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Isopiestic and Volumetric Study of $CuCl_2$ + Ethanol at 25 °C

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Osmotic coefficients and densities of solutions of $CuCl_2$ in ethanol are reported at 25 °C. Osmotic coefficients have been measured using an improved isopiestic method and correlated with the Pitzer and NRTL models. Densities have been measured using a vibrating-tube densimeter and fitted with equations obtained from the Pitzer and NRTL models. Both the Pitzer and NRTL models successfully correlate the experimental osmotic coefficient and density data.

Introduction

Activity coefficient data of binary electrolyte solutions are required to describe the thermodynamic behavior of electrolyte solutions with organic solvents. These data are also useful to predict thermodynamic properties of electrolytes in mixed solvents.[1−3] The volumetric behavior of solutes has been shown to be very useful in elucidating the various interactions that are observed in aqueous and nonaqueous solutions.[4] However, accurate thermodynamic data are very scarce for salts in nonaqueous electrolyte solutions, in contrast to aqueous solutions. For salt + alcohol solutions, reported accurate osmotic coefficient data for lithium and calcium salts in ethanol and methanol[5−7] at 25 °C are measured with an isopiestic technique. This work is the continuation of a systematic thermodynamic investigation of (salt + alcohol) systems. In this work, we report the osmotic coefficients and densities of solutions of $CuCl_2$ in ethanol. Osmotic coefficients have been reported previously by Mato and Cocero.[8] Martinez-Andreu et al.[9] have reported densities for the solution of $CuCl_2$ in ethanol at 25 °C. However, only a few data points have been reported in the dilute region. Unfortunately, since the density data measured in the dilute region are scattered, meaningful values cannot be derived for the partial molal volume at infinite dilution for $CuCl_2$ in ethanol. In this work, we focused on the dilute region as well as the concentrated region and reported density data, which can be used to derive the partial molal volume at infinite dilution for $CuCl_2$ in ethanol.

In the isopiestic method we used sodium iodide as the isopiestic reference. The osmotic coefficients for the reference system were previously calculated[5] from accurate vapor pressure data of Barthel and Lauermann.[10] The osmotic coefficients obtained from isopiestic experiments were correlated with the Pitzer ion interaction model[11] and the electrolyte NRTL model of Chen and Evans.[12]

Densities were measured with a vibrating-tube densimeter. The excess volume equations derived by Rogers and Pitzer[13] from the Pitzer model[11] and by Humffray[14] from the electrolyte NRTL model[12] were used for the correlation of the experimental densities.

Experimental Section

Materials. The alcohol and salts were obtained from Merck. They were all analytical pure grade reagents (absolute ethanol, GR, minimum 99.8% by mass; NaI, GR, minimum 99.5% by mass; $CuCl_2{\cdot}2H_2O$, GR, minimum 99.5% by mass). Both NaI and $CuCl_2$ were used without further purification. Ethanol was dried by the method described by Vogel.[15] The density, d, of pure ethanol was measured with a vibrating-tube densimeter as $d_s = 785.12$ kg·m^{-3}, which is in reasonable agreement with the literature value[10] of 785.08 kg·m^{-3}. NaI was dried in a free convection oven at about 125 °C for 24 h prior to use, and copper(II) chloride was dehydrated at about 180 °C according to Duval.[16]

Apparatus and Procedure. The isopiestic apparatus employed is essentially the same as the one used previously.[5] This apparatus consisted of a five-leg manifold attached to round-bottom flasks. The five flasks were typically used as follows. Two flasks contained the standard NaI solutions, two flasks contained $CuCl_2$ solutions, and the central flask was used as an ethanol reservoir. The apparatus was held in a constant-temperature bath at least 120 h for equilibration at (25.0 ± 0.005) °C. The temperature was controlled to within ±0.005 °C with a Heto temperature controller (Hetotherm PF, Heto Lab Equipment, Denmark). After equilibrium had been reached, the manifold assembly was removed from the bath and each flask was weighed with a high precision (10^{-4} kg) analytical balance (Shimadzu, 321-34553, Shimadzu Co., Japan). It was assumed that the equilibrium condition was reached when the differences between the mass fractions of each duplicate were less than 1%. In all cases, averages of the duplicates are reported as the total isopiestic mass fraction. The uncertainty in the measurement of solvent activity was estimated to be ±0.0002.

