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Activity Coefficients of Lithium Chloride in ROH/Water Mixed Solvent (R = Me, Et) Using the Electromotive Force Method at 298.15 K

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The mean activity coefficients of LiCl in ROH/water mixed solvents (where R = Me and Et) were determined using the electromotive force (EMF) method at 298.15 K. The Pitzer equation and Pitzer−Simonson−Clegg equation were applied to the experimental data.

1. Introduction

Over the past century, the study of the thermodynamic properties of electrolytes in aqueous or aqueous–organic mixed solvents has received considerable attention. Hamer and Wu (1972) have produced tables for the osmotic coefficients and mean activity coefficients of 79 electrolytes[1] in water at 25 °C. In 1985, Koh et al.[2] obtained the activity coefficients of the alkali metal chlorides (MCl = LiCl, NaCl, KCl, RbCl, CsCl, and HCl) in methanol–water mixtures at 25 °C. Recent investigations have showed that there is renewed interest in the study of the mean activity coefficients of alkali metal chlorides in water−alcohol mixtures.[3–6]

In our previous work, we have completed the phase diagrams for about 50 ternary or quaternary systems, such as aliphatic alcohols (methanol, ethanol, 1-propanol, and 2-propanol) + cesium carbonate + water,[7] cesium chloride + 1-propanol or 2-propanol + water ternary systems,[8] water + 1-propanol + cesium sulfate + cesium chloride quaternary systems,[9] and so on. Recently, our group has focused on the thermodynamic properties of these ternary or quaternary systems. We had obtained the activity coefficients of CsCl in methanol–water mixtures and ethanol–water mixtures,[10] activity coefficients of RbCl in methanol–water mixtures,[11] and the activity coefficients of CsCl in the $CsCl + Cs_2SO_4 + H_2O$[12] system. As an extension of this work, we have now carried out the investigation on the ternary systems LiCl + methanol + water and LiCl + ethanol + water at 298.15 K with molalities up to near 2 $mol \cdot kg^{-1}$ by EMF measurement. The experimental data were fitted by the Pitzer and Pitzer−Simonson−Clegg models. Our goal was to enrich the available data on water + alkali chloride + organic systems. It is expected that such a study could be of much use in industry, medical science, and other areas.

2. Experimental

2.1. Materials. Analytical grade methanol, ethanol (purity > 99.5 %, Xi'an), and lithium chloride (purity > 99.5 %, Guangdong) were used without further purification. The specific conductance of double-distilled–deionized water used in our experiments was approximately $(1.0 \text{ to } 1.2) \cdot 10^{-4}\ S \cdot m^{-1}$.

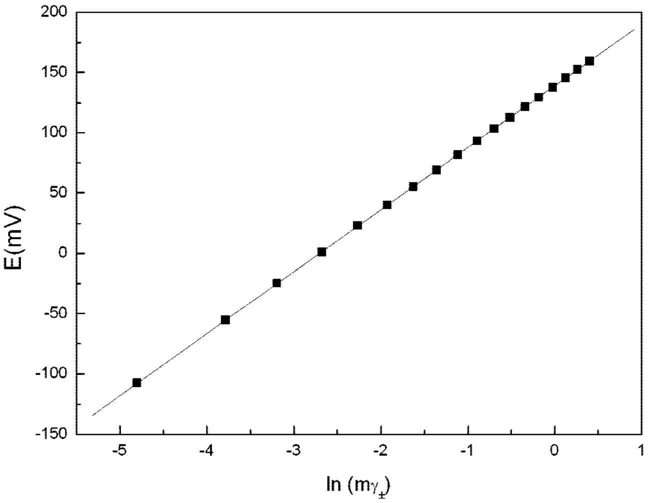

Figure 1. Response of the Li−ISE and AgAgCl electrode pair in the mixtures.

Table 1. Electromotive Force and the Mean Activity Coefficients $\gamma_\pm$ at Different LiCl Molalities in Aqueous Solution at 298.15 K

$\frac{m_{LiCl}}{mol \cdot kg^{-1}}$	$\frac{E}{mV}$	$\gamma_\pm$	$\frac{m_{LiCl}}{mol \cdot kg^{-1}}$	$\frac{E}{mV}$	$\gamma_\pm$
0.0091	−107.7	0.9078	0.5520	93.1	0.7409
0.0264	−55.4	0.8610	0.6697	103.1	0.7452
0.0495	−25.1	0.8288	0.7949	112.7	0.7523
0.0861	1.0	0.7994	0.9308	121.6	0.7623
0.1336	23.1	0.7771	1.0773	129.5	0.7750
0.1913	40.0	0.7610	1.2375	137.7	0.7908
0.2620	55.1	0.7497	1.4002	145.3	0.8086
0.3459	69.0	0.7428	1.5697	152.5	0.8286
0.4442	81.8	0.7399	1.7535	159.6	0.8519

2.2. Apparatus and Procedure. The apparatus used in the experiment has been described in a previous paper,[10] so only a brief description of the experimental procedure is presented here. The ion analyzer used was an Orion-868 (USA), with a precision of ± 0.1 mV. All measurements were performed under stirring conditions, and the temperature was kept constant at 298.15 K (± 0.02 K).

