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Solubilities of Sodium, Potassium, and Copper(II) Sulfates in Ethanol–Water Solutions

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ABSTRACT: The solubilities of (sodium and copper(II)) sulfate + ethanol + water mixtures have been determined at (278.15, 288.15, and 298.15) K and for the potassium sulfate + ethanol + water system at the same temperatures and also at (308.15 and 318.15) K. The equilibrium composition for different points has been calculated by means of refraction index and density measurements. An empirical correlation for the solubilities of the ternary mixtures has been used to correlate experimental values as a function of the solvent composition. Data fitting shows a good agreement with experimental values.

INTRODUCTION

A large amount of salts are obtained from aqueous solutions. A common method for this is evaporative crystallization, but the method presents the problem of energy needs and the consequent financial outlay involved by vaporizing water to saturate the solution to obtain the solid salt. One solution to this problem could be the introduction of an "organic solvent" to decrease the solubility of the salt and thereby cause its precipitation, and this procedure is called antisolvent or extractive crystallization.[1−3]

In this article, solubility data for sodium, potassium, and copper(II) sulfates in ethanol–water solutions are presented to observe the effect of the ethanol addition on the solubility of sulfates in water. This study was conducted at atmospheric pressure and at (273.15, 288.15, and 298.15) K for ternary systems containing sodium sulfate and copper sulfate and at two additional temperatures [(308.15 and 318.15) K] in the case of potassium sulfate. Physical properties (density and refractive index) were used to determine the compositions of the liquid phase at the equilibrium points. The natural logarithm of the solubility has been correlated by an application of a solvent composition-dependent polynomial equation.

In the literature, solubility data for sodium[4] and potassium sulfates[5−8] in ethanol and water solutions were found. For the copper(II) sulfate system in ethanol and water solutions, no data could be found.

EXPERIMENTAL SECTION

Materials. The ethanol employed was supplied by Merck (Lichrosolv quality) with a stated minimum purity of 0.995, degassed with ultrasound, and stored over freshly activated molecular sieves (type 4a or 3a, 1/16 in., Aldrich cat. N° 20.860-4 or 20.858-2, respectively) for several days before use. The water was Milli-Q quality (resistivity, 18.2 MΩ·cm), and sodium sulfate (Merck, mass fraction > 0.99), potassium sulfate (Merck, mass fraction > 0.99), and copper(II) sulfate (Merck, mass fraction > 0.99) were used in sample preparation. The chemicals were recently acquired and stored under sun and humidity protection conditions.

Apparatus and Procedure. The saturation of the solutions was achieved by stirring (magnetic stirrer) for 2 days in closed glass vessels with an external jacket which was thermostatted using a Polyscience controller bath (model 9510), and the temperature stability inside the container was approximately ± 0.1 K. The salt present in the prepared solutions was added in excess to reach solution saturation. To obtain saturated solutions free of suspended solids, suspended matter was settled for a half-day after agitation. The masses of ethanol and water of the potassium sulfate + ethanol + water solution were weighed on a Mettler AT261 Delta Range balance with an uncertainty better than $\pm 10^{-4}$ g, to have a value for the salt-free mass fractions of ethanol. Due to reasons that will be discussed in the next section, for this system, this parameter was not calculated from physical properties. The salt-free mass fractions of ethanol for the potassium sulfate + ethanol + water had an uncertainty better than $\pm 5 \cdot 10^{-5}$ and for the ternary systems containing sodium sulfate and copper sulfate give an uncertainty better than $\pm 2.5 \cdot 10^{-3}$. The increase in uncertainty with respect to the ternary system containing potassium sulfate is because this parameter is calculated from the physical property for both systems and by weighing in the case of potassium sulfate, as discussed above, which generates a smaller error. The molality of the solutions is determined from physical properties in all cases, yielding an uncertainty better than $\pm 10^{-2}$ $\text{mol}\cdot\text{kg}^{-1}$ in the case of sodium and copper sulfate in ethanol–water solution, and in the case of potassium sulfate in ethanol–water the uncertainty is better than $\pm 1.5 \cdot 10^{-2}$ $\text{mol}\cdot\text{kg}^{-1}$.