Densities were measured with a vibrating-tube densimeter (Kyoto Electronic DA-210, Japan). It was calibrated with air and distilled water as reference fluids before each measurement. The apparatus was also tested with the density of a known molality of aqueous NaCl using the data given by Pitzer et al.[17] The temperature was held to within ±0.01 °C with a temperature controller (Eyela, UA-10, Tokyo Rikakiai Co., Japan). The uncertainty in the measurement of density was estimated to be $\pm 2 \times 10^{-2}$ kg·m^{-3}.

Results and Discussion

Isopiestic Results. Isopiestic equilibrium molalities with reference standard solutions of NaI in ethanol as reported in Table 1 enabled the calculation of the osmotic

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Table 1. Isopiestic Equilibrium Molalities, Osmotic Coefficients, Solvent Activities, and Vapor Pressures of $CuCl_2$ in Ethanol at 25 °C

m_{NaI}/mol·kg^{-1}	m_{CuCl_2}/mol·kg^{-1}	Φ_{exp}	a_{exp}	p_{exp}/kPa
0.0000	0.0000	1.000	1.0000	7.870
0.0910	0.1572	0.292	0.9958	7.837
0.1242	0.2233	0.277	0.9943	7.825
0.1820	0.3343	0.267	0.9918	7.805
0.2469	0.4450	0.269	0.9890	7.783
0.2580	0.4821	0.260	0.9885	7.779
0.3236	0.5915	0.265	0.9857	7.756
0.4024	0.7299	0.268	0.9821	7.728
0.4685	0.8517	0.269	0.9791	7.704
0.6347	1.1563	0.277	0.9709	7.639
0.7568	1.3943	0.282	0.9644	7.588
0.8357	1.5565	0.285	0.9600	7.552
0.9492	1.7627	0.296	0.9531	7.498
1.0101	1.9011	0.298	0.9492	7.467
1.2053	2.2645	0.319	0.9356	7.359
1.3012	2.4091	0.334	0.9286	7.303
1.4516	2.6384	0.358	0.9167	7.209
1.6008	2.9188	0.375	0.9041	7.109
1.7550	3.2051	0.394	0.8902	6.999
1.8802	3.4260	0.410	0.8787	6.907

coefficient, Φ, of the solutions of $CuCl_2$ in ethanol from

$$\Phi = \frac{\nu^* \Phi^* m^*}{\nu m} \tag{1}$$

where ν^* and ν are the sums of the stoichiometric numbers of anions and cations in the reference solution and the solution of $CuCl_2$, respectively, m is the molality of the $CuCl_2$ solution, m^* is the molality of the reference standard in isopiestic equilibrium with this solution, and Φ^* is the osmotic coefficient of the isopiestic reference standard, calculated at m^*. The necessary Φ^* values at any m^* were obtained from the fitted Pitzer equation, including the $\beta^{(2)}$ term,[18] as described in our previous paper.[5] It was shown[5] that, by using $\alpha_1 = 0.2$, $\alpha_2 = 1.4$, $\beta^{(0)} = 1.05886$, $\beta^{(1)} = 6.89558$, $\beta^{(2)} = -6.25702$, and $C^{\phi} = -0.133017$, the osmotic coefficients, Φ^*, are reproducible with a standard deviation of 0.005. From the calculated osmotic coefficient data, the activity of ethanol in $CuCl_2$ solution and the vapor pressure of this solution were determined at isopiestic equilibrium molalities, with the help of the following relations:

$$\Phi = -\frac{\ln(a_s)}{\nu m M_s} \tag{2}$$

$$\ln(a_s) = \ln\left(\frac{p}{p^*}\right) + \frac{(B - V_s^*)(p - p^*)}{RT} \tag{3}$$

where a_s is the activity of solvent, M_s is the molar mass of the ethanol, B is the second virial coefficient, V_s^* is the molar volume, and p^* is the vapor pressure of pure ethanol. The values of $M_s = 0.046\,040\,69$ kg·mol^{-1}, $B = -2.981 \times 10^{-5}$ m^3·mol^{-1}, $V_s^* = 5.868 \times 10^{-5}$ m^3·mol^{-1}, and $p^* = 7.8703$ kPa (from Barthel and Lauermann[10]) were used at 25 °C. The obtained activity and vapor pressure data are also given in Table 1.

From the solvent activity data reported by Mato and Cocero[8] for the $CuCl_2$ in ethanol, osmotic coefficients were calculated using eq 2. A comparison of our osmotic coefficient data to that of Mato and Cocero[8] is shown in Figure 1. This figure shows that our data agree well with the literature data.

