CT 52 thermostatic bath, with a temperature precision of ±0.05 K. The dynamic viscosity was obtained by multiplying the kinematic viscosity by the corresponding density. The results given in Table 1 are the average of three determinations for each solution. The reproducibility of the measured viscosities was better than $\pm 5 \times 10^{-3}$ mPa·s.

Results

The solubilities, densities, viscosities, electrical conductivities, and refractive indices of the saturated solutions for potassium sulfate + water + 1-propanol at three different temperatures are given in Table 1.

Measurements of the solubilities and physical properties for the binary potassium sulfate + water agreed with literature values,[1,3−5,7] as shown in Table 2. In the narrow range of possible comparison, the agreement is within ±0.9%. Comparison of the present solubility results with those of Mydlarz and Jones,[7] who studied 2-propanol as a cosolvent at temperatures of 303.15 and 313.15 K, showed similar tendencies, with small differences due to the fact that potassium sulfate was less soluble in the aqueous solution with 2-propanol than with 1-propanol.

The solubility results expressed as % mass of potassium sulfate may be correlated as a function of the propanol composition and temperature, according to the equation

$$\ln s/(\text{kg}/100 \text{ kg of solution}) = A_0(\omega) + B_0(\omega)/(T/\text{K}) \quad (1)$$

with

$$A_0(\omega) = a_{00} + a_{01}\omega + a_{02}\omega^2 + a_{03}\omega^3$$

$$B_0(\omega) = b_{00} + b_{01}\omega + b_{02}\omega^2$$

The a_{0i} and b_{0i} coefficient values for eq 1 with the 1-propanol mass fraction between 0 and 0.6 are presented in Table 3.

The mean absolute deviation between the calculated and experimental solubility values is 0.06 kg of salt/100 kg of solution. The maximum absolute deviation is 0.22 kg of salt/100 kg of solution.

The values for saturation density were correlated as a function of composition and temperature following the equation

$$\rho/(\text{kg}\cdot\text{m}^{-3}) = A_1(\omega) + B_1(\omega)\,(T/\text{K}) \quad (2)$$

with

$$A_1(\omega) = a_{10} + a_{11}\omega + a_{12}\omega^2 + a_{13}\omega^3$$

$$B_1(\omega) = b_{10} + b_{11}\omega + b_{12}\omega^2$$

The a_{1i} and b_{1i} coefficient values for eq 2 are presented in Table 3.

Table 1. Solubility *s*, Density *ρ*, Refractive Index n_D, Electrical Conductivity *k*, and Viscosity *η* of Potassium Sulfate Saturated Solutions for Various Mass Fractions *w* in (1 − *w*)Water + *w*1-Propanol at 298.15, 308.15, and 318.15 K