The lithium ion-selective electrode and AgAgCl electrode were prepared in our laboratory. The preparation technique was described by Wu.[13] Aqueous solutions of LiCl were measured

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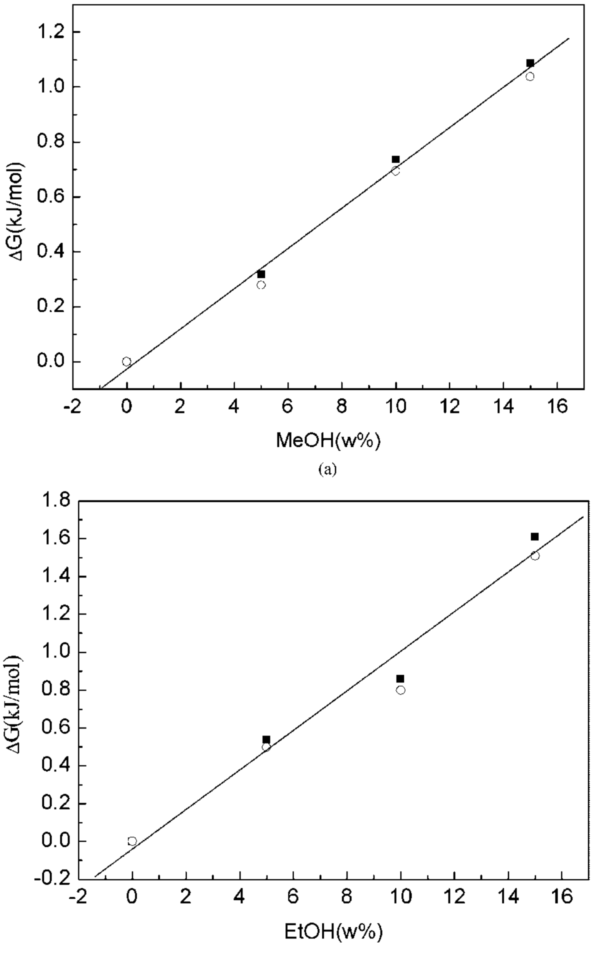
Table 2. Electromotive Force and the Mean Activity Coefficients $\gamma_{\pm}$ at Different LiCl Molalities and Weight Percent of Methanol in the Methanol–Water System at 298.15 K

m_{LiCl} / mol·kg^{-1}	E / mV	$\gamma_{\pm}$	m_{LiCl} / mol·kg^{-1}	E / mV	$\gamma_{\pm}$
5 % Methanol					
0.0124	−89.3	0.8915	0.5744	96.5	0.7203
0.0284	−49.1	0.8517	0.6947	106.5	0.7239
0.0577	−15.8	0.8127	0.8192	115.8	0.7303
0.0995	10.3	0.7816	0.9476	123.6	0.7392
0.1512	30.1	0.7590	1.0835	131.3	0.7506
0.2147	47.3	0.7422	1.2224	138.0	0.7641
0.2882	61.5	0.7308	1.3681	145.1	0.7800
0.3726	74.6	0.7236	1.5293	152.1	0.7995
0.4660	86.0	0.7203			
10 % Methanol					
0.0234	−55.3	0.8561	0.5327	95.7	0.7066
0.0507	−18.7	0.8128	0.6406	105.1	0.7079
0.0932	10.5	0.7767	0.7508	113.2	0.7118
0.1419	30.4	0.7527	0.8674	121.0	0.7180
0.2002	47.5	0.7349	0.9944	129.0	0.7266
0.2711	62.2	0.7217	1.1250	136.1	0.7373
0.3502	74.5	0.7131	1.2619	143.0	0.7501
0.4394	85.9	0.7082	1.4050	149.4	0.7651
15 % Methanol					
0.0041	−137.7	0.9250	0.3630	77.6	0.6848
0.0118	−85.3	0.8823	0.4717	90.5	0.6779
0.0653	−3.7	0.7830	0.5988	102.7	0.6759
0.1000	15.9	0.7551	0.7381	113.9	0.6785
0.1459	33.5	0.7310	0.8904	124.1	0.6854
0.2021	48.6	0.7118	1.0743	133.4	0.6979
0.2747	63.9	0.6961			