Properties used to determine the system compositions were density and refraction index. The refraction index was the property used for systems that needed only one property to be determined. The densities of the mixtures were measured with an oscillating-tube Anton Paar DMA-60/602 densimeter with a precision better than $\pm 10^{-4}$ $\text{g}\cdot\text{cm}^{-3}$. The apparatus was calibrated periodically using degassed Millipore quality water

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and air. The temperature in the cell was measured by means of a digital precision Anton Paar MKT 100 thermometer, with a resolution of ± 10^{-3} K. The densimeter was thermostatted with a polyscience controller bath model 9510 with a temperature stability of ± 10^{-2} K. The refractive indices were measured with an automatic refractometer ABBEMAT-HP Dr. Kernchen with a precision of ± 10^{-5}. Refractometer calibration was performed periodically (Milli-Q quality water and ambient air were used for calibration). The measurement device was thermostatted using a Polyscience controller bath (model 9510).

Table 1. Solubility, Density (298.15 K), and Refractive Index (318.15 K) for the Ternary Mixtures of Copper(II) Sulfate for Various Mass Fractions w_e in w_e Ethanol + (1 − w_e) Water at (278.15, 288.15, and 298.15) K

w_e	$m/(\mathrm{mol \cdot kg^{-1}})$	$\rho/(\mathrm{g \cdot cm^{-3}})$	n_D
	T = 278.15 K		
0.0000	1.063	1.15973	1.35746
0.0277	0.737	1.10659	1.35126
0.0522	0.529	1.07032	1.34726
0.0799	0.363	1.04009	1.34445
0.1108	0.242	1.01652	1.34300
0.1322	0.182	1.00406	1.34264
0.1538	0.135	0.99363	1.34262
0.1747	0.101	0.98543	1.34290
0.2039	0.073	0.97686	1.34376
	T = 288.15 K		
0.0000	1.243	1.18585	1.36172
0.0267	0.909	1.13244	1.35551
0.0513	0.684	1.09389	1.35121
0.0779	0.496	1.06052	1.34782
0.1084	0.348	1.03303	1.34570
0.1330	0.254	1.01483	1.34463
0.1589	0.184	1.00038	1.34429
0.1856	0.130	0.98821	1.34434
0.2025	0.100	0.98118	1.34446
	T = 298.15 K		
0.0000	1.431	1.21266	1.36606
0.0259	1.123	1.16404	1.36070
0.0487	0.889	1.12490	1.35625
0.0781	0.652	1.08391	1.35189
0.1016	0.503	1.05752	1.34941
0.1279	0.371	1.03335	1.34752
0.1473	0.289	1.01806	1.34651
0.1702	0.220	1.00410	1.34600
0.1976	0.158	0.99066	1.34588

RESULTS AND DISCUSSION

In this paper, the compositions of the saturated salt systems in solution were calculated from measurements of physical properties.[9−11] The composition of a two-component homogeneous system is defined by measuring a single physical property. In the case of three components, two physical properties are required. This is true for the case of sodium and copper sulfate salts in solution of ethanol and water, but in the case of potassium sulfate in ethanol and water a simplification which reduces the calculation to a single physical property can be done.

The potassium sulfate salt contains no coordination water when it is in equilibrium with an aqueous solution or in a solution of water and ethanol,[5−8] thus the only substance to be transferred between the solid phase and the aqueous is potassium sulfate. This has the effect that the relationship between the amount of water and ethanol at equilibrium is constant and equal to that before the salt was added. So, once the solid-free solution is extracted from the equilibrium cell, only the measurement of a physical property is needed because one datum of the solution composition is already known (the ratio between the amount of water and ethanol is known by weight before it was placed in the equilibrium cell). In the case of sodium and copper sulfates in ethanol−water solution, the salt is hydrated, and there are no conclusive data about the number of water molecules in the salt. It can be seen how the copper sulfate salt changes from blue (pentahydrated salt) to white when an increasing amount of ethanol is present in the solution, whereas in the case of sodium sulfate it can be observed that the salt moves from a transparent crystalline appearance (decahydrated salt) to be white in color, which indicates the transition from the hydrated to the anhydrous salt. The fact these salts can trap a part of the solution water results in the variation of the initial amount of water in the solution, thus the measurement of two physical properties is needed to determine the composition of the system. Finally, for the three binary systems of salts in aqueous solution only one physical property is needed to determine its composition.