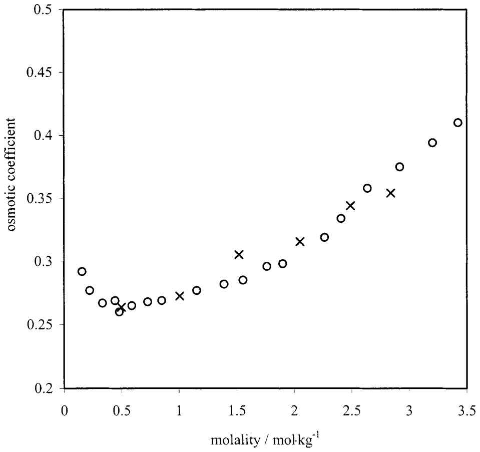

Figure 1. Comparison of osmotic coefficient data for $CuCl_2$ + ethanol solutions at 25 °C: ○, this work; ×, Mato and Cocero.[8]

Table 2. Densities, d, of Solutions of $CuCl_2$ in Ethanol at 25 °C

m/mol·kg^{-1}	d/kg·m^{-3}	m/mol·kg^{-1}	d/kg·m^{-3}
0.0123	786.45	0.6729	848.32
0.0265	787.93	0.7053	851.12
0.0405	789.40	0.7847	858.28
0.0497	790.37	0.8408	863.21
0.0593	791.26	0.8419	863.32
0.0625	791.50	1.0642	882.61
0.0667	792.05	1.1005	885.72
0.0693	792.26	1.1282	888.14
0.1380	799.01	1.1559	890.47
0.2064	805.50	1.3263	905.16
0.2843	812.95	1.5563	924.41
0.2990	814.31	1.6028	928.48
0.3190	816.10	1.7321	939.13
0.3445	818.58	2.0671	967.12
0.3558	819.59	2.2113	979.16
0.3629	820.20	2.4628	999.78
0.3823	822.06	2.6992	1019.29
0.4268	826.12	2.8553	1032.17
0.4699	830.07	2.9068	1036.41
0.4863	831.56	3.099	1052.32
0.5699	839.14	3.3159	1070.06
0.5842	840.43	3.8015	1110.60
0.6344	844.79	4.0127	1128.52

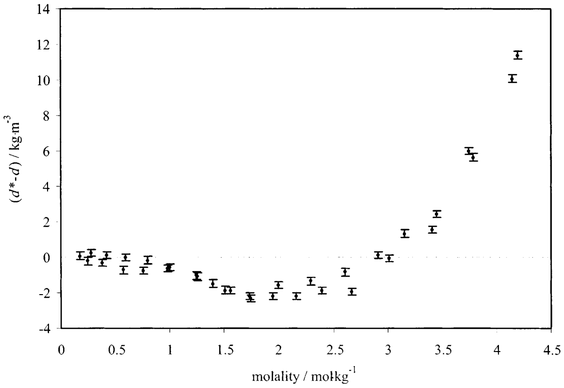

Figure 2. Density difference between the data of Martinez-Andreu et al.[9] and those of this work, d^*-d, versus molality for $CuCl_2$ + ethanol at 25 °C.

Volumetric Results. Table 2 summarizes the density data for solutions of $CuCl_2$ in ethanol in the molality range 0.0123 to 4.0127 mol·kg^{-1}. A comparison of the density data, d^*, reported by Martinez-Andreu et al.[9] and the corresponding data, d, obtained using the Pitzer model (eq 11a) with the coefficients given in the first row of Table 5 is shown in Figure 2.

Apparent molal volumes in the dilute region ($m < 0.1$) evaluated from eq 4 can be used along with the Redlich−Mayer equation[19] (eq 5) for evaluation of the limiting apparent molal volume of $CuCl_2$ in ethanol solutions, ϕ_v° (equal to the partial molal volume at infinite dilution, V_2°). The necessary equations have the following forms:

$$\phi_v = \left[\frac{M_2}{d} + \frac{1}{m}\left(\frac{1}{d} - \frac{1}{d_s}\right)\right] \tag{4}$$

$$\phi_v = \phi_v^\circ + S_v\sqrt{m} + b_v m \tag{5}$$

where b_v is an empirical parameter and S_v is defined as

$$S_v = A_v\left[\frac{1}{2}\left(\sum_i \nu_i z_i^2\right)\right]^{3/2} \tag{6}$$