w	*s* (kg of salt/ (100 kg of solution)	*ρ* (kg/m³)	n_D	*k* (S/m)	*η* (mPa·s)
		T = 298.15 K			
0.0000	10.8416	1085.8	1.3453	10.43	1.0432
0.0000	10.8508	1085.9	1.3453	10.46	1.0343
0.1668	3.0743	995.5	1.3504	1.70	1.7302
0.1710	3.0628	995.5	1.3505	1.68	1.7163
0.2857	1.6571	961.2	1.3570	0.65	2.1970
0.2859	1.6585	961.2	1.3570	0.65	2.1863
0.3749	1.0317	938.0	1.3616	0.31	2.4717
0.3720	1.0282	937.9	1.3617	0.31	2.4665
0.3749	1.0136	938.3	1.3614	0.31	2.4359
0.4449	0.6483	921.3	1.3645	0.16	2.5903
0.4434	0.6675	921.0	1.3649	0.16	2.5618
0.4445	0.6597	921.1	1.3650	0.16	2.5956
0.5017	0.4264	907.9	1.3673	0.09	2.6788
0.4981	0.4419	908.0	1.3673	0.09	2.6284
0.5448	0.2937	897.6	1.3694	0.05	2.6803
0.5463	0.2890	898.1	1.3695	0.05	2.6528
		T = 308.15 K			
0.0000	12.3416	1095.3	1.3457	13.94	0.8716
0.0000	12.3569	1096.6	1.3456	13.94	0.8802
0.1686	3.8985	996.7	1.3480	2.62	1.4366
0.1681	3.9203	996.6	1.3484	2.70	1.2994
0.2850	2.2296	959.0	1.3546	1.07	1.6198
0.2861	2.2202	958.5	1.3546	1.07	1.6323
0.3757	1.3965	933.2	1.3587	0.50	1.8081
0.3750	1.3986	933.5	1.3588	0.50	1.8233
0.3754	1.3708	933.3	1.3587	0.50	1.8237
0.4443	0.8936	915.2	1.3614	0.25	1.9032
0.4446	0.8893	915.1	1.3617	0.25	1.9172
0.4446	0.8875	915.0	1.3614	0.26	1.9138
0.5005	0.5830	901.1	1.3639	0.13	1.9378
0.4998	0.5817	901.2	1.3640	0.14	1.9563
0.5441	0.3939	890.8	1.3660	0.08	1.9337
0.5443	0.3923	890.6	1.3661	0.08	1.9579
		T = 318.15 K			
0.0000	13.5877	1100.8	1.3457	17.51	0.7543
0.0000	13.6830	1101.1	1.3456	17.48	0.7469
0.1668	4.8242	997.5	1.3452	3.90	1.0286
0.1675	4.7422	997.2	1.3455	3.90	1.0189
0.2855	2.8256	956.7	1.3513	1.61	1.2703
0.2855	2.8102	956.7	1.3514	1.61	1.2704
0.3752	1.7737	929.5	1.3558	0.76	1.4174
0.3742	1.7873	930.0	1.3553	0.76	1.3852
0.3781	1.7768	929.7	1.3549	0.76	1.3860
0.4454	1.1285	909.9	1.3582	0.37	1.4695
0.4468	1.1124	909.6	1.3586	0.37	1.4396
0.4438	1.1447	910.6	1.3586	0.38	1.4494
0.5011	0.7257	895.3	1.3607	0.20	1.4576
0.4996	0.7387	895.7	1.3607	0.20	1.5050
0.5449	0.4814	884.3	1.3626	0.12	1.4640
0.5461	0.4772	884.0	1.3626	0.12	1.4780

The mean absolute deviation between all of the calculated and experimental density values is 1.1 kg·m⁻³. The maximum absolute deviation is 2.9 kg·m⁻³.

The refractive index (n_D) results may be correlated as a function of the propanol composition and temperature, according to the equation

$$n_D = A_2(\omega) + B_2(\omega)/(T/\text{K}) \quad (3)$$

with

$$A_2(\omega) = a_{20} + a_{21}\omega + a_{22}\omega^2 + a_{23}\omega^3$$

$$B_2(\omega) = b_{20} + b_{21}\omega + b_{22}\omega^2 + b_{23}\omega^3$$

Table 2. Comparisons of Experimental Results for Potassium Sulfate + Water with Literature Values

	T/K	this work	ICT[3]	Perry[4]	Linke and Seidell[5]	Mydlarz and Jones[7]	Ishii and Fujita[1]
s/(kg/100 kg of solution)	298.15	10.85	10.83	10.75	10.75		
	308.15	12.35	12.27	12.18	12.20		
	318.15	13.63	13.63	13.52	13.55		
ρ/(kg/m^3)	298.15	1085.9	1086.3			1085.5	
	308.15	1096.0	1094.8			1093.9	1086.6 at 303.15 K[a]
	318.15	1101.0	1102.0				1090.8 at 313.43 K[a]
n_D	298.15	1.3453	1.3444 at 293.15 K[a]				
	308.15	1.3457	1.3422 at 303.15 K[a]				
	318.15	1.3457					
η/(mPa·s)	298.15	1.039					1.025 at 298.29 K[a]
	308.15	0.876					0.933 at 303.15 K[a]
	318.15	0.751					0.771 at 313.43 K[a]

[a] No saturated solutions.