Physical property correlations (density and refractive index) drawn from earlier work[12−15] were used for the determination of the composition in the different systems. Density correlations (298.15 K) are to slight salt supersaturation at 298.15 K, and refractive index correlations (318.15 K) are at a higher salt concentration than density correlations. To calculate the composition, one variable Newton−Raphson method was used when only one physical property was necessary to be measured. When two physical properties were necessary, the same two-variable method was used.

The solubilities for the salt + water + ethanol ternary mixtures were determined at (278.15, 288.15, and 298.15) K, except for the system containing potassium sulfate which has two additional temperatures [(308.15 and 318.15) K]. This is because the measurement of one physical property is only necessary, and the refractive index is used because correlations are at a higher solubility (318.15 K). Tables 1 to 3 show the solubility values for the molality of salts at different salt-free mass fractions and temperatures, together with the refraction index and density (when necessary for the calculation of the composition). Figure 1 shows a comparison between the experimental data obtained and those found in the literature[5−8] for the system ethanol + water + potassium sulfate at 298.15 K. A good agreement between them is shown. Ethanol + water + sodium sulfate system data were also found,[4] and in these data the emergence of a liquid−liquid−solid equilibrium at 298.15 K can be seen. This behavior does not appear in the data provided in this article. The high concentration of sodium sulfate for equilibrium points in bibliographic data is remarkable. The possible cause of this experimental behavior was investigated, and it was found that this equilibrium with two liquid phases is a metastable equilibrium. At the temperatures used in this article, the thermodynamically more stable form of sodium sulfate in aqueous solution is the decahydrated salt; however, at about

Table 2. Solubility, Density (298.15 K), and Refractive Index (318.15 K) for the Ternary Mixtures of Sodium Sulfate for Various Mass Fractions w_e in w_e Ethanol + $(1 - w_e)$ Water at (278.15, 288.15, and 298.15) K

w_e	$m/(\mathrm{mol \cdot kg^{-1}})$	$\rho/(\mathrm{g \cdot cm^{-3}})$	n_D
	$T = 278.15$ K		
0.0000	0.450	1.05159	1.33855
0.0290	0.347	1.03401	1.33824
0.0548	0.276	1.02101	1.33842
0.0806	0.219	1.00999	1.33890
0.1094	0.171	0.99986	1.33972
0.1351	0.136	0.99188	1.34056
0.1566	0.111	0.98585	1.34133
0.1749	0.097	0.98152	1.34208
0.2028	0.073	0.97468	1.34316
0.2276	0.058	0.96915	1.34418
0.2542	0.048	0.96377	1.34532
0.2803	0.039	0.95846	1.34640
0.3057	0.032	0.95327	1.34742
	$T = 288.15$ K		
0.0000	0.932	1.10514	1.34651
0.0260	0.747	1.07974	1.34488
0.0524	0.602	1.05877	1.34397
0.0755	0.489	1.04203	1.34339
0.1096	0.372	1.02311	1.34330
0.1329	0.300	1.01133	1.34335
0.1563	0.244	1.00136	1.34363
0.1761	0.210	0.99441	1.34407
0.2039	0.168	0.98540	1.34477
0.2263	0.139	0.97862	1.34540
0.2551	0.110	0.97070	1.34632
0.2854	0.088	0.96303	1.34738
	$T = 298.15$ K		
0.0000	1.954	1.20701	1.36054
0.0278	1.651	1.17197	1.35800
0.0515	1.408	1.14320	1.35591
0.0689	1.229	1.12188	1.35430
0.0965	1.016	1.09483	1.35261
0.1221	0.830	1.07081	1.35110
0.1428	0.696	1.05305	1.35005
0.1764	0.539	1.03056	1.34917
0.1928	0.458	1.01908	1.34867
0.2298	0.320	0.99792	1.34824
0.2517	0.272	0.98891	1.34851
0.2737	0.222	0.97961	1.34879
0.3001	0.170	0.96926	1.34928

