Thermodynamic Properties of Aqueous Mixtures $LiCl + KCl + NH_4Cl + H_2O$. Water Activity and Osmotic and Activity Coefficients at 298.15 K[†]

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The thermodynamic properties of the quaternary aqueous system $LiCl + KCl + NH_4Cl + H_2O$ have been studied using the hygrometric method by measuring the diameter of droplets of the reference solution of NaCl(aq) as a function of the surrounding relative humidity of the studied system. The water activities of aqueous electrolyte mixtures of $LiCl + KCl + NH_4Cl + H_2O$ were experimentally determined at $T = 298.15$ K at a total ionic strength from 0.6 $mol\cdot kg^{-1}$ to 4.8 $mol\cdot kg^{-1}$ for different ionic strength fractions y of one of the three solutes ($y = I_{XCl}/I_{tot}$), ranging from 1/3, 1/2, to 2/3 with the constant ratio r of molality of the two other solutes of unity ($r = m_{YCl}/m_{ZCl}$). The data allow the deduction of osmotic coefficients. The results obtained were correlated using Pitzer's model, Dinane−Pitzer's model, the Robinson−Stokes (RS) equation, the Lietzke−Stoughton (LS II) model, and Dinane's mixing rules ECA I and ECA II. The solute activity coefficients of the components in the mixture were also determined for different ionic strength fractions y of solutes.

Introduction

The thermodynamic properties of mixed aqueous electrolyte solutions are of great practical interest in the fields of chemical oceanography, seawater desalination, geochemical calculations in brines, geothermal energy recovery, and industrial processes.

The parameters in this area that have received considerable attention are the osmotic and activity coefficients of species in mixed aqueous solutions containing several electrolytes. Such data have been found to be very useful for verification or parametrization of thermodynamic models.

As a continuation of previous investigations on mixed electrolyte systems with a common chloride ion, we were prompted to perform measurements on the system $LiCl + KCl + NH_4Cl + H_2O$ using the hygrometric method, which is described in our previous paper.[1] These measurements yield the water activity in aqueous solutions containing electrolytes from the measured relative humidity.

Measurements of water activities over the total ionic strength range from 0.6 $mol\cdot kg^{-1}$ to 4.8 $mol\cdot kg^{-1}$ were performed for quaternary aqueous solutions $LiCl + KCl + NH_4Cl + H_2O$ of different ionic strength fractions y of LiCl(aq), KCl(aq), and NH_4Cl(aq), ranging from 1/3, 1/2, to 2/3, with the constant ratio r of molality, of NH_4Cl(aq) and LiCl(aq) ($r = m_{NH_4Cl}/m_{LiCl}$), of KCl(aq) on LiCl(aq) ($r = m_{KCl}/m_{LiCl}$), of KCl(aq) on NH_4Cl(aq) ($r = m_{KCl}/m_{NH_4Cl}$) of one, respectively, at $T = 298.15$ K. The osmotic coefficients were also determined from these measurements. To our knowledge, no water activity and osmotic coefficient data for this system are available in the literature. Measurements of the water activity of binary solutions of LiCl(aq), KCl(aq), and NH_4Cl(aq) have been reported previously.[2] Also, ternary mixtures with a common chloride ion, $LiCl + KCl + H_2O$, $LiCl + NH_4Cl + H_2O$, $LiCl + NH_4Cl + H_2O$, were investigated in our previous work.[3−5]

It has been demonstrated in our earlier studies that many mixed-electrolyte solutions[6,7] obey the Dinane's ECA rule of water activity.[8] This rule states that the water activities of the electrolyte mixtures can be predicted from those of the aqueous solutions of the individual component electrolytes. In the same way, another modified form of the ECA rule called the ECA II rule has been developed and applied to the quaternary solutions.

The equations developed by Pitzer[9−12] for aqueous mixed electrolytes with three numbers of components include interaction parameters between ions considered two and three. The equation of Pitzer can be converted for the osmotic coefficient into a form based upon the same quantities, but we use, instead of binary and ternary interaction parameters, two terms involving ternary and quaternary interactions of the ions.[13] This formalism is used for treating experimental data for this quaternary mixed electrolyte system.

On the other hand, the available parameter values of the Pitzer equation, in the presence of the electrolyte NH_4Cl, can be used to estimate the activity coefficient of species in the mixture.

Experimental

The experimental setup and procedures used to measure the relative humidity over aqueous solutions containing nonvolatile electrolytes were described in our earlier work.[1]

From measurements of reference droplet diameters $D\{a_{w(ref)}\}$ above the reference solution and the same diameters $D(a_w)$ above the studied solution, the growth ratio $K = D(a_w)/D\{a_{w(ref)}\}$ was calculated, and the relative humidity based upon the variation of the ratio K as a function of the water activity of these reference solutions was determined. The droplets of the reference salt solution of NaCl(aq) or LiCl(aq) are suspended by a spider-thin thread over a cup containing the solution to be studied. The diameter of these droplets is measured by a microscope with an ocular equipped with a micrometric screw.

At equilibrium, the activity of water of solution equals the relative humidity of the surrounding vapor. Generally, the

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Table 1. Growth Ratios K of the NaCl(aq) Droplets, Water Activities a_w, and Osmotic Coefficients ϕ of KCl + NH_4Cl + LiCl(aq) at Total Ionic Strength I for Different Ionic Strength Fractions y ($y = I_{solute}/I_{tot}$) of Different Solutes