In these equations ϕ_v, M_2, m, and d are the apparent molal volume in $m^3 \cdot mol^{-1}$, the molar mass of electrolyte in $kg \cdot mol^{-1}$, the molality of the solution in $mol \cdot kg^{-1}$, and the density of solution in $kg \cdot m^{-3}$, respectively. ν_i and z_i are the stoichiometric number and absolute charge of ion i, respectively, and A_v is the Debye–Hückel slope for the apparent molal volume. A_v is calculated with the equation[20]

$$A_v = -4RT\left(\frac{\partial A_\Phi}{\partial P}\right)_T = 6RTA_\Phi\left(\left(\frac{\partial \ln D}{\partial p}\right)_T - \frac{\kappa_T}{3}\right) \tag{7}$$

where A_Φ is the Debye–Hückel constant for the osmotic coefficient on the molal basis. D is the dielectric constant, and κ_T is the isothermal compressibility. For ethanol, using the values of $(\partial \ln D/\partial p)_T = 1.18\ GPa^{-1}$ (from Srinivasan and Kay[21]), the isothermal compressibility $\kappa_T = 1.14\ GPa^{-1}$ (from Kawaizumi and Zana[22]), and $A_\Phi = 2.006\ kg^{1/2} \cdot mol^{-1/2}$ (calculated in our previous work[5] by using eq 8d), we obtain $A_v = 23.873 \times 10^{-6}\ m^3 \cdot mol^{-1} \cdot kg^{-1/2}$ at 25 °C. The limiting apparent molal volume of $CuCl_2$ in ethanol was obtained by fitting eq 5 to the data in the dilute region. The obtained value of ϕ_v° is $-16.43 \times 10^{-6}\ m^3 \cdot mol^{-1}$, and b_v is $-181.44 \times 10^{-6}\ m^3 \cdot mol^{-2} \cdot kg$.

Correlation of Osmotic Coefficients. In this work, for the correlation of the osmotic coefficient data of $CuCl_2$ in ethanol solutions, we used the ion interaction model of Pitzer[11] and the electrolyte NRTL model of Chen and Evans.[12]

The model of Pitzer[11] has been used for aqueous and, in a few cases, for nonaqueous electrolyte solutions.[5,6,10,18,23] The NRTL model has been used for the correlation of mean ionic activity coefficients of the solute and the vapor pressure of aqueous and a few nonaqueous electrolyte solutions.[5,6,12]

The Pitzer model has the following form for a binary 2:1 electrolyte solution:[11]

$$\Phi - 1 = 2f^\Phi + \frac{4m}{3}B^\Phi + m^2\frac{2^{3/2}}{3}C^\Phi \tag{8a}$$

where

$$f^\Phi = -\frac{A_\Phi\sqrt{I}}{1 + b\sqrt{I}} \tag{8b}$$

$$B^\Phi = \beta^{(0)} + \beta^{(1)}\exp(-\alpha_1\sqrt{I}) \tag{8c}$$

$$A_\Phi = \frac{1}{3}\sqrt{2\pi N_A d_s}\left(\frac{e^2}{4\pi\epsilon_0 DkT}\right) \tag{8d}$$

In these equations $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ are Pitzer's ion interaction parameters obtained by fitting of experimental data; α_1 and b are adjustable parameters. N, e, k, and ϵ_0 are Avogadro's number, the electronic charge, Boltzmann's constant, and the permittivity of vacuum, respectively. For $CuCl_2$ in ethanol solutions at 25 °C the values of $\alpha_1 = 2.0\ kg^{1/2} \cdot mol^{-1/2}$ and $b = 3.2\ kg^{1/2} \cdot mol^{-1/2}$ were used. Table 3 summarizes the Pitzer ion interaction parameters obtained from fitting of the experimental osmotic coefficient data with the Pitzer model.

Table 3. Pitzer Model Parameters for Osmotic Coefficients of $CuCl_2$ in Ethanol at 25 °C ($\alpha_1 = 2$ and $b = 3.2$)

$\beta^{(0)}$	$\beta^{(1)}$	C_ϕ	$\sigma(\Phi)$
0.1792 ± 0.0056	2.5358 ± 0.0969	$-0.013\,33 \pm 0.001\,33$	0.010

In the NRTL model the excess Gibbs energy of an electrolyte solution and consequently the activity coefficients of species have been written as the sum of long-range and short-range contributions,[12]

$$\ln \gamma_i = \ln \gamma_i^{LR} + \ln \gamma_i^{SR} \tag{9a}$$

where LR and SR refer to the long-range and short-range contributions, respectively.