Table 3. Solubility and Refractive Index (318.15 K) for the Ternary Mixtures of Potassium Sulfate for Various Mass Fractions w_e in w_e Ethanol + $(1 - w_e)$ Water at (278.15, 288.15, 298.15, 308.15, and 318.15) K

w_e	$m/(\mathrm{mol \cdot kg^{-1}})$	n_D
	$T = 278.15$ K	
0.0000	0.490	1.33885
0.0259	0.371	1.33833
0.0500	0.290	1.33831
0.0731	0.221	1.33844
0.0965	0.174	1.33895
0.1246	0.123	1.33966
0.1511	0.097	1.34072
0.1649	0.083	1.34126
0.1829	0.068	1.34198
0.1945	0.056	1.34240
0.2293	0.040	1.34395
0.2447	0.038	1.34467
	$T = 288.15$ K	
0.0000	0.597	1.34065
0.0265	0.462	1.33996
0.0501	0.360	1.33960
0.0745	0.283	1.33966
0.0959	0.227	1.33990
0.1208	0.175	1.34041
0.1529	0.133	1.34147
0.1754	0.105	1.34222
0.2016	0.084	1.34325
0.2232	0.067	1.34407
0.2434	0.051	1.34480
	$T = 298.15$ K	
0.0000	0.705	1.34240
0.0253	0.557	1.34152
0.0486	0.448	1.34104
0.0728	0.356	1.34086
0.0991	0.277	1.34099
0.1272	0.215	1.34150
0.1496	0.174	1.34202
0.1765	0.133	1.34275
0.2016	0.110	1.34368
0.2240	0.088	1.34443
0.2466	0.072	1.34526
	$T = 308.15$ K	
0.0000	0.800	1.34392
0.0244	0.645	1.34293
0.0487	0.519	1.34228
0.0736	0.412	1.34189
0.1014	0.314	1.34179
0.1256	0.249	1.34201
0.1488	0.203	1.34247
0.1765	0.160	1.34322
0.2023	0.125	1.34396
0.2248	0.100	1.34466
0.2482	0.081	1.34547

305.55 K the anhydrous salt is more stable, so it is normal that when sodium sulfate in aqueous solution at 298.15 K has previously been at a temperature above 305.55 K metastable equilibrium with the anhydrous salt will occur. Liquid−liquid−solid equilibrium shows up because of the addition of ethanol. It was found that at 308.15 K this behavior is stable, which permits the conclusion that the higher concentration of sodium sulfate in ethanol−water solution that allows the

Table 3. Continued

w_e	$m/(\mathrm{mol \cdot kg^{-1}})$	n_D
	$T = 318.15$ K	
0.0000	0.908	1.34560
0.0226	0.746	1.34447
0.0487	0.596	1.34358
0.0775	0.471	1.34314
0.1014	0.384	1.34300
0.1256	0.310	1.34306
0.1488	0.249	1.34326
0.1765	0.200	1.34388
0.2016	0.166	1.34457
0.2251	0.135	1.34521
0.2482	0.108	1.34586