Table 3. Electromotive Force and the Mean Activity Coefficients $\gamma_{\pm}$ at Different LiCl Molalities and Weight Percent of Ethanol in the Ethanol–Water Systems at 298.15 K

m_{LiCl} / mol·kg^{-1}	E / mV	$\gamma_{\pm}$	m_{LiCl} / mol·kg^{-1}	E / mV	$\gamma_{\pm}$
5 % Ethanol					
0.0342	−38.5	0.8367	0.4577	85.6	0.7007
0.0599	−11.5	0.8034	0.5597	96.2	0.6987
0.0990	12.0	0.7725	0.6735	105.7	0.6999
0.1488	31.1	0.7482	0.8020	114.9	0.7043
0.2110	47.5	0.7292	0.9388	123.6	0.7119
0.2840	61.8	0.7153	1.0816	130.9	0.7221
0.3667	74.6	0.7061			
10 % Ethanol					
0.0399	−28.5	0.8176	0.6097	101.6	0.6741
0.0707	−1.6	0.7807	0.7228	110.3	0.6753
0.0994	14.0	0.7582	0.8459	118.5	0.6794
0.1533	34.0	0.7302	0.9766	126.7	0.6861
0.2215	51.6	0.7084	1.1189	134.2	0.6957
0.3028	66.4	0.6926	1.2622	140.9	0.7074
0.3949	79.4	0.6822	1.4154	148.0	0.7218
0.4992	91.5	0.6761			
15 % Ethanol					
0.0162	−64.2	0.8614	0.3843	83.5	0.6606
0.0390	−23.3	0.8085	0.4745	94.5	0.6530
0.0708	4.4	0.7675	0.5723	103.8	0.6486
0.1154	27.2	0.7330	0.6829	113.0	0.6470
0.1707	45.4	0.7062	0.8182	122.0	0.6486
0.2344	60.5	0.6862	0.9717	131.1	0.6538
0.3020	72.4	0.6720	1.1354	139.4	0.6624

at several molalities to check the response of the electrodes. The mean activity coefficients of different systems were calculated using the Pitzer model. As shown in Figure 1, a plot of E against $\ln(m\gamma_{\pm})$ produced a straight line, with a linear correlation coefficient of 0.9999; the values of E^0 and k were 138.9 mV and 25.67 mV (theoretical value: 25.69 mV), respectively. Thus, it can be concluded that the electrode pairs used in this work have good Nernstian response.



(a)

(b)

Figure 2. Standard free energy of transference, ΔG^0_t, from water to methanol–water and ethanol–water mixtures for LiCl at 298.15 K: ■, Pitzer equation; ○, Pitzer−Simonson−Clegg equation.

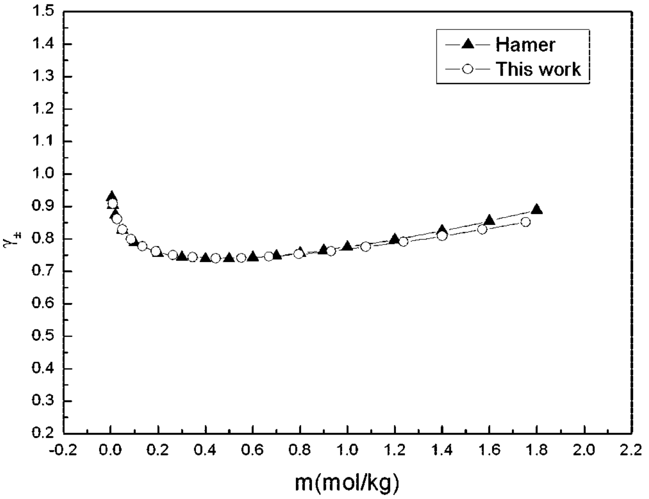


Figure 3. Comparisons between this work and the reference data for mean activity coefficients of LiCl in water at 298.15 K: ▲, ref 1; ○, this work.

3. Results and Discussion

The cell arrangement in this work was a galvanic cell without liquid junction:

$$\text{Li-ISE}|\text{LiCl}(m),\ \text{alcohol}(Y),\ \text{water}(100-Y)|\text{Ag}|\text{AgCl} \quad \text{(a)}$$

where Y stands for the mass fraction percent of methanol or ethanol and m for the molality of LiCl. The cell was employed to determine