The long-range contribution is represented by the Pitzer–Debye–Hückel (PDH) equation,[24] and the short-range contribution is represented by the NRTL model. The PDH equation for the solvent activity coefficient is

$$\ln \gamma_s^{PDH} = \frac{2A_x I_x^{3/2}}{1 + \rho I_x^{1/2}} \tag{9b}$$

where A_x is the Debye–Hückel constant for the osmotic coefficient on a mole fraction basis. For ethanol the value of $A_x = 9.349$ has been reported in previous work.[5] I_x is the ionic strength on a mole fraction basis, $I_x = {}^1/_2\sum_{i=ions} x_i z_i^2$, where x_i and z_i are the mole fraction and absolute value of charge for the ith ion. ρ is the closest distance parameter; for aqueous solutions its value has been set to 14.9 by Chen and Evans[12] and Pitzer.[24] Fitting the osmotic coefficient data for $CuCl_2$ in ethanol with the NRTL model with $\rho = 14.9$ gives unreliable results. From analysis of the experimental osmotic coefficient data, the optimum value of 21 was obtained for ρ; so that choosing this value for ρ gives the smallest value for the standard deviation of the fit in the NRTL model. In principle, the value of ρ can be obtained from the equation[25]

$$\rho = a\sqrt{\frac{2e^2 N d_s}{M_s \epsilon_0 DkT}} \tag{9c}$$

An important parameter in the above equation is the hard core collision diameter or distance of closest approach of ions in solution, a. To calculate a for some electrolytes in propanol solutions, Barthel[26] has used the following relation

$$a = a_+ + a_- + S \tag{9d}$$

When the above relation is used for the calculation of a for $CuCl_2$ in ethanol solution, a value of about 20 is obtained for ρ, which is close to the optimum value of 21 obtained using the trial and error method. In the above equation, a_+ and a_- are the cationic and anionic radii, respectively. S is the contribution of the shape and size of the solvent molecule. For $CuCl_2$ in ethanol solution, $a_+ = 0.072$ nm, $a_- = 0.181$ nm, and $S = 0.57$ (from Barthel[26]) were used.

Table 4. NRTL Model Parameters for Osmotic Coefficients of $CuCl_2$ in Ethanol at 25 °C ($\rho = 21$ and $\alpha = 0.2$)

$\tau_{ca,m}$	$\tau_{m,ca}$	$\sigma(\Phi)$
-3.7202 ± 0.008	7.5403 ± 0.0273	0.015

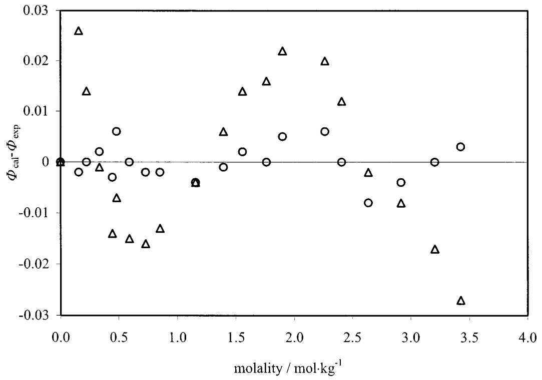

Figure 3. Difference between the experimental and calculated osmotic coefficients: ○, Pitzer model; △, NRTL model.

The short-range contribution in the activity of the solvent according to the NRTL model is

$$\ln \gamma_s^{NRTL} = 8x_c^2\left\{\frac{2\tau_{ca,m}\exp(-2\alpha\tau_{ca,m})}{[1-3x_c+4x_c\exp(-\alpha\tau_{ca,m})]^2} - \frac{\tau_{m,ca}\exp(-\alpha\tau_{m,ca})}{[(1-3x_c)\exp(-\alpha\tau_{m,ca})+2x_c]^2}\right\} \qquad (9e)$$

In this equation there are two fitting parameters: $\tau_{ca,m}$ (salt−solvent parameter) and $\tau_{m,ca}$ (solvent−salt parameter). α is the nonrandomness factor, and x_c is the mole fraction of cation, defined as

$$x_c = \frac{n_c}{n_s + n_c + n_a} \qquad (9f)$$

where n_c, n_a, and n_s are the numbers of cation, anion, and solvent molecules, respectively.

According to eq 9a, addition of the long-range term (eq 9b) to eq 9e gives the corresponding expression for $\ln \gamma_s$ for the NRTL model. From this expression for solvent activity coefficient, together with the relation $\ln a_s = \ln \gamma_s + \ln x_s$ we obtain the corresponding expression for the osmotic coefficient. The binary fit parameters obtained from the fitting of the experimental osmotic coefficient data for $CuCl_2$ in ethanol solution at 25 °C to the NRTL model are presented in Table 4. The difference between the experimental osmotic coefficient data and those calculated from the Pitzer and the NRTL models is shown in Figure 3.