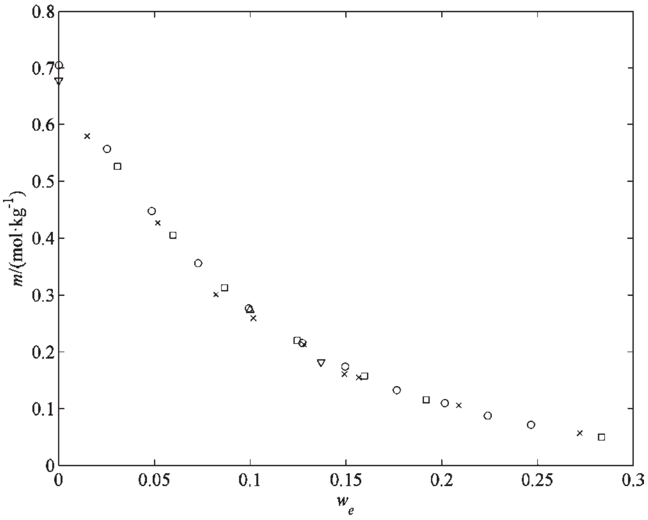

Figure 1. Comparison of experimental saturation molalities (m) of potassium sulfate in ethanol—water with literature data at 298.15 K: ×, ref 5; □, ref 6; △, ref 7; ▽, ref 8; ○, this work.

Table 4. Fitting Parameters of Equation 1 and the Standard Deviation (σ) of Equation 2 for Salt + Ethanol + Water Ternary Systems

T/K	278.15	288.15	298.15	308.15	318.15
			$CuSO_4$ + Ethanol + Water		
A_1	−13.3671	−11.4819	−9.24369		
A_2		−3.61756	−10.3160		
σ	0.0020	0.0031	0.0030		
			K_2SO_4 + Ethanol + Water		
A_1	−10.8168	−9.97443	−9.34902	−9.14913	−8.55459
σ	0.0027	0.0027	0.0018	0.0036	0.0030
			Na_2SO_4 + Ethanol + Water		
A_1	−8.89301	−8.41900	−6.13181		
A_2			−7.04339		
σ	0.0014	0.0031	0.0082		

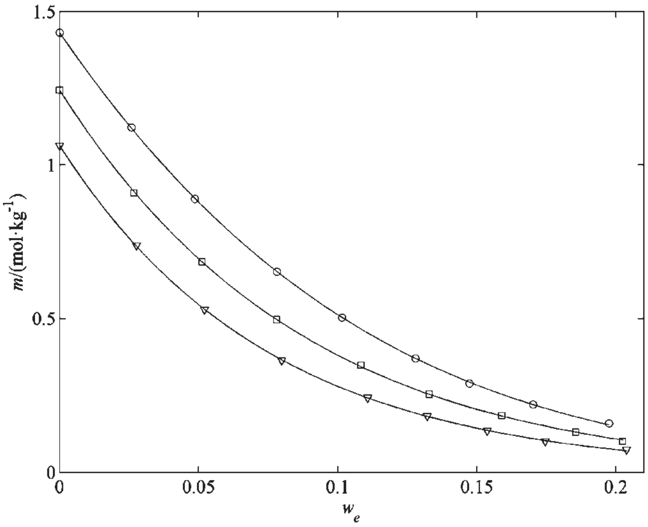

Figure 2. Saturation molalities of copper sulfate, m, vs salt-free mass fraction of ethanol, w_e, in ethanol—water solution at different temperatures: ○, 298.15 K; □, 288.15 K; ▽, 278.15 K.

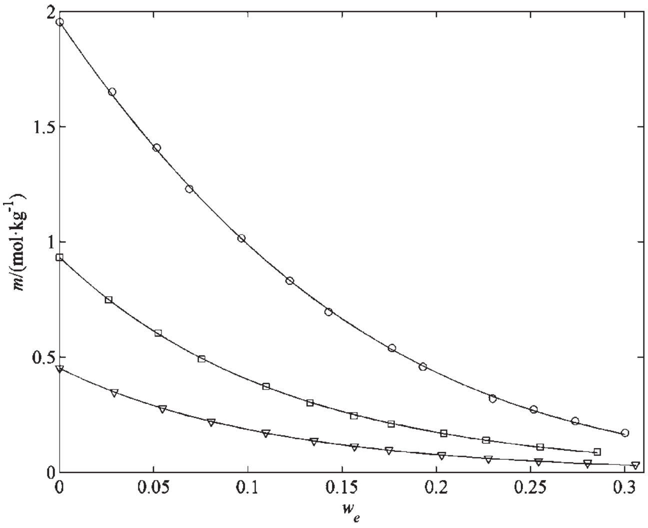

Figure 3. Saturation molalities of sodium sulfate, m, vs salt-free mass fraction of ethanol, w_e, in ethanol—water solution at different temperatures: ○, 298.15 K; □, 288.15 K; ▽, 278.15 K.

anhydrous salt allows the system to reach this liquid—liquid—solid equilibrium. In the case of the decahydrated sodium sulfate salt, due to its lower solubility, it could not be reached at the temperatures of this work.