m_{KCl} (mol·kg^{-1})	m_{NH_4Cl} (mol·kg^{-1})	m_{LiCl} (mol·kg^{-1})	I (mol·kg^{-1})	K	a_w	ϕ
		$y = 1/3$				
0.2	0.2	0.2	0.6	1.005[a]	0.9803	0.920
0.4	0.4	0.4	1.2	1.498	0.960	0.944
0.6	0.6	0.6	1.8	1.303	0.938	0.987
0.8	0.8	0.8	2.4	1.191	0.916	1.015
1.0	1.0	1.0	3.0	1.113	0.893	1.047
1.2	1.2	1.2	3.6	1.051	0.868	1.091
1.4	1.4	1.4	4.2	1.005	0.842	1.136
1.6	1.6	1.6	4.8	0.965	0.815	1.183
		$y = 1/2$ (KCl)				
0.4	0.2	0.2	0.8	1.713	0.973_8	0.921
0.6	0.3	0.3	1.2	1.498	0.960	0.944
0.8	0.4	0.4	1.6	1.356	0.946	0.963
1.0	0.5	0.5	2.0	1.267	0.932	0.977
1.2	0.6	0.6	2.4	1.200	0.918	0.989
1.6	0.8	0.8	3.2	1.093	0.887	1.040
2.0	1.0	1.0	4.0	1.026	0.855	1.087
2.4	1.2	1.2	4.8	0.975	0.822	1.133
		$y = 2/3$ (KCl)				
0.4	0.1	0.1	0.6	1.008[a]	0.980_5	0.909
0.8	0.2	0.2	1.2	1.509	0.961	0.920
1.2	0.3	0.3	1.8	1.315	0.940	0.954
1.6	0.4	0.4	2.4	1.204	0.919	0.977
2.0	0.5	0.5	3.0	1.124	0.897	1.006
2.4	0.6	0.6	3.6	1.066	0.875	1.029
2.8	0.7	0.7	4.2	1.021	0.852	1.058
3.2	0.8	0.8	4.8	0.984	0.829	1.084
		$y = 1/2$ (NH_4Cl)				
0.2	0.4	0.2	0.8	1.713	0.973_8	0.921
0.3	0.6	0.3	1.2	1.498	0.960	0.944
0.4	0.8	0.4	1.6	1.356	0.946	0.963
0.6	1.2	0.6	2.4	1.200	0.918	0.989
0.8	1.6	0.8	3.2	1.099	0.888	1.030
1.0	2.0	1.0	4.0	1.028	0.856	1.079
1.2	2.4	1.2	4.8	0.976	0.823	1.126
		$y = 2/3$ (NH_4Cl)				
0.1	0.4	0.1	0.6	1.008[a]	0.980_5	0.911
0.2	0.8	0.2	1.2	1.509	0.961	0.920
0.3	1.2	0.3	1.8	1.322	0.941	0.938
0.4	1.6	0.4	2.4	1.206	0.920	0.964
0.5	2.0	0.5	3.0	1.127	0.898	0.995
0.6	2.4	0.6	3.6	1.069	0.876	1.021
0.7	2.8	0.7	4.2	1.024	0.854	1.043
0.8	3.2	0.8	4.8	0.989	0.832	1.063
		$y = 1/2$ (LiCl)				
0.2	0.2	0.4	0.8	1.696	0.973	0.950
0.4	0.4	0.8	1.6	1.342	0.944	1.000
0.6	0.6	1.2	2.4	1.175	0.912	1.065
0.8	0.8	1.6	3.2	1.073	0.878	1.128
1.0	1.0	2.0	4.0	1.003	0.841	1.202
1.1	1.1	2.2	4.4	0.975	0.822	1.236
1.2	1.2	2.4	4.8	0.947	0.801	1.283
		$y = 2/3$ (LiCl)				
0.1	0.1	0.4	0.6	0.999[a]	0.979_8	0.944
0.2	0.2	0.8	1.2	1.473	0.958	0.992
0.3	0.3	1.2	1.8	1.278	0.934	1.053
0.4	0.4	1.6	2.4	1.164	0.909	1.103
0.5	0.5	2.0	3.0	1.081	0.881	1.172
0.6	0.6	2.4	3.6	1.021	0.852	1.235
0.7	0.7	2.8	4.2	0.973	0.821	1.303
0.8	0.8	3.2	4.8	0.933	0.788	1.378

[a] The reference solution is NaCl(aq). Reference water activity 0.98. Other K values are for reference water activity 0.84. $\phi = -1000 \ln a_w / 18.015\ (2I)$.

Table 2. Coefficients from the Polynomial Fit of Water Activity a_w[a]

	a_w(LiCl(aq))	a_w(KCl(aq))	a_w(NH_4Cl(aq))
a_0	9.9901 (−1)	9.9953 (−1)	9.9996 (−1)
a_1	−2.9537 (−2)	−3.0855 (−2)	−3.0993 (−2)
a_2	−5.0464 (−3)	−3.711 (−4)	−3.8250 (−4)
a_3	1.7812 (−4)	0	5.1788 (−5)
σ	0.0009	0.0006	0.00137
m	0.1 to 8	0.1 to 4.8	0.1 to 6
source	ref 2, 14	ref 2, 14	ref 2, 14

[a] Standard deviation σ, molality range for which coefficients are valid, and sources of literature data used in polynomial fits.

Table 3. Pitzer Binary Parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} and Standard Deviation σ for Different Single Electrolytes at Maximum Molality Max m used in Evaluation and Sources of Literature

system	Max m (mol·kg^{-1})	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	σ	source
LiCl + H_2O	6.0	0.1494	0.3074	0.00359	0.001	ref 10
KCl + H_2O	4.8	0.04835	0.2122	−0.00084	0.0005	ref 10
NH_4Cl + H_2O	6.0	0.0522	0.1918	−0.003	0.001	ref 10

Table 4. Mixing Ion-Interaction Parameters θ and ψ for Different Ternary Mixtures used in Evaluation and Sources of Literature

system	Max I (mol·kg^{-1})	$>\theta$	ψ	σ	source
LiCl + KCl + H_2O	4.8	−0.022	−0.0100	0.003	ref 11
KCl + NH_4Cl + H_2O	6.0	0.0516	−0.000847	0.001	ref 5
NH_4Cl + LiCl + H_2O	6.0	0.0563	0.0089	0.001	ref 4

reference relative humidity is 0.84. For moderately dilute solution, the reference value is 0.98.