Correlation of Density Data. A power series in (molality)$^{1/2}$ is usually employed for correlation of densities of aqueous electrolytes. In this method, an adequate description of experimental density data may require a large number of parameters. Recently, there is a growing interest in using theoretical methods such as the Pitzer and the electrolyte NRTL models for correlation of density and apparent molal volume data for aqueous electrolyte solutions.[13,14,27,28] However, these models have not been applied for volumetric properties of nonaqueous electrolytes. To see the reliability of each method in the correlation of the density data for $CuCl_2$ in ethanol solutions, all of the aforementioned methods were considered.

The density data were fitted to the following equation with a power series in the (molality)$^{1/2}$

$$d/\text{kg}\cdot\text{m}^{-3} = d_s + a_1\sqrt{m} + a_2 m + a_3\sqrt{m^3} + a_4 m^2 + a_5\sqrt{m^5} \qquad (10)$$

The obtained coefficients a_1, a_2, a_3, a_4, and a_5 are respectively 1.9222, 96.9324, −2.5561, −6.8353, and 2.5308. From the obtained standard deviation of the fit, $\sigma(d) = 0.08$ kg·m^{-3}, we conclude that eq 10 can be satisfactorily employed for the representation of the experimental density data for $CuCl_2$ in ethanol solutions.

The Pitzer equation for the apparent molal volume of a binary solution of a 2:1 electrolyte has the following form[27]

$$\phi_v = V_0^{\,2} + \frac{A_v I}{mb}\ln(1 + b\sqrt{I}) + 2RTm\left(2B^v + \frac{4m}{2\sqrt{2}}C^v\right) \qquad (11a)$$

where

$$B^v = \beta^{(0),v} + \beta^{(1),v}g(\alpha_1\sqrt{I}) \qquad (11b)$$

$$g(x) = \frac{2}{x^2}[1 - (1 + x)\exp(-x)] \qquad (11c)$$

In these equations, the superscript v indicates the differentiation of the corresponding ion interaction parameter with respect to pressure at constant temperature [for example $\beta^{(0),v} = (\partial\beta^{(0)}/\partial p)_T$]. The Pitzer model can be written in terms of $1/d$ versus molality using eq 4. Fitting of density data with the Pitzer model was carried out as $1/d$ versus molality. As in the case of correlation of osmotic coefficients, the values of $b = 3.2$ kg$^{1/2}$·mol$^{-1/2}$ and $\alpha_1 = 2.0$ kg$^{1/2}$·mol$^{-1/2}$ give the best fitting of the density data. The results of fitting to the Pitzer model are given in Table 5.

For most aqueous electrolytes, it has been shown[28] that the Pitzer model with only two parameters ($\beta^{(0),v}$ and C^v) can be satisfactorily used for the correlation of apparent molal volume data. It has been stated[28] that, including the $\beta^{(1),v}$ term does not significantly improve the overall fit. To examine the role of the $\beta^{(1),v}$ terms in the quality of fitting of the density data as $1/d$ versus molality for the investigated nonaqueous system, the Pitzer model was used in two forms: with only two parameters ($\beta^{(0),v}$ and C^v) and with three parameters ($\beta^{(0),v}$, $\beta^{(1),v}$ and C^v). The results are given in Table 5. From the obtained standard deviations, we conclude that, for the $CuCl_2$ + ethanol system, it is better to include the $\beta^{(1),v}$ term. The limiting apparent molal volume of $CuCl_2$ in ethanol, V_2°, obtained from the Pitzer model is also given in Table 5. Table 5 shows that the difference between the V_2° value obtained from eq 5 and those obtained from different forms of the Pitzer model is less than 2×10^{-6} m^3·mol^{-1}. In addition, we note that when the limiting apparent molal volume of solution was fixed to -16.43×10^{-6} m^3·mol^{-1}, the Pitzer model again provides a good correlation of the experimental density data. Therefore, the results of Table 5 prove that the Pitzer model is a powerful tool for correlation of volumetric properties of the investigated system.