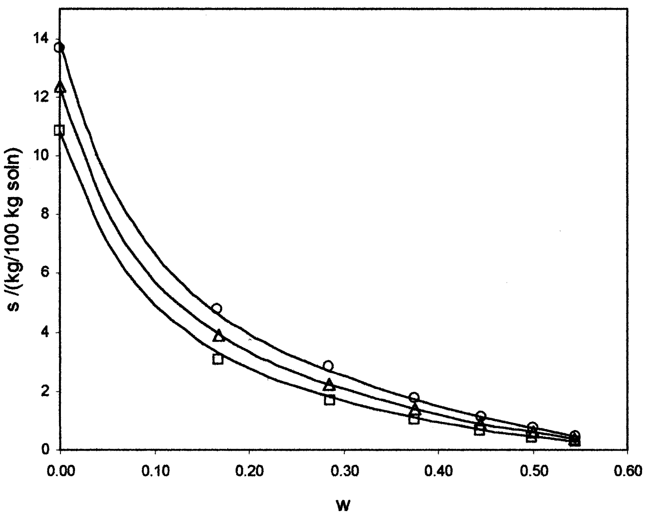

Figure 1. Solubility of potassium sulfate in 1-propanol + water at different temperatures: (□) 298.15 K; (△) 308.15 K; (○) 318.15 K.

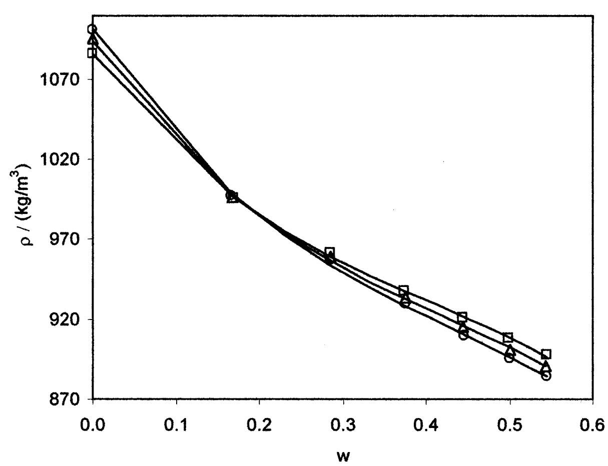

Figure 2. Density of potassium sulfate in 1-propanol + water at the same temperatures as those used in Figure 1.

The a_{2i} and b_{2i} coefficients for eq 3 are presented in Table 3.

The mean absolute deviation between all of the calculated and experimental refractive index values is 0.0005. The maximum absolute deviation is 0.0014.

The electrical conductivity (k) results may be correlated with both the 1-propanol composition and temperature, according to the equation

$$\ln k/(\mathrm{S{\cdot}m^{-1}}) = A_3(\omega) + B_3(\omega)/(T/\mathrm{K}) \qquad (4)$$

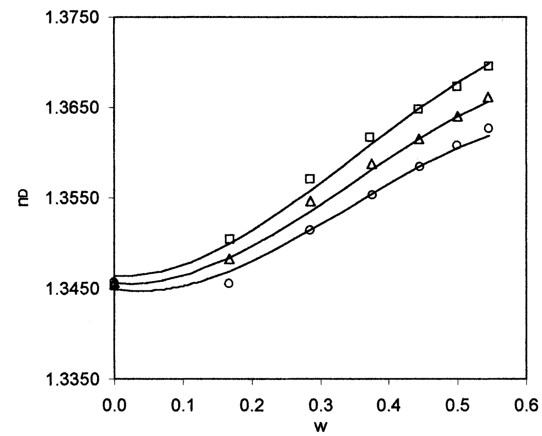

Figure 3. Refractive index of potassium sulfate in 1-propanol + water at the same temperatures as those used in Figure 1.