Reference solutions of NaCl(aq) were prepared by mass from reagent grade crystals dried at 453.15 K. The concentration was controlled by conductivity measurements. The uncertainties of the molality of the solutes are less than ± 0.01 mol·kg^{-1}. The solutions were prepared by mass from Merck extrapure-grade chemicals (mass fraction > 0.995) without further purification and deionized distilled water.

Hygrometric Equilibrations. The relative humidities for the mixture LiCl + KCl + NH_4Cl + H_2O are measured as a function of total ionic strength ranging from 0.6 mol·kg^{-1} to 4.8 mol·kg^{-1}, for different ionic strength fractions y of KCl(aq) (where $y = I_{KCl}/I_{tot}$) of 1/3, 1/2, and 2/3 with the constant molal ratio r of KCl(aq) and NH_4Cl(aq) of unity (where $r = m_{KCl}/m_{NH_4Cl}$) at T = 298.15 K. The reference solution is NaCl(aq). The measurements were made at (298.15 ± 0.02) K. In most cases, measurements for a given solution were made on several droplets. The uncertainty in the water activity depends on the uncertainty of the diameter measurements and graphical determination of water activities from growth ratio K versus a_w for the reference solution. Then the relative error incurred in these measurements is therefore less than ± 0.02 % for $a_w > 0.97$, ± 0.05 % for $a_w > 0.95$, ± 0.09 % for $a_w > 0.90$, ± 0.2 % for $a_w > 0.85$, and ± 0.5 % for $a_w > 0.75$.

The experimental values of water activity are listed in Table 1. The water activities of pure electrolytes are determined in our previous work.[2]

On the basis of the experimental water activities, we evaluated the osmotic coefficients for different ionic strength fractions. There are no studies of the present system which are available for comparison with our results.

Results and Discussion

Many different mixing rules have been proposed to determine the thermodynamic properties of mixed aqueous electrolyte solutions from those of the aqueous solutions of the individual component salts. In this work, five models are used to determine these properties: the extended composed additivity (ECA) rule from Dinane, the ion-interaction model from Pitzer, the

Pitzer−Dinane model from Dinane, the RS equation from Robinson and Stokes, and the LS II model from Lietzke and Stoughton.

1. ECA Rule. Dinane[8] has proposed the ECA rule, which calculates the water activity in mixed electrolyte solutions from those of the aqueous solutions of the individual salts. The ECA equation applied to the quaternary system studied in the present work is given by

$$a_w = -2 + a_{w(\mathrm{LiCl})} + a_{w(\mathrm{KCl})} + a_{w(\mathrm{NH_4Cl})} - I_{\mathrm{LiCl}} I_{\mathrm{KCl}} \lambda_{\mathrm{LiK}} - I_{\mathrm{LiCl}} I_{\mathrm{NH_4Cl}} \lambda_{\mathrm{LiNH_4}} - I_{\mathrm{KCl}} I_{\mathrm{NH_4Cl}} \lambda_{\mathrm{KNH_4}} - I_{\mathrm{LiCl}} I_{\mathrm{KCl}} I \delta_{\mathrm{LiKCl}} - I_{\mathrm{LiCl}} I_{\mathrm{NH_4Cl}} I \delta_{\mathrm{LiNH_4Cl}} - I_{\mathrm{KCl}} I_{\mathrm{NH_4Cl}} I \delta_{\mathrm{KNH_4Cl}} \quad (1)$$

where I_{LiCl}, I_{KCl}, $I_{\mathrm{NH_4Cl}}$, and I are, respectively, the ionic strengths of the electrolytes LiCl(aq), KCl(aq), and NH_4Cl(aq) in the mixture and the total ionic strength. Here, $a_{w(\mathrm{LiCl})}$, $a_{w(\mathrm{KCl})}$, $a_{w(\mathrm{NH_4Cl})}$, and a_w are, respectively, the water activities of binary solution of