Humffray[14] extended the electrolyte NRTL model for correlation of the densities of aqueous electrolytes. The excess volume of an electrolyte solution according to the NRTL model has the form

$$V^{ex} = V_{PDH}^{ex} + V_{NRTL}^{ex} \qquad (12a)$$

Table 5. Pitzer Model Parameters for Densities of $CuCl_2$ in Ethanol at 25 °C

$\beta_{ca}^{(0),v} \times 10^4$	$\beta_{ca}^{(1),v} \times 10^4$	$C^v \times 10^6$	$V_2^\circ \times 10^6/m^3 \cdot mol^{-1}$	$\sigma(d) \times 10^2$
−0.2498 ± 0.0458	−3.3112 ± 0.02882	−2.6458 ± 1.3629	−14.88[a]	5.5
−0.2973 ± 0.0480	−1.9033 ± 0.3023	−0.5716 ± 1.4298	−16.43[b]	7.3
−0.3725 ± 0.1065	0	−0.0605 ± 0.3079	−18.39[a]	13.1
−0.5375 ± 0.0104	0	4.3842 ± 0.4429	−16.43[b]	41.4

[a] Obtained from the Pitzer model. [b] Fixed to the value obtained from the Redlich−Mayer equation.

where V_{PDH}^{ex} is the long-range interaction contribution to the excess volume, which is the pressure derivative of the Pitzer−Debye−Hückel equation, and V_{NRTL}^{ex} is the contribution of short-range forces to the excess volume. These terms are

$$V_{PDH}^{ex} = \frac{A_v I_x}{\rho\sqrt{M_1}} \ln(1 + \rho\sqrt{I_x}) \tag{12b}$$

and

$$V_{NRTL}^{ex} = RT[A_1\tau_{ca,m}^{v} + B_1\tau_{m,ca}^{v}] \tag{12c}$$

where

$$A_1 = 2z_c x_c G_{ca,m}\left[\frac{x_1}{\theta_1}\left(1 - \frac{\alpha\tau_{ca,m}}{\theta_1}\right) - (1 - \alpha\tau_{ca,m})\right] \tag{12d}$$

and

$$B_1 = 2z_c x_c\left[\frac{x_1 G_{m,ca}}{\theta_2}\left(1 - \frac{\alpha z_c x_c \tau_{m,ca}}{\theta_2}\right) - 1\right] \tag{12e}$$

In these equations the following definitions have been used:

$$\theta_1 = x_1 + 2x_c G_{ca,m} = x_1 + 2x_a G_{ca,m} \tag{12f}$$

and

$$\theta_2 = x_a + x_1 G_{m,ca} = x_c + x_1 G_{m,ca} \tag{12g}$$

$$G_{ca,m} = \exp(-\alpha\tau_{m,ca}) \tag{12h}$$

$$G_{m,ca} = \exp(-\alpha\tau_{m,ca}) \tag{12i}$$

In the above equations x_1, x_c, and x_a are the mole fractions of solvent, cation, and anion, respectively. $\tau_{ca,m}^{v}$ and $\tau_{m,ca}^{v}$ are pressure derivatives of the interaction parameters of the NRTL model for the excess Gibbs energy. For the $CuCl_2$ + ethanol system, the two NRTL interaction parameters, $\tau_{ca,m}$ and $\tau_{m,ca}$, have already been determined from the fitting of the VLE data to the NRTL model (Table 4). The two remaining parameters, $\tau_{ca,m}^{v}$ and $\tau_{m,ca}^{v}$, were obtained from the correlation of experimental density data as 1/*d* versus molality to the model. As in the case of the osmotic coefficients, the same values of $\rho = 21$ and $\alpha = 0.2$ were used in fitting of the density data to the NRTL model. To express 1/*d* versus molality in the NRTL model, we use eq 4. The necessary ϕ_v expression is obtained by inserting the corresponding V^{ex} expression in the following relation:

$$\phi_v = V_2^\circ + \frac{V^{ex}}{m} \tag{13}$$

The results of fitting the experimental data, as 1/*d* versus molality, to the NRTL model are shown in Table 6.

Table 6. NRTL Model Parameters for Densities of $CuCl_2$ in Ethanol at 25 °C

$\tau_{ca,m}^{v} \times 10^4$	$\tau_{m,ca}^{v} \times 10^4$	$V_2 \times 10^6/m^3 \cdot mol^{-1}$	$\sigma(d) \times 10^2$
1.5689 ± 0.1680	−3.9937 ± 0.4031	−16.70 ± 0.20[a]	29.3[c]
1.5323 ± 0.1529	−3.8706 ± 0.3669	−16.43[b]	30.1[c]
3.8974 ± 0.3470	−8.5448 ± 0.7561	−15.47 ± 0.10[a]	19.8[d]
4.3422 ± 0.5180	−9.6668 ± 1.1297	−16.43[b]	19.3[d]
1.2615 ± 0.1423	−3.4867 ± 0.3630	−17.06 ± 0.17[a]	31.8[e]
1.1987 ± 0.1156	−3.2479 ± 0.2949	−16.43[b]	33.9[e]

[a] Obtained from the NRTL model. [b] Fixed to the value obtained from the Redlich−Mayer equation. [c] The NRTL model parameters, $\tau_{ca,m} = -3.7202$ and $\tau_{m,ca} = 7.5403$, were used. [d] $\tau_{ca,m} = -3$; $\tau_{m,ca} = 6$. [e] $\tau_{ca,m} = -4$; $\tau_{m,ca} = 8$.