The experimental values for solubility (molality) of the ternary systems may be correlated as a function of the salt-free mass fractions for each temperature, according to the equation[16]

$$\ln(m) = \ln(m_0) + \sum_{i=1}^{P} A_i w_e^i \qquad (1)$$

where m is the molality of the saturated solution; w_e is the ethanol mass fraction of the salt-free solution; A_i are adjustable parameters, which are given in Table 4; P is the number of terms in the polymonial; and m_0 is the molality of the saturated salt + water binary system.

The saturation concentration (molality) versus salt-free mass fraction of ethanol for the three sulfates in ethanol—water

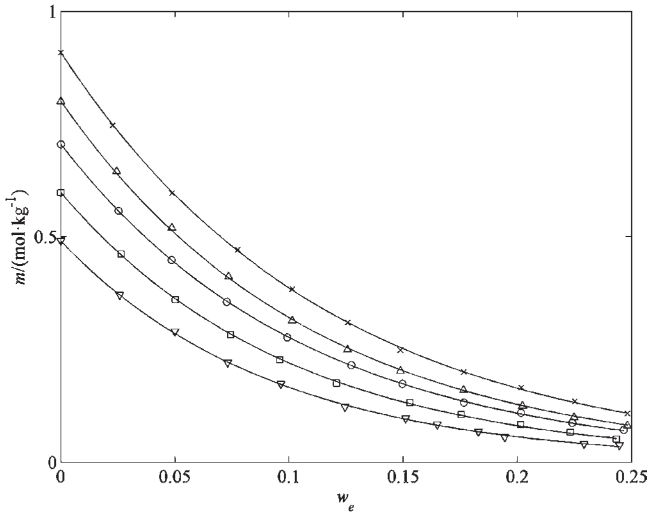

Figure 4. Saturation molalities of potassium sulfate, *m*, vs salt-free mass fraction of ethanol, w_e, in ethanol−water solution at different temperatures: ×, 318.15 K; △, 308.15K; ○, 298.15 K; □, 288.15 K; ▽, 278.15 K.

solution has been shown in Figures 2 to 4. It was observed that the solubility increases with an increase in temperature, and the increase in the salt-free mass fraction of ethanol led to a decrease of the salt solubility. This decline in solubility with the ethanol amount was expected due to the insolubility of sulfates in ethanol. The same behavior was observed for all systems.

All parameters were obtained by a fitting algorithm from Marquardt.[17] In Table 4, the experimental and estimated solubilities are compared showing standard deviations (eq 2).

$$\sigma = \sqrt{\frac{\sum_{i}^{n} (m_{i,\,\text{experimental}} - m_{i,\,\text{predicted}})^2}{n-p}} \qquad (2)$$

The value of the saturated molality, the number of experimental data, and the number of parameters are represented in this equation by *m*, *n*, and *p*, respectively. The root-mean-square deviation values between the experimental data of this work and those predicted show good agreement.

■ CONCLUSION

In this article, the solubility of sodium and copper sulfates in ethanol−water solutions are presented at (278.15, 228.15, and 298.15) K. Data of potassium sulfate at the same temperatures and at (308.15 and 318.15) K are presented too. The natural logarithm of salt molality of the saturated solutions was correlated to solvent composition-dependent polynomials by use of the least-squares method. The average absolute deviations between calculated values and experimental values are satisfactory. A decrease in all solubilities was observed with an increase in mass fraction of ethanol, and an increase was observed with an increase in temperature.

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