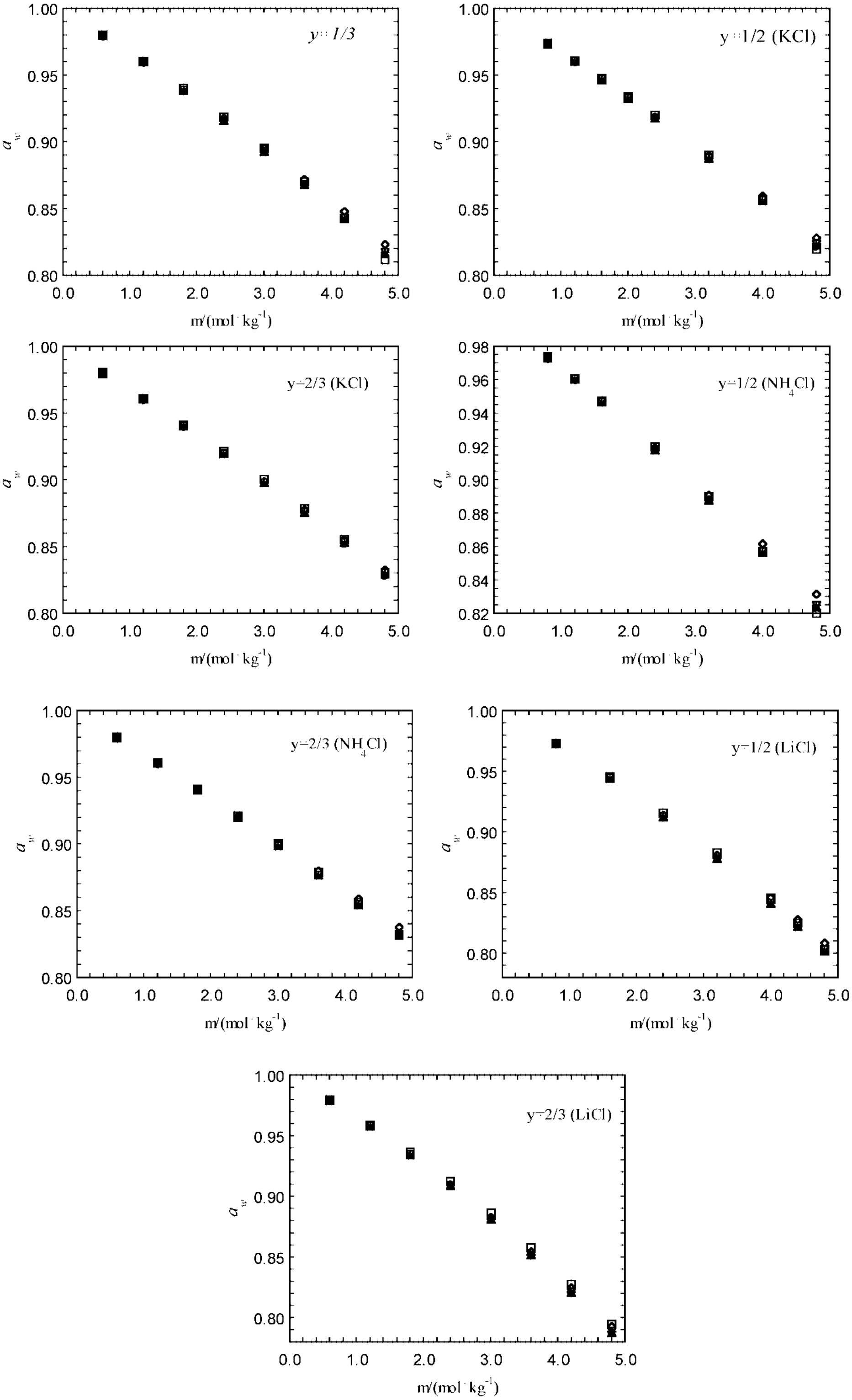

Figure 1. Water activity a_w of KCl + NH_4Cl + LiCl(aq) plotted against total molality m at different ionic strength fractions y of solutes. ×, experimental points; ◇, ECA I rule; □, ECA II rule; ○, Pitzer; +, Dinane−Pitzer; Δ, LS II; ▽, RS.

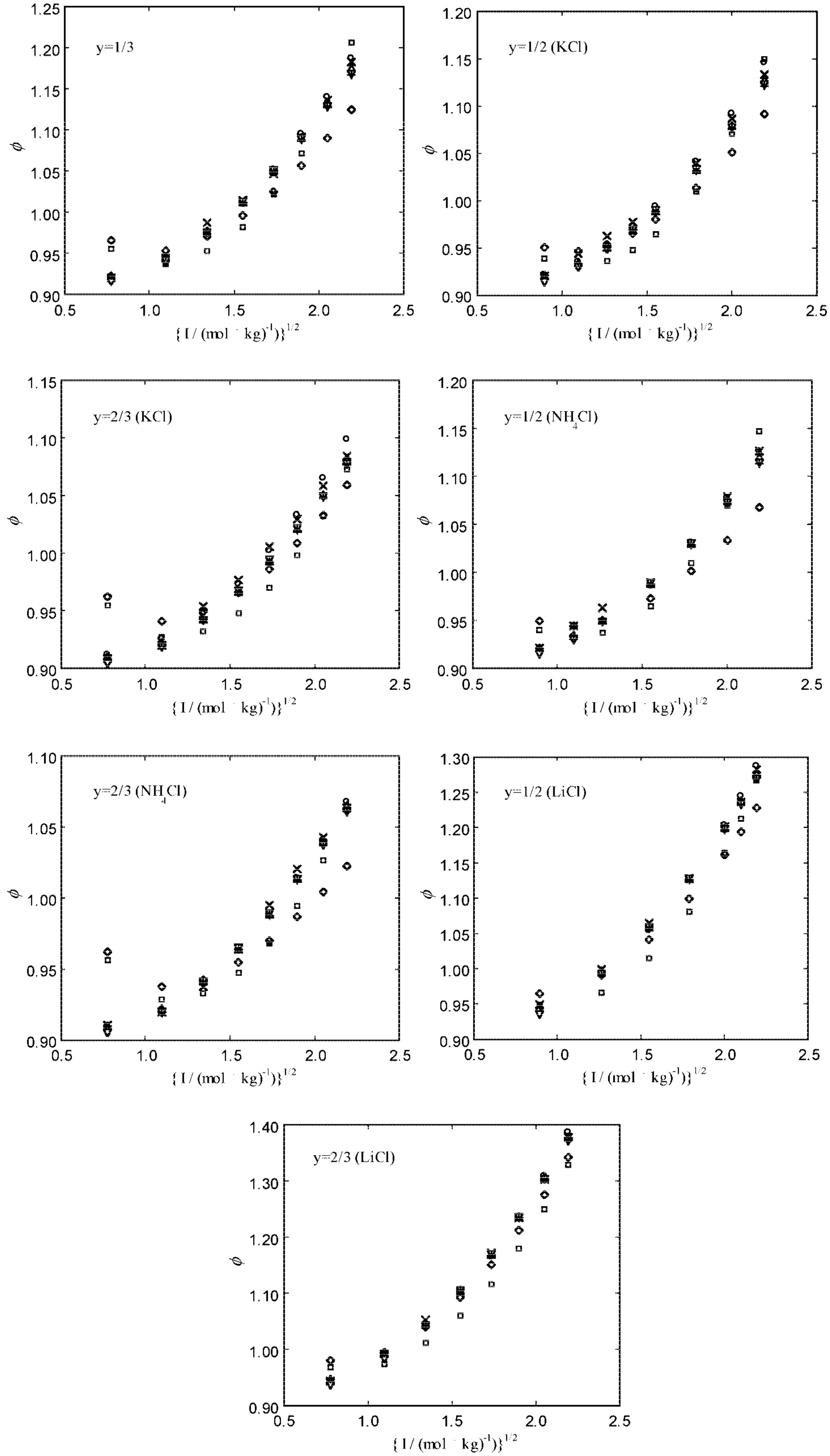

Figure 2. Osmotic coefficient ϕ of KCl + NH_4Cl + LiCl(aq) plotted against square root of total ionic strength $I^{1/2}$ at different ionic strength fractions y of solutes. ×, experimental points; ◇, ECA I rule; □, ECA II rule; ○, Pitzer; +, Dinane-Pitzer; Δ, LS II; ▽, RS.