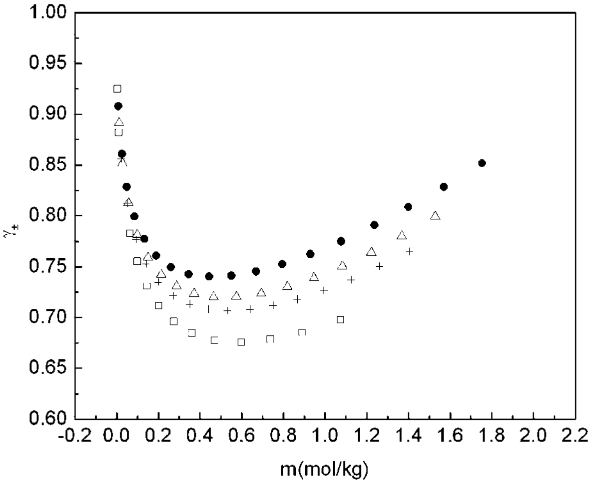


Figure 4. Variation of mean activity coefficient $\gamma_{\pm}$ with molality of LiCl in methanol–water solvents at 298.15 K: ●, water; Δ, 5 % methanol; +, 10 % methanol; □, 15 % methanol.

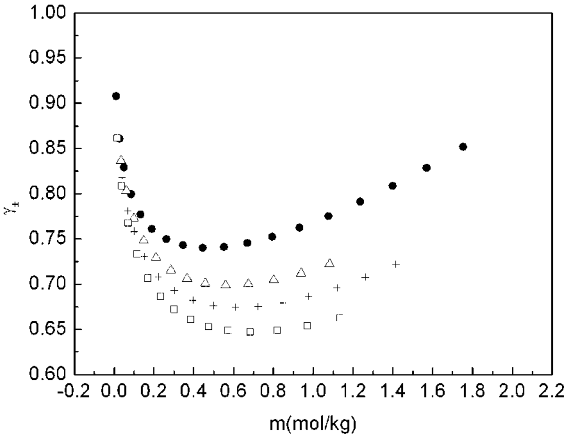


Figure 5. Variation of mean activity coefficient $\gamma_{\pm}$ with molality of LiCl in ethanol–water solvents at 298.15 K: ●, water; △, 5 % ethanol; +, 10 % ethanol; ■, 15 % ethanol.

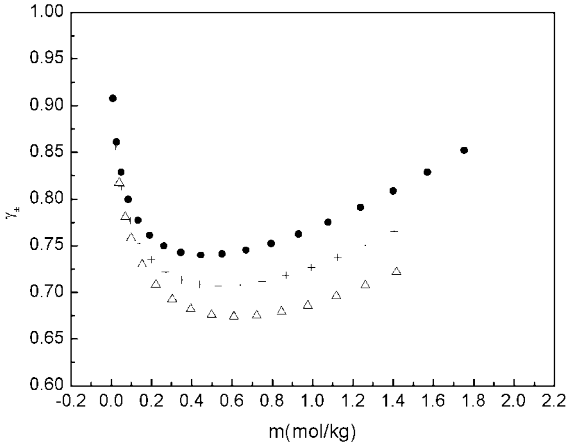


Figure 6. Mean activity coefficient for LiCl in 10 % mass fraction of ROH in water mixed solvents (with R = Me or Et) at 298.15 K: ●, water; Δ, 10 % MeOH; +, 10 % EtOH.

Table 4. Pitzer Parameters for LiCl in Methanol–Water Solvents at 298.15 K

wt %	β^0	β^1	C^{φ}	E^0 mV	Sd mV	ΔG^0_t kJ·mol^{-1}
0	0.1563	0.2947	−0.0070	138.9	0.20	0.000
5	0.1502	0.2753	−0.0003	141.8	0.27	0.319
10	0.1531	0.2843	−0.0017	145.7	0.25	0.736
15	0.1617	0.2256	−0.0016	148.9	0.40	1.087

Table 5. Pitzer Parameters for LiCl in Methanol–Water Solvents at 298.15 K

wt %	β^0	β^1	C^{φ}	E^0 mV	Sd mV	ΔG^0_t kJ·mol^{-1}
0	0.1563	0.2947	−0.0070	138.9	0.20	0.000
5	0.1514	0.2103	−0.0011	144.1	0.30	0.537
10	0.1549	0.1920	−0.0010	147.0	0.26	0.859
15	0.1520	0.1965	−0.0010	154.4	0.36	1.610

the EMF values E of LiCl in mixed solvents at 298.15 K. The experimental mean activity coefficients of LiCl in the mixtures were calculated from the following Nernstian equation

$$E = E^0 + 2k\ln(m\gamma_{\pm}) \tag{1}$$

where $\gamma_{\pm}$ is the mean activity coefficient of LiCl; $k = (RT/F)$ is the ideal Nernstian slope in which the symbols (R, T, and F) have their usual meanings. E^0 is the standard potential of the cell (a). The EMF values for each system and the molalities are listed in Tables 1, 2, and 3.