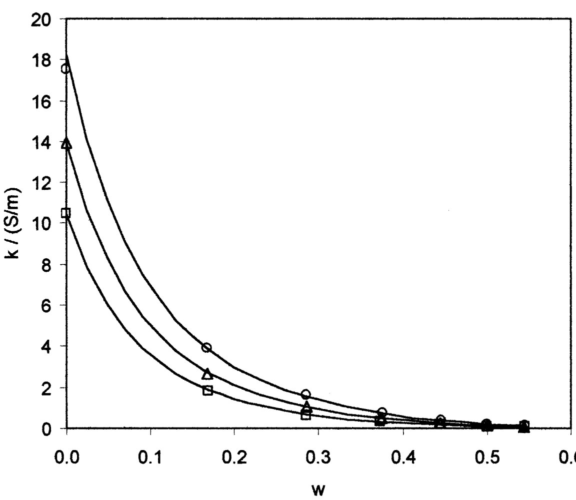

Figure 4. Conductivity of potassium sulfate in 1-propanol + water at the same temperatures as those used in Figure 1.

with

$$A_3(\omega) = a_{30} + a_{31}\omega + a_{32}\omega^2$$

$$B_3(\omega) = b_{30} + b_{31}\omega + b_{32}\omega^2 + b_{33}\omega^3$$

The a_{3i} and b_{3i} coefficients for eq 4 are presented in Table 3.

The mean absolute deviation between all of the experimental and calculated conductivity values is 0.06 S/m. The maximum absolute deviation is 0.77 S/m.

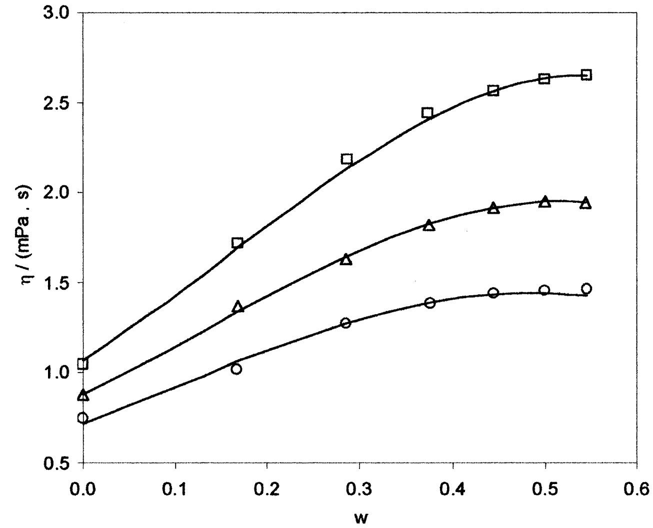

Figure 5. Viscosity of potassium sulfate in 1-propanol + water at the same temperatures as those used in Figure 1.

The viscosity results of the saturated solution (η) may be correlated with both the propanol composition and temperature by the following equation

$$\ln \eta/(\mathrm{mPa{\cdot}s}) = A_4(\omega) + B_4(\omega)\,(T/\mathrm{K}) \qquad (5)$$

with

$$A_4(\omega) = a_{40} + a_{41}\omega + a_{42}\omega^2 + a_{43}\omega^3$$

$$B_4(\omega) = b_{40} + b_{41}\omega$$

The a_{4i} and b_{4i} coefficients for eq 5 are presented in Table 3.

The mean absolute deviation between all of the experimental and calculated viscosity values is 0.017 mPa·s. The maximum absolute deviation is 0.054 mPa·s.

Table 3. Coefficients of Equations 1−5

a_{i0}	a_{i1}	a_{i2}	a_{i3}	b_{i0}	b_{i1}	b_{i2}	b_{i3}
6.26	−0.70	14.83	−21.67	−1155.08	−2552.99	541.79	
865.52	819.34	−173.15	−983.44	0.81	−5.10	4.56	
1.32	−0.14	0.10	−0.20	6.60	41.74	21.53	13.34
11.25	6.34	−10.97	−2654.82	−5448.90	7306.57	−5264.89	
5.97	9.34	−2.37	0.61	−0.02	−0.02		

These results confirmed the good fit between experimental values for concentrations of the salt and the physical properties of the saturated solutions at three temperature levels, in a broad range of concentrations.

For better visualization, experimental data and fitting results from eqs 1−5 are presented as solid lines in Figures 1−5.

Acknowledgment

Financial support from Conicyt-Chile (Fondecyt Project 1011049) is gratefully acknowledged.

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Received for review February 1, 2002. Accepted June 27, 2002.

JE020024G