LiCl(aq) at the ionic strength I_{LiCl}, the water activities of binary solution of KCl(aq) at the ionic strength I_{KCl}, the water activities of binary solution of NH_4Cl(aq) at the ionic strength I_{NH_4Cl}, and the water activity of ternary solution at the total ionic strength I. The parameters λ and δ, determined experimentally for each system, characterize the binary and ternary deviation from ideality in the mixture in a concentrated solution. The parameters λ_{LiK}, λ_{LiNH_4}, λ_{KNH_4}, δ_{LiKCl}, δ_{LiNH_4Cl}, and δ $_{KNH_4Cl}$ are given in our previous work.[3−5]

The water activities for the binary solutions were calculated using polynomial fits of water activity data obtained in our previous work[2] and those from Robinson and Stokes.[14] The general equation of these polynomial fits is $a_w = a_0 + a_1 m + a_2 m^2 + a_3 m^3 + a_4 m^4 + ...$ The coefficients (a_i) for each electrolyte are listed in Table 2. The mean values determined for different ternary solutions, derived from a combination of electrolytes studied in this work, LiCl + KCl(aq),[3] LiCl + NH_4Cl(aq),[4] KCl + NH_4Cl(aq),[5] are, respectively, $\lambda_{LiK} = 0.004$ $(mol \cdot kg^{-1})^{-2}$, $\lambda_{LiNH_4} = 0.00264$ $(mol \cdot kg^{-1})^{-2}$, $\lambda_{KNH_4} = 0.0001757$ $(mol \cdot kg^{-1})^{-2}$, and $\delta_{LiKCl} = - 0.000$ $(mol \cdot kg^{-1})^{-3}$, $\delta_{LiNH_4Cl} = - 0.00016$ $(mol \cdot kg^{-1})^{-3}$, $\delta_{KNH_4Cl} = -0.000016$ $(mol \cdot kg^{-1})^{-3}$. The water activities for the studied quaternary solutions were calculated using the ECA rule with these parameters. The standard deviation for the fit is $\sigma_{a_w} = 0.003$.

Equation 2 involves parameters $\lambda_{cc'}$ and $\delta_{cc'a}$ characterizing binary interactions between two cations and interactions between two cations and the anion. Or, in the solution, the three cations interact simultaneously. To characterize ternary and quaternary interactions in the quaternary solution, another form of the ECA equation containing only two unknown terms is proposed

$$a_w = -2 + a_{w(LiCl)} + a_{w(KCl)} + a_{w(NH_4Cl)} - I_{LiCl} I_{KCl} I_{NH_4Cl} \lambda_{LiKNH_4} - I_{LiCl} I_{KCl} I_{NH_4Cl} I \delta_{LiKNH_4Cl} \quad (2)$$

where the parameters λ_{LiKNH_4} and δ_{LiKNH_4Cl} may be estimated by a graphical procedure.

The mean values determined for LiCl + KCl + NH_4Cl(aq) are $\lambda_{LiKNH_4} = 0.0045$ $(mol \cdot kg^{-1})^{-3}$ and $\delta_{LiKNH_4Cl} = -0.0004$ $(mol \cdot kg^{-1})^{-4}$. The standard deviation for the fit is $\sigma_{a_w} = 0.0027$.

2. Pitzer's Model. Pitzer's model[9-12] for the calculation of water activity of the mixtures has been used to treat the results from experiments. The osmotic coefficient is given by the Pitzer model as

$$\phi - 1 = \frac{2}{\sum_i m_i} \Big\{ -\frac{A_\phi I^{3/2}}{1 + 1.2\sqrt{I}} + m_{Li} m [B^\phi_{LiCl} + m C^\phi_{LiCl}] + m_K m [B^\phi_{KCl} + m C^\phi_{KCl}] + m_{NH_4} m [B^\phi_{NH_4Cl} + m C^\phi_{NH_4Cl}] + m_{Li} m_K [\theta_{LiK} + m \psi_{LiKCl}] + m_{Li} m_{NH_4} [\theta_{LiNH_4} + m \psi_{LiNH_4Cl}] + m_K m_{NH_4} [\theta_{KNH_4} + m \psi_{KNH_4Cl}] \Big\} \quad (3)$$

where A_ϕ is the Debye–Hückel osmotic coefficient parameter and has the value of 0.392 for water at $T = 298.15$ K; m is the total molality; m with a subscript is the molality of the subscripted ion; and θ and ψ are, respectively, the binary mixing parameter and ternary mixing parameter involving different ions. The second virial coefficient B^ϕ of the subscripted ions is defined as

$$B^\phi = \beta^{(0)} + \beta^{(1)} \exp(-2\sqrt{I}) \quad (4)$$

where $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ are ion interaction parameters of the specified ions which are dependent on temperature and pressure. These parameters are given by Pitzer and Mayorga[10] for LiCl(aq), KCl(aq), and NH_4Cl(aq). The values of these ion interaction parameters are listed in Table 3. The mixing parameters θ and ψ are given in Table 4.

