

Densities of (Lithium, Magnesium, or Copper(II)) Sulfates in Ethanol–Water Solutions

Martín F. Hervello and Angel Sánchez*

Departamento de Ingeniería Química, Universidad de Vigo, 36200, Vigo, Spain

The densities of (lithium, magnesium, and copper(II)) sulfates + ethanol + water mixtures have been measured with an oscillating-tube densimeter in the temperature range of (283.15 to 298.15) K and at atmospheric pressure. An empirical correlation for the densities of ternary mixtures has been used to correlate experimental values as a function of the molality of the salt and solvent composition. Data fitting show a good agreement with experimental values.

Introduction

The knowledge of the influence of electrolytes in the phase equilibria of water + alcohol has been treated in numerous papers.^{1–3} Also, g^E models have been developed for the reliable prediction of phase equilibria, osmotic coefficients, and mean ionic activity coefficients.^{4–7} But the study of densities of these type of mixtures is more scarce than the above properties.

One of the research activities of our group is the physical characterization of the salt effect in ethanol–water solutions.⁸ Generally, the densities of electrolyte solutions have been determined at low molalities of salt for using a fitting equation⁹ elucidating the nature of solute–solvent interactions by partial molar volume at infinite dilution. But the aim of this work is to obtain densities of the studied systems in a broad range of molalities of salt and mass fraction of ethanol. So, we present densities from (283.15 to 298.15) K, at 5 K intervals, of (lithium, magnesium, or copper(II)) sulfate + ethanol + water mixtures. These values were fitted to polynomials as a function of the molality of the salt and the salt-free mass fraction of the solution. The three systems present good agreement with the experimental values. For the systems treated in this paper, we have not been able to find more data in the literature on experimental values for these ternary systems, except data on MgSO₄ mixtures at dilute concentrations of salt^{10,11} and data on Li₂SO₄-saturated solutions.¹²

Experimental Section

Materials. The chemicals were ethanol (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 Catalog No. 20.860-4 or 20.858-2, respectively) for several days before use. The water was Milli-Q quality (resistivity, 18.2 MΩ·cm). Lithium sulfate monohydrate (Merck, mass fraction >0.99), magnesium sulfate (Aldrich, 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.

The molality of the MgSO₄ and CuSO₄ aqueous stock solutions was determined by gravimetric sulfate analysis. Li₂SO₄ stock aqueous solutions were prepared by weight. Final

Table 1. Density for the Binary Mixtures of Salt + Water as a Function of Molality in the Temperature Range from (283.15 to 298.15) K

$m/\text{mol}\cdot\text{kg}^{-1}$	t/298.15 K	t/293.15 K	t/288.15 K	t/283.15 K
Li ₂ SO ₄ + Water, $\rho/\text{g}\cdot\text{cm}^{-3}$				
0.2142	1.01689	1.01816	1.01921	1.02000
0.3987	1.03324	1.03460	1.03578	1.03671
0.7939	1.06675	1.06826	1.06962	1.07078
1.1787	1.09756	1.09915	1.10066	1.10196
1.5748	1.12768	1.12933	1.13093	1.13231
1.9713	1.15622	1.15791	1.15958	1.16103
2.3607	1.18289	1.18460	1.18629	1.18776
2.7455	1.20801	1.20969	1.21140	1.21292
3.0903	1.22951	1.23119	1.23284	1.23434
MgSO ₄ + Water, $\rho/\text{g}\cdot\text{cm}^{-3}$				
0.1933	1.02013	1.02138	1.02246	1.02324
0.3842	1.04203	1.04339	1.04461	1.04558
0.7688	1.08485	1.08638	1.08785	1.08917
1.1636	1.12702	1.12869	1.13034	1.13193
1.5096	1.16237	1.16413	1.16590	1.16767
1.9000	1.20080	1.20266	1.20452	1.20643
2.2691	1.23575	1.23759	1.23958	1.24157
2.6781	1.27267	1.27456		
3.0440	1.30455			
CuSO ₄ + Water, $\rho/\text{g}\cdot\text{cm}^{-3}$				
0.1346	1.01879	1.02008	1.02112	1.02188
0.3007	1.04485	1.04629	1.04751	1.04845
0.4408	1.06656	1.06813	1.06947	1.07055
0.5896	1.08933	1.09104	1.09250	1.09372
0.7359	1.11135	1.11318	1.11477	1.11610
0.8590	1.12972	1.13165	1.13334	1.13478
1.0160	1.15285	1.15490	1.15670	1.15827
1.1791	1.17668	1.17880	1.18077	1.18245
1.3008	1.19409	1.19632	1.19832	
1.4565	1.21625			

solutions were prepared gravimetrically one by one by dilutions of water and ethanol. All mixtures were prepared using a Mettler AT261 Delta Range balance with a precision of $\pm 10^{-4}$ g, yielding an error better than $\pm 5 \cdot 10^{-5}$ in the salt-free mass and molar fraction and better than $\pm 5 \cdot 10^{-4}$ mol·kg⁻¹ in the molality of the salt.

Measurements. The densities of the mixtures were measured with an oscillating-tube Anton Paar DMA-60/602 densimeter with an uncertainty better than $\pm 10^{-4}$ g·cm⁻³. The apparatus was calibrated periodically using degassed Millipore quality water and air. The temperature in the cell was measured by means of a digital precision Anton Paar MKT 100 thermometer,

* Corresponding author. Fax: +34 986812022. E-mail: asanchez@uvigo.es

the root-mean-square deviation values between the experimental data of this work and the corresponding ones from the proposed equations show a good agreement, and all values are less than 10^{-4} g·cm $^{-3}$ at all temperatures. So, the density solutions are described adequately by these equations, and these polynomials can be used for density prediction to salt saturation.

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