3.1. Pitzer Equation. Pitzer equations were used to describe the mean activity coefficient in our calculation. For a 1–1 type electrolyte, the Pitzer equations for the mean activity coefficient ($\gamma_{\pm}$) can be written as follows[14]

$$\ln\gamma_{\pm} = f^{\gamma} + mB^{\gamma} + m^2C^{\gamma} \tag{2}$$

where

$$f^{\gamma} = -A^{\varphi}[I^{1/2}/(1+bI^{1/2}) + (2/b)\ln(1+bI^{1/2})] \tag{2-1}$$

$$B^{\gamma} = 2\beta^{(0)} + 2\beta^{(1)}\{[1-\exp(-\alpha I^{1/2})(1+\alpha I^{1/2} - 1/2\alpha^2 I)]/(\alpha^2 I)\} \tag{2-2}$$

$$C^{\gamma} = 1.5C^{\varphi} \tag{2-3}$$

In these equations, I is the ionic strength in the molarity scale and m is the concentration of the electrolyte in molarity. $\beta^{(0)}$, $\beta^{(1)}$, C^{φ}, and the constants $\alpha = 2.0$ kg$^{1/2}$·mol$^{-1/2}$ and $b = 1.2$ kg$^{1/2}$·mol$^{-1/2}$ are the parameters of the Pitzer equations. A^{φ} is the Debye–Hückel constant for the osmotic coefficient defined by

$$A^{\varphi} = (1/3)[(2\pi N_0 d)/1000]^{1/2} \cdot [e^2/(DKT)]^{3/2} \tag{3}$$

where N_0, d_N, D, and K are Avogadro's number, the density of solvent mixtures, the dielectric constant, and Boltzmann's constant, respectively.

3.2. Pitzer−Simonson−Clegg Equation. The Pitzer−Simonson−Clegg equation was also used for these ternary systems. This model for electrolyte activity coefficients was proposed by Pitzer and Simonson.[15] The Pitzer−Simonson−Clegg model for a mixture of two neutral species, 1 and 2, and a 1–1 type electrolyte has been discussed in great detail.[4] For a MX(electrolyte) + alcohol (1) + water (2) system, the activity coefficient $\gamma_{\pm\,\mathrm{MX}}$can be written as

$$\ln\gamma_{\pm}{}^{S} = x_1x_2/f^2\cdot\{(1-f^2)W_{12} + (1-f^3)/f\cdot 2(x_1 - x_2)U_{12} + [f^2(1-2x_S) - 1]Z_{12\mathrm{MX}}\} + (f^2-1)/f(x_1W_{1\mathrm{MX}} + x_2W_{2\mathrm{MX}}) + x_1/(3f^2)\cdot[f^3(2-2x_1+x_S) + x_Sf^2(3x_1+x_2) - 2x_2]U_{1\mathrm{MX}} + x_2/(3f^2)\cdot[f^3(2-2x_2+x_S) + x_Sf^2(3x_2+x_1) - 2x_1]U_{2\mathrm{MX}} \tag{4}$$

and

Table 6. Parameters B_{MX}, W_{2MX}, U_{2MX}, W_{1MX}, U_{1MX}, Z_{12MX}, and E^0 Calculated by the Pitzer−Simonson−Clegg Equation

	water	5 % MeOH	10 % MeOH	15 % MeOH	5 % EtOH	10 % EtOH	15 % EtOH
B_{MX}	−3.9813	−3.9813	−3.9813	−3.9813	−3.9813	−3.9813	−3.9813
W_{12}		0.4926	0.4926	0.4926	1.2051	1.2051	1.2051
U_{12}		0.0032	0.0032	0.0032	0.2583	0.2583	0.2583
W_{1MX}		−41.4216	−25.1343	−37.5853	−250.1364	−190.4730	−69.6337
W_{2MX}	−1.2961	−1.2961	−1.2961	−1.2961	−1.2961	−1.2961	−1.2961
Z_{12MX}		29.3487	17.1568	27.4559	199.6791	149.2392	57.0734
U_{1MX}		−48.3247	−32.0072	−47.2195	−320.5084	−242.6263	−85.4868
U_{2MX}	3.6875	3.6875	3.6875	3.6875	3.6875	3.6875	3.6875
E^0/mV	140.5	143.0	146.8	150.0	145.2	147.9	154.9
Sd/mV	0.23	0.26	0.26	0.44	0.31	0.32	0.29
ΔG^0_t (kJ·mol^{-1})	0.000	0.279	0.695	1.038	0.498	0.798	1.509

$$\ln \gamma_{\pm}^{DH} = -A_X[(2/\rho)\ln(1+\rho I_X^{1/2}) + I_X^{1/2}(1-2I_X)/(1+\rho I_X)] + x_X B_{MX} g(\alpha I_X^{1/2}) - x_X x_M B_{MX}[g(\alpha I_X^{1/2})/2I_X + (1-1/(2I_X))\exp(-\alpha I_X^{1/2})] \quad (5)$$