3. Dinane-Pitzer Model. The Pitzer equation[11] used for calculating the osmotic coefficients of mixed-electrolyte solutions contains several mixing ionic parameters. To simplify this equation, we have proposed a modified Pitzer's equation containing only the reduced parameters corresponding to all ionic interactions in the mixed-electrolyte solution. The osmotic coefficient of a mixed solution of three salts LiCl(aq), KCl(aq), and NH_4Cl(aq) is given by the Dinane–Pitzer equation[13] as

Table 5. Activity Coefficients γ_{KCl} of KCl(aq), γ_{NH_4Cl} of NH_4Cl(aq), and γ_{LiCl} of LiCl(aq) in KCl + NH_4Cl + LiCl(aq) at Total Ionic Strength I for Different Ionic Strength Fractions y ($y = I_{solute}/I_{tot}$) of Different Solutes

y = 1/3				y = 1/2 (KCl)				y = 2/3 (KCl)			
I(mol·kg^{-1})	γ_{KCl}	γ_{NH_4Cl}	γ_{LiCl}	I(mol·kg^{-1})	γ_{KCl}	γ_{NH_4Cl}	γ_{LiCl}	I(mol·kg^{-1})	γ_{KCl}	γ_{NH_4Cl}	γ_{LiCl}
0.6	0.654	0.649	0.696	0.8	0.633	0.634	0.688	0.6	0.644	0.650	0.688
1.2	0.625	0.617	0.702	1.2	0.616	0.619	0.693	1.2	0.608	0.620	0.685
1.8	0.619	0.611	0.734	1.6	0.608	0.613	0.709	1.8	0.595	0.614	0.705
2.4	0.624	0.615	0.782	2.0	0.606	0.612	0.731	2.4	0.593	0.618	0.738
3.0	0.634	0.627	0.842	2.4	0.608	0.616	0.759	3.0	0.596	0.626	0.780
3.6	0.648	0.642	0.914	3.2	0.617	0.630	0.828	3.6	0.603	0.638	0.829
4.2	0.664	0.662	0.999	4.0	0.631	0.650	0.913	4.2	0.612	0.652	0.884
4.8	0.682	0.684	1.097	4.8	0.649	0.673	1.015	4.8	0.623	0.667	0.946

y = 1/2 (NH_4Cl)				y = 2/3 (NH_4Cl)			
I(mol·kg^{-1})	γ_{KCl}	γ_{NH_4Cl}	γ_{LiCl}	I(mol·kg^{-1})	γ_{KCl}	γ_{NH_4Cl}	γ_{LiCl}
0.8	0.640	0.628	0.684	0.6	0.654	0.641	0.682
1.2	0.625	0.610	0.689	1.2	0.625	0.604	0.676
1.6	0.620	0.602	0.704	1.8	0.620	0.591	0.696
2.4	0.624	0.602	0.755	2.4	0.625	0.589	0.730
3.2	0.638	0.613	0.828	3.0	0.634	0.593	0.775
4.0	0.657	0.630	0.921	3.6	0.646	0.600	0.831
4.8	0.678	0.652	1.035	4.2	0.659	0.609	0.897
				4.8	0.673	0.621	0.974

y = 1/2 (LiCl)				y = 2/3 (LiCl)			
I(mol·kg^{-1})	γ_{KCl}	γ_{NH_4Cl}	γ_{LiCl}	I(mol·kg^{-1})	γ_{KCl}	γ_{NH_4Cl}	γ_{LiCl}
0.8	0.646	0.637	0.709	0.6	0.664	0.655	0.720
1.6	0.631	0.619	0.752	1.2	0.642	0.628	0.748
2.4	0.640	0.629	0.833	1.8	0.644	0.629	0.807
3.2	0.662	0.653	0.943	2.4	0.657	0.642	0.888
4.0	0.689	0.687	1.084	3.0	0.677	0.665	0.990
4.4	0.705	0.708	1.168	3.6	0.702	0.696	1.115
4.8	0.722	0.730	1.260	4.2	0.731	0.734	1.266
				4.8	0.763	0.779	1.446

$$\phi - 1 = \frac{2}{\sum_i mi}\left\{-\frac{A_\phi I^{3/2}}{1+1.2\sqrt{I}} + m_{\mathrm{LiCl}}m[B^{\phi}_{\mathrm{LiCl}} + mC^{\phi}_{\mathrm{LiCl}}] + m_{\mathrm{KCl}}m[B^{\phi}_{\mathrm{KCl}} + mC^{\phi}_{\mathrm{KCl}}] + m_{\mathrm{NH_4Cl}}m[B^{\phi}_{\mathrm{NH_4Cl}} + mC^{\phi}_{\mathrm{NH_4Cl}}] + m_{\mathrm{LiCl}}m_{\mathrm{KCl}}m_{\mathrm{NH_4Cl}}[\eta_{\mathrm{LiKNH_4}} + m\chi_{\mathrm{LiKNH_4Cl}}]\right\} \quad (5)$$

where $\eta_{\mathrm{LiKNH_4}}$ is a ternary mixing parameter involving unlike ions of the same sign and $\chi_{\mathrm{LiKNH_4Cl}}$ is a quaternary mixing parameter for the three unlike ions of the same sign with a forth ion of the opposite sign.

These quantities are evaluated by a graphical procedure which defines the quantity $\Delta\phi$ as the difference between the experimental value ϕ_{exp} and that calculated from eq 5, ϕ_{calc}, without mixing ionic parameters. This yield

$$\frac{m}{m_{\mathrm{LiCl}}m_{\mathrm{KCl}}m_{\mathrm{NH_4Cl}}}\Delta\phi = \eta_{\mathrm{LiKNH_4}} + \chi_{\mathrm{LiKNH_4Cl}}m_{\mathrm{Cl}} \quad (6)$$

so that a plot of $\Delta\phi$ versus total molality m should give a straight line with intercept $\eta_{\mathrm{LiKNH_4}}$ and slope $\chi_{\mathrm{LiKNH_4Cl}}$. We have evaluated the unknown mixing ionic parameters for the Dinane−Pitzer equation. The values are $\eta_{\mathrm{LiKNH_4}} = 0.001$ and $\chi_{\mathrm{LiKNH_4Cl}} = -0.005$, and the standard deviation is $\sigma_\phi = 0.007$.