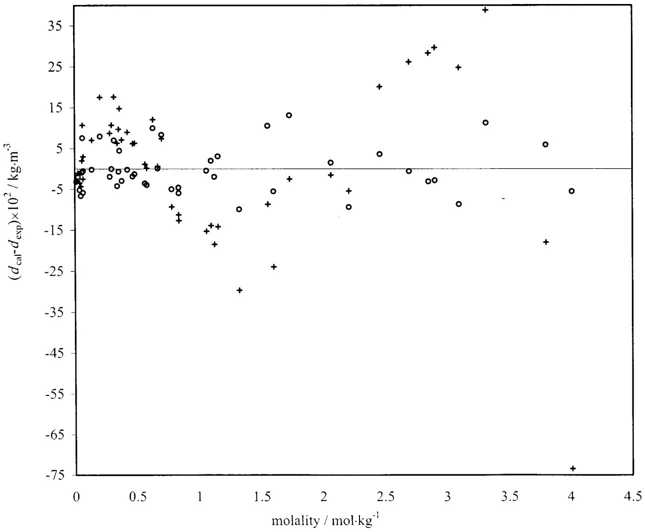

Figure 4. Difference between experimental and calculated densities: ○, Pitzer model; + NRTL model.

In the correlation of some density data for aqueous electrolyte solutions, Humffray[14] showed that if the Gibbs energy parameters are not known for a system, one can set them to a fixed value and use the approximate relation $\tau_{m,ca} = -2\tau_{ca,m}$. Following Humffray,[14] the value of $\tau_{ca,m}$ has been set to −3 and −4, and the correlation of density data has been repeated with the results shown in Table 6. These results show that this simplification gives a reasonable correlation of densities for the $CuCl_2$ + ethanol system. The limiting apparent molal volume of $CuCl_2$ in ethanol, V_2°, obtained from the NRTL model is also given in Table 6. Table 6 shows that the V_2° values obtained from the NRTL model with different choices of $\tau_{ca,m}$ and $\tau_{m,ca}$ values are in good agreement with the value $V_2^\circ = -16.43 \times 10^{-6}$ $m^3 \cdot mol^{-1}$ obtained using the Redlich−Mayer equation. In addition, when the limiting apparent molal volume of the solution was fixed to -16.43×10^{-6} $m^3 \cdot mol^{-1}$, the NRTL model again provided a good correlation of the experimental density data. These results indicate that the NRTL model is also a powerful tool in correlation of density data and estimating the limiting apparent volume value for the $CuCl_2$ + ethanol system. Using the Pitzer and NRTL parameters presented in the first row of the Tables 5 and 6, respectively, the densities were calculated. The differences between the calculated and the experimental densities are shown in Figure 4.

Conclusions

Experimental osmotic coefficient and density data were obtained for $CuCl_2$ + ethanol solutions at 25 °C. The activity of ethanol, the vapor pressure of the solutions, and the apparent partial molal volumes were evaluated from the osmotic coefficient and density data. Fitting of the dilute region density data with the Redlich−Mayer equation gave a value for the limiting apparent molal volume of this solution.

Osmotic coefficients and densities of this system were correlated satisfactorily with the Pitzer ion interaction model and the electrolyte NRTL model of Chen and Evans. In fitting the density data with the Pitzer model, when the limiting apparent molal volume of the solution was regarded as a model parameter, the obtained value was close to the value evaluated from the Redlich−Mayer equation.

The NRTL model was also found to correlate the experimental osmotic coefficient and density data for the solution of $CuCl_2$ in ethanol with good accuracy when the calculated value of $\rho = 21$ and the nonrandomness factor $\alpha = 0.2$ were used. The interaction parameters of the excess Gibbs energy equation, appearing in the density equation of the NRTL model, were obtained by correlation of experimental osmotic coefficients to the NRTL model or were set to the fixed values. For both choices, the model provides a satisfactory correlation of the density data. The limiting apparent molal volume of the solution obtained from the NRTL model is in good agreement with the Redlich−Mayer value.

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