By combining eq 4 and eq 5, the mean activity coefficient of MX in mixed solvents is

$$\ln \gamma_{\pm} = \ln \gamma_{\pm}^{DH} + \ln \gamma_{\pm}^{S} \quad (6)$$

where W_{12} and U_{12} are parameters for the alcohol (1) + water (2) binary system; W_{iMX} and U_{iMX} are parameters for the solvent i + MX binary system (i = 1 or 2); and Z_{12MX} and B_{MX} are the parameters of the Pitzer−Simonson−Clegg equation. α is given as a fixed value of 13.[15]

In the above equations

$$g(y) = 2[1-(1+y)\exp(-y)]/y^2 \quad (5\text{-}1)$$

$$I_X = 1/2(x_+ + x_-) \quad (5\text{-}2)$$

$$f = 1 - x_S$$
$$\rho = 2150(d_S/DT)^{1/2} \quad (5\text{-}3)$$

$$A_X = (1000/M_{sol})^{1/2}A^{\varphi} \quad (5\text{-}4)$$

where $y = \alpha I^{1/2}$ in eq 5-1; I_X is the ionic rational strength; x_S is the mole fraction of the total ions in the solution; d_S and D are density and dielectric constant of the solvent; ρ is the parameter of the Pitzer−Simonson−Clegg equation; and M_{sol} is the mean molecular mass of the solvent.

In this work, the parameters B_{MX}, W_{2MX}, and U_{2MX} were obtained from the activity coefficients of LiCl in aqueous solutions. They were evaluated using the equation

$$\ln \gamma_{\pm} = -A_X[(2/\rho)\cdot\ln(1+\rho I_X^{1/2}) + I_X^{1/2}(1-2I_X)/(1+\rho I_X^{1/2})] + x_X B_{MX} g(I_X^{1/2}) - x_X x_M B_{MX}\cdot[g(\alpha I_X^{1/2})/2I_X + (1-1/(2I_X))\exp(-\alpha I_X)] + (x_2^2-1)W_{2MX} + 2x_2^2(1-x_2)U_{2MX} \quad (7)$$

The mean ionic rational activity coefficient (γ_X) can be related to the mean ionic molal activity coefficient (γ) by

$$\gamma_X = (1 + 0.002M_{sol}m) \quad (8)$$

where m is the molality of the solution.

3.3. Discussion. The standard free energy of transference is one of the most useful available thermodynamic properties of solution. It can be calculated from E^0 values using eq 9:[16]

$$\Delta G^0_t = F(E^0_m - E^0_w) + 2RT\ln(d_w/d_m) \quad (9)$$

where subscripts w and m refer to the water and mixed solvent, respectively. Other symbols have their usual meaning. Figure 2 is given to describe the values of ΔG^0_t for these alcohol + water + LiCl systems. This figure illustrates that both systems have a similar variation, and the energies for methanol–water are less than for ethanol–water at a given percentage. This phenomenon may be explained by the fact that LiCl is more solvated in the former system. These values are always positive, which indicates that the transference of LiCl from water to the alcohol−water mixed solvents is not spontaneous.

The EMF values and the molalities for each system, together with the activity coefficients of lithium chloride, are listed in Tables 1, 2, and 3. For comparison, the published values[1] and our data for the activity coefficients of lithium chloride are both depicted in Figure 3. Figure 3 shows that the two results are consistent. Plots of $\gamma_{\pm}$ versus m for both mixed solvents are shown in Figures 4 and 5. It can be seen that $\gamma_{\pm}$ decreases with an increase of alcohol content in the solvent mixture. These profiles were observed in similar systems, such as NH_4Cl in 2-PrOH/water mixed solvent.[17] One possible explanation for this phenomenon is ion–ion and ion–solvent interactions in the mixture. From the figures, it can be assumed that for the