4. Robinson−Stokes Equation. Robinson and Stokes[14] have proposed a relation for the vapor pressure of a mixture involving the additivity of the lowerings of vapor pressures of the solutes in the ternary mixture. This equation can be rewritten in terms of water activity for the quaternary mixture as

$$(1 - a_{\mathrm{w}}) = \{(1 - y_{\mathrm{NX}} - y_{\mathrm{ZX}})(1 - a_{\mathrm{w(MX)}}) + y_{\mathrm{NX}}(1 - a_{\mathrm{w(NX)}}) + y_{\mathrm{ZX}}(1 - a_{\mathrm{w(ZX)}})\} \quad (7)$$

where a_{w}, $a_{\mathrm{w(MX)}}$, $a_{\mathrm{w(NX)}}$, and $a_{\mathrm{w(ZX)}}$ are, respectively, the water activities of quaternary solution of both solutes MX, NX, and ZX, of the pure solution of MX, NX, and ZX at the same ionic strength I as the mixed solution. y is the ionic strength fractions of subscript solutes.

5. Lietzke−Stoughton Model. The Lietzke and Stoughton model[15] named (LS II) predicts the osmotic coefficient of a multicomponent solution by

$$(\nu_{\mathrm{MX}}m_{\mathrm{MX}} + \nu_{\mathrm{NX}}m_{\mathrm{NX}} + \nu_{\mathrm{ZX}}m_{\mathrm{ZX}})\phi = \nu_{\mathrm{MX}}m_{\mathrm{MX}}\phi_{\mathrm{MX}} + \nu_{\mathrm{NX}}m_{\mathrm{NX}}\phi_{\mathrm{NX}} + \nu_{\mathrm{ZX}}m_{\mathrm{ZX}}\phi_{\mathrm{ZX}} \quad (8)$$

where ν_{MX}, ν_{NX}, and ν_{ZX} are, respectively, the number of ions released by the complete dissociation of one molecule of component MX, NX, and ZX. m_{MX}, m_{NX}, and m_{ZX} are, respectively, their molality. ϕ, ϕ_{MX}, ϕ_{NX}, and ϕ_{ZX} are, respectively, the osmotic coefficients of the mixed solution and the binary solutions of components MX, NX, and ZX at the total ionic strength of the multicomponent solution.

The comparison of the water activities shows that the values calculated with ECA(I) and ECA(II) rules, RS model, and LS II model and those predicted by Pitzer's and Dinane−Pitzer's models are relatively close over the molality range (Figure 1). The standard deviation is $\sigma_{a_{\mathrm{w}}} = 0.0006$ for Pitzer's model, $\sigma_{a_{\mathrm{w}}} = 0.0008$ for Dinane−Pitzer's model, $\sigma_{a_{\mathrm{w}}} = 0.0030$ for the ECA(I) rule, $\sigma_{a_{\mathrm{w}}} = 0.0005$ for the LSII model, and $\sigma_{a_{\mathrm{w}}} = 0.0007$ for the RS equation.

The calculations of the osmotic coefficients by ECA rules have been generalized for different mixtures. The standard deviation for the osmotic coefficient is $\sigma_\phi = 0.006$ for Pitzer's model, $\sigma_\phi = 0.007$ for the Dinane−Pitzer model, $\sigma_\phi = 0.029$ for ECA II, $\sigma_\phi = 0.029$ for ECA I, $\sigma_\phi = 0.006$ for the LS II model, and $\sigma_\phi = 0.008$ for the RS model. The comparison of our results with those of different models is shown in Figure 2. The predictions by the ECA rules are very similar to those of Pitzer's model at medium and high concentrations, but the deviations for ECA become quite large at very low molality. These deviations are due to the parameters λ and δ which are introduced in the ECA rules for moderated and concentrated solutions and also to the a_{w}, ϕ relationship by the term 1000/

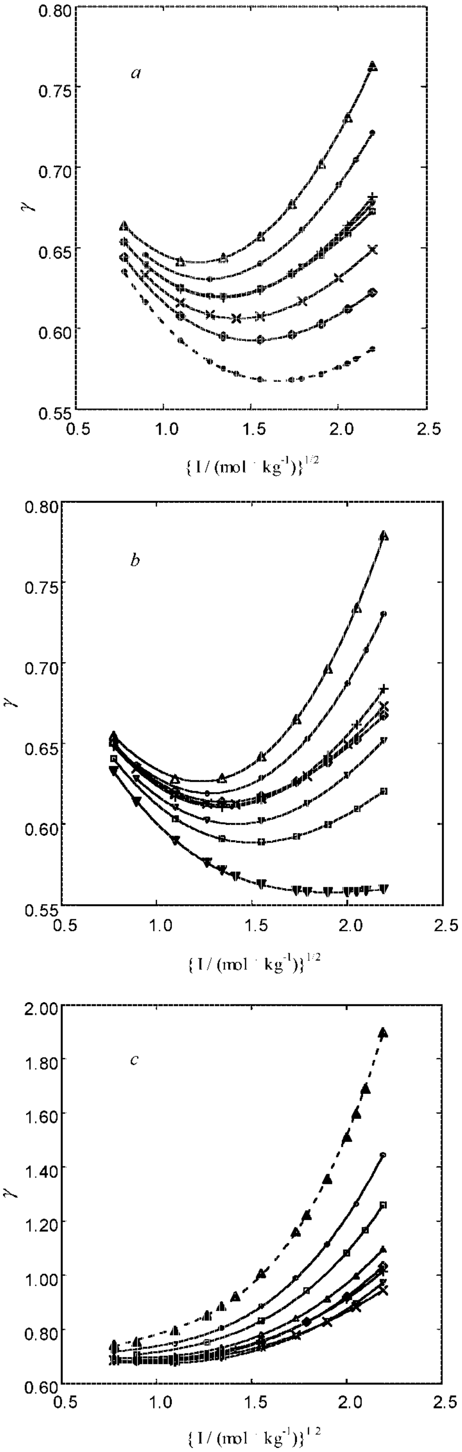

Figure 3. Activity coefficients γ_{KCl} of KCl(aq), $\gamma_{\mathrm{NH_4Cl}}$ of NH$_4$Cl(aq), and γ_{LiCl} of LiCl(aq) in KCl + NH$_4$Cl + LiCl(aq) plotted against square root of total ionic strength $I^{1/2}$ at different ionic strength fractions y of solutes. *a*, γ_{KCl}; *b*, $\gamma_{\mathrm{NH_4Cl}}$; *c*, γ_{LiCl}: +, $y = 1/3$; ×, $y = 1/2$ (KCl); ◇, $y = 2/3$ (KCl); ▽, $y = 1/2$ (NH$_4$Cl); □, $y = 2/3$ (NH$_4$Cl); ○, $y = 1/2$ (LiCl); Δ, $y = 2/3$ (LiCl).