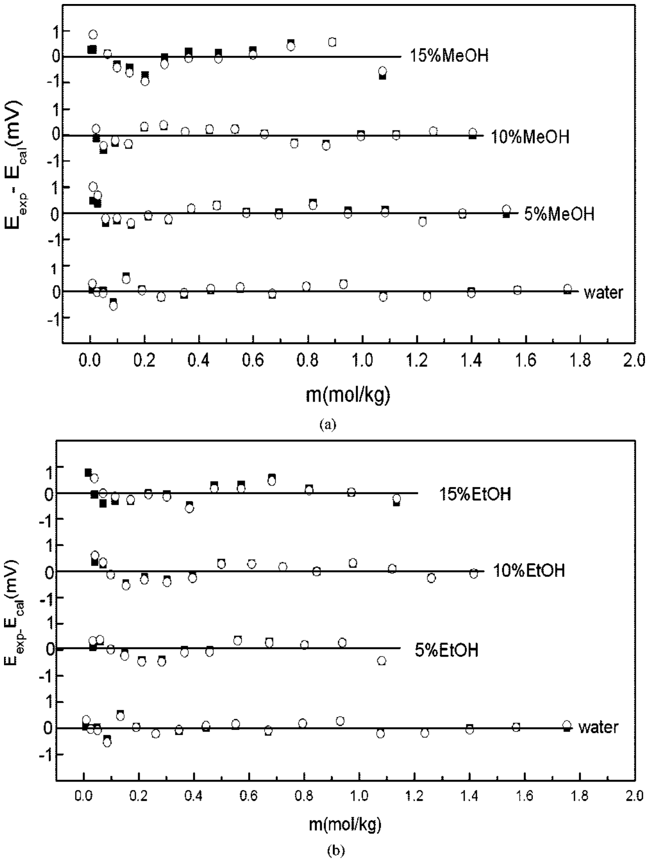


Figure 7. $E_{exptl} - E_{calcd}$ values obtained from each measured EMF reading and the fitted activity coefficient equations: ■, $E_{exptl} - E_{calcd}$ (Pitzer equation); □, $E_{exptl} - E_{calcd}$ (Pitzer−Simonson−Clegg equation).

methanol–water mixture the relative permittivity of the mixed solvent decreases when the mass fraction of methanol increases, while the ion–ion interaction was more significant than the ion–solvent interaction. For interpolation, Figure 6 gives the mean activity coefficients vs LiCl molality in water and 10 % mass fraction of ROH in water mixed solvents (R = Me and Et) at 298.15 K. Significantly, the activity coefficients of LiCl in water were larger than the alcohol−water solvents (R = Me and Et).

The values for E^0 and the Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} of each alcohol−water mixture could be optimized using a simplex method from the EMF data. Tables 4 and 5 present the parameters for the Pitzer equation together with the fitting standard deviation and the standard potential E^0. It can be observed from the Tables 4 and 5 that the standard potential E^0 increases when the mass fraction of methanol increases.

Table 6 shows the parameters B_{MX}, $W_{2\mathrm{MX}}$, $U_{2\mathrm{MX}}$, $W_{1\mathrm{MX}}$, $U_{1\mathrm{MX}}$, $Z_{12\mathrm{MX}}$, and E^0 calculated using the Pitzer−Simonson−Clegg equation with the Nernstian equation, from the experimental data for the alcohol−water−LiCl system. Then, the parameters W_{12} and U_{12} for the methanol–water and ethanol–water binary system were regressed using the Margules equation for the activity coefficients of the mixtures and the known values taken from refs 18 and 5.

Figure 7 illustrates the difference $E_{\mathrm{exptl}} - E_{\mathrm{calcd}}$ obtained from each measured EMF reading and the fitted activity coefficient equations. From Figure 7, it was clear that both the Pitzer equation and the Pitzer−Simonson−Clegg equation can be used to explain the ternary system MX(electrolyte) + alcohol (1) + water (2).

4. Conclusion

The results presented in this work show the galvanic cell consisting of a lithium ion-selective electrode and AgAgCl electrode could be used to study the thermodynamic properties of the LiCl + ROH (R = Me and Et) + water ternary system. Both the Pitzer equation and the Pitzer−Simonson−Clegg equation can be used to estimate the measured values well.

List of Symbols.

A^{φ}: Debye−Hückel constant for the osmotic coefficient in the Pitzer equation

D: dielectric constant

d_{N}: density of solvent mixtures

d_{s}: density of the solvent

E: electromotive force

E^0: standard potential of cell (a)

F: Faraday constant

I: ionic strength in the molarity scale

I_{x}: ionic rational strength

K: Boltzmann's constant

m: molality of LiCl

M_{sol}: mean molecular mass of the solvent

N_0: Avogadro's number

R: gas constant

T: absolute temperature

W_{12}, U_{12}: parameters for the alcohol (1) + water (2) binary system

$W_{i\mathrm{MX}}$, $U_{i\mathrm{MX}}$: parameters for the solvent i + MX binary system

x_{S}: the mole fraction of the total ions in the solution

$Z_{12\mathrm{MX}}$, B_{MX}: parameters of Pitzer−Simonson−Clegg equation

Greek letters

$\beta^{(0)}$, $\beta^{(1)}$, C^{φ}: parameters of Pitzer equation

$\gamma_{\pm}$: ionic mean activity coefficients of the electrolyte LiCl in the mixture

γ_{x}: ionic rational activity coefficient

ρ: parameter of the Pitzer−Simonson−Clegg equation

$\Delta G_{\mathrm{t}}^{0}$: standard free energy of transference

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Literature Cited

(1) Hamer, W. J.; Wu, Y. C. Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25°C. *J. Phys. Chem. Ref. Data.* **1972**, *1*, 1047–1100.

(2) Koh, D. S. P.; Khoo, K. H.; Chan, C. Y. The application of the Pitzer equations to 1–1 electrolytes in mixed solvents. *J. Solution Chem.* **1985**, *14*, 635–651.

(3) Yao, J.; Yan, W. D.; Xu, Y.J.; Han, S. J. Activity coefficients for NaCl in MeOH + H_2O by electromotive force measurements at 308.15 K and 318.15K. *J. Chem. Eng. Data* **1999**, *44*, 497–500.

(4) Lopes, A.; Farelo, F.; Ferra, M. I. Activity Coefficients of Potassium Chloride in Water-Ethanol Mixtures. *J. Solution Chem.* **1999**, *28*, 117–131.

(5) Lopes, A.; Farelo, F.; Ferra, M. I. A. Activity Coefficients of sodium chloride in water-ethanol mixtures: A Comparative study of Pitzer and Pitzer-Simonson Model. *J. Solution Chem.* **2001**, *30*, 757–770.

(6) Boukhalfa, N.; Méniai, A.-H. Activity coefficients for salts in water-methanol mixed solvent solutions. *Fluid Phase Equilib.* **2007**, *206*, 380–393.

(7) Hu, M. C.; Jin, L. H.; Zhai, Q. G.; Li, S. N.; Liu, Z. H. Liquid-liquid equilibria for some aliphatic alcohols + cesium carbonate + water systems. *Fluid Phase Equilib.* **2005**, *232*, 57–61.

(8) Hu, M. C.; Jin, L. H.; Li, S. N.; Jiang, Y. C. Equilibrium Phase Behavior of Water + Propan-1-ol or Propan-2-ol + Cesium Chloride at (298.15, 308.15, and 318.15) K. *J. Chem. Eng. Data* **2005**, *50*, 2049–2052.

(9) Hu, M. C.; Jin, L. H.; Li, S. N.; JiangY. C. Quaternary liquid-liquid equilibrium for water + 1-propanol + cesium sulfate + cesium chloride at 25 °C. *Fluid Phase Equilib.* **2006**, *242*, 136–140.

(10) Hu, M. C.; Cui, R. F.; Li, S. N.; Jiang, Y. C.; Xia, S. P. Determination of Activity Coefficients for Cesium Chloride in Methanol-Water and Ethanol-Water Mixed Solvents by Electromotive Force Measurements at 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 357–362.

(11) Cui, R. F.; Hu, M. C.; Jin, L. H.; Li, S. N.; Jiang, Y. C.; Xia, S. P. Activity coefficients of rubidium chloride and cesium chloride in methanol-water mixtures and a comparative study of Pitzer and Pitzer-Simonson-Clegg models (298.15 K). *Fluid Phase Equilib.* **2007**, *251*, 137–144.

(12) Hu, M. C.; Tang, J.; Li, S. N.; Xia, S. P. Cui, R. F. Activity Coefficients of Cesium Chloride and Cesium Sulfate in Aqueous Mixtures Using an Electromotive Force Method at 298 K. *J. Chem. Eng. Data*, ASAP.

(13) Wu, G.; Gao, S.; Lü, C.; Wang, F. Construction and application of valinomycin potassium electrodes. *Chem. World (Chin.)* **1981**, *10*, 291–295.

(14) Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **1973**, *77*, 268–277.

(15) Pitzer, K. S.; Simonson, J. M. Thermodynamics of Multicomponent, Mlsclble, Ionic systems: Theory and Equations. *J. Phys. Chem.* **1986**, *90*, 3005–3009.

(16) Hernández-Luis, F.; Vázquez, M. V.; Esteso, M. A. Activity Coefficients for NaF in Methanol-Water and Ethanol-Water Mixtures at 25°C. *J. Mol. Liq.* **2003**, *108*, 283–301.

(17) Deyhimi, F.; Ghalami-Choobar, B. Activity coefficients for NH_4Cl in 2-PrOH/water mixted solvent and some thermodynamic correlations for NH_4Cl in ROH/water mixed solvents (R = Me, Et, 1-Pr and 2-Pr). *Fluid Phase Equilib.* **2007**, *246*, 185–190.

(18) Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection Aqueous-Organic Systems Part 1, Chemistry Data Series [M]*; DECHEMA, FRG: Frank-furt/Main, 1997.

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