$\Sigma_i \nu_i m_i M_w$ which becomes greater for $m < 1.0$ mol·kg^{-1} and yields large deviations for the lower variation of water activity.

The comparison of the osmotic coefficient shows that the values calculated with the Dinane−Pitzer equation and those predicted by other models are relatively close over the molality range (Figure 2).

The activity coefficient γ_{MX} of MX(aq) in mixtures is given by the Pitzer model.[11] For a mixture of just three symmetrical electrolytes of charge $z = 1$ and with a common anion, the expression of activity coefficient is considerably simplified. Thus, the activity coefficient γ_{KCl} of KCl(aq) in mixtures with NH_4Cl(aq) and LiCl(aq) is given by the Pitzer model as the simplified form

$$\ln \gamma_{KCl} = F + m_2(\theta_{KNH_4} + m\psi_{KNH_4Cl}) + m_3(\theta_{KLi} + m\psi_{KLiCl}) + P \quad (9)$$

where F is given by

$$F = f^{\gamma} + \sum_i m_i B_i + 2m\sum_i m_i C_i + m\sum_i m_i B_i' \quad (10)$$

and P by

$$P = \frac{1}{2}(m_1 m_2 \psi_{KNH_4Cl} + m_1 m_3 \psi_{KLiCl} + m_2 m_3 \psi_{NH_4LiCl}) \quad (11)$$

m is the total molality; m with subscripted i is the molality of the subscripted electrolyte ($i = 1$ for KCl, 2 for NH_4Cl, and 3 for LiCl).

The activity coefficient γ_{NH_4Cl} of NH_4Cl(aq) in mixtures with KCl(aq) and LiCl(aq) is given by

$$\ln \gamma_{NH_4Cl} = F + m_1(\theta_{KNH_4} + m\psi_{KNH_4Cl}) + m_3(\theta_{NH_4Li} + m\psi_{NH_4LiCl}) + P \quad (12)$$

The activity coefficient γ_{LiCl} of LiCl(aq) in mixtures with KCl(aq), and NH_4Cl(aq) is given by

$$\ln \gamma_{LiCl} = F + m_2(\theta_{NH_4Li} + m\psi_{NH_4LiCl}) + m_1(\theta_{KLi} + m\psi_{KLiCl}) + P \quad (13)$$

The activity coefficients γ_{KCl}, γ_{NH_4Cl}, and γ_{LiCl} in the mixture are listed in Table 5.

Figure 3 is the plot of γ_{KCl}, γ_{NH_4Cl}, and γ_{LiCl} as a function of $I^{1/2}$. A cursory comparison of these results shows that the activity coefficients for KCl(aq) in the mixture increase with increasing ionic strength fractions y in the following order: $\gamma_{KCl(bin)} < \gamma_{KCl(y = 2/3\ (KCl))} < \gamma_{KCl(y = 1/2\ (KCl))} < \gamma_{KCl(y = 2/3\ (NH_4Cl))} < \gamma_{KCl(y = 1/2\ (NH_4Cl))} < \gamma_{KCl(y = 1/3)} < \gamma_{KCl(y = 1/2\ (LiCl))} < \gamma_{KCl(y = 2/3\ (LiCl))}$. The activity coefficients of NH_4Cl(aq) in the mixture increase with increasing ionic strength fractions y from the activity coefficient of pure NH_4Cl(aq) in the order: $\gamma_{NH_4Cl(bin)} < \gamma_{NH_4Cl(y = 2/3\ (NH_4Cl))} < \gamma_{NH_4Cl(y = 1/2\ (NH_4Cl))} < \gamma_{NH_4Cl(y = 2/3\ (KCl))} < \gamma_{NH_4Cl(y = 1/2\ (KCl))} < \gamma_{NH_4Cl(y = 1/3)} < \gamma_{NH_4Cl(y = 1/2\ (LiCl))} < \gamma_{NH_4Cl(y = 2/3\ (LiCl))}$. The activity coefficients of KCl(aq) and NH_4Cl(aq) in the mixture show a minimum for the ionic strength fractions between (1.4 and 2.4) mol·kg^{-1}. For LiCl(aq), the activity coefficients of LiCl(aq) in the mixture decrease with increasing ionic strength fractions y in the order: $\gamma_{LiCl(bin)} > \gamma_{LiCl(y = 1/2\ (LiCl))} > \gamma_{LiCl(y = 2/3\ (NH_4Cl))} > \gamma_{LiCl(y = 2/3\ (LiCl))} > \gamma_{LiCl(y = 2/3\ (KCl))} > \gamma_{LiCl(y = 1/3)} > \gamma_{LiCl(y = 1/2\ (NH_4Cl))} > \gamma_{LiCl(y = 1/2\ (KCl))}$.

Conclusion

The hygrometric method has been used to determine water activity at $T = 298.15$ K for aqueous electrolyte mixtures of LiCl + KCl + NH_4Cl + H_2O to total ionic strengths from 0.6 mol·kg^{-1} to 4.8 mol·kg^{-1}. The data allow the deduction of new osmotic coefficients of this mixture. The solute activity coefficients of the components in the mixture were also determined for different ionic strength fractions y of different solvents.

Five different mixing rules were evaluated in their ability to predict the water activity and osmotic coefficient as a function of solute concentration for the mixed electrolyte solutions studied. The Pitzer, the RS, the LSII, and the Dinane−Pitzer models were generally able to predict the mixture's water activity and osmotic coefficient to within the uncertainty of the experimental data for the LiCl + KCl + NH_4Cl + H_2O system. The predictions by the ECA rules give good results for water activity, but the deviations become quite large for osmotic coefficients with accepted errors.

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