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Thermodynamic Properties of Aqueous Mixtures $NaCl-KCl-NH_4Cl-H_2O$: Water Activity and Osmotic and Activity Coefficients at 298.15 K

Abderrahim Dinane*

Ecole Royale Navale, Département de Recherches et Projets, Laboratoire de Thermodynamique, Boulevard Sour Jdid, Casablanca 20000, Maroc

The water activities of aqueous electrolyte mixtures of $NaCl-KCl-NH_4Cl-H_2O$ were experimentally determined at $T = 298.15$ K by the hygrometric method at a total ionic strength from 0.4 $mol\cdot kg^{-1}$ to about saturation of the solutes for different ionic strength fractions y of NaCl(aq) ($y = I_{NaCl}/I_{tot}$) of 1/3, 1/2, and 2/3 with the constant rapport molal ratio r of KCl(aq) on NH_4Cl(aq) of unity ($r = m_{KCl}/m_{NH_4Cl}$). The data allow the deduction of new osmotic coefficients. The results obtained were correlated using Pitzer's model and Dinane's mixing rules ECA I and ECA II for calculations of the water activity in mixed aqueous electrolytes. A new Dinane−Pitzer model is proposed for the calculation of osmotic coefficients in quaternary aqueous mixtures using the evaluated ternary and quaternary ionic mixing parameters obtained from the system studied. The solute activity coefficients of the components in the mixture were also determined for different ionic strength fractions y of NaCl(aq).

Introduction

In many industrial, geochemical, biological, and environmental systems, aqueous mixed electrolyte solutions are of considerable importance due to their application in these areas to solve environmental problems and optimize industrial processes. There has been a resurgence of interest in the thermodynamic properties of aqueous NH_4 and of its mixtures with other electrolytes. The properties of the water-soluble compounds of the ammonium ion are of considerable interest in studies related to waste disposal.[1] Thermodynamic data for their ammonium chloride salts and mixtures with NaCl(aq) may help to understand the transport of the ion in the natural environment. The system investigated in this work is of special interest for constructing a model for calculating mineral−solution equilibria in brine systems. One of the problems in this area that has received considerable attention is the osmotic and activity coefficients of species in mixed aqueous solutions containing NH_4Cl(aq). Recent developments of electrolyte solution theories have also generated added interest in this aspect of solution chemistry. Although the experimental thermodynamic data for mixed electrolyte solutions of high soluble ammonium salts in acid solutions and in combination of sea type ions are of special interest in constructing the comprehensive model for high concentration aqueous inorganic aerosols. Such data have been found to be very useful for verification or parametrization of thermodynamic models. There are no studies of these properties of the present system in the literature.

In the experimental determination of thermodynamic properties in mixed electrolyte solutions, isopiestic vapor pressure and electromotive force (emf) methods have been widely used. In this work, we use the hygrometric method described in our previous paper,[2] which yields the water activity in aqueous solution containing electrolytes from the measured relative humidity. This method has been used for determining thermodynamic properties of binary aqueous chlorides including NaCl(aq), KCl(aq), and NH_4Cl(aq)[3] and of ternary mixed chloride electrolytes such as $NaCl-KCl-H_2O$,[4] $NaCl-NH_4Cl-H_2O$,[5] and $KCl-NH_4Cl-H_2O$.[6] Measurements of water activities over the total ionic strength range of (0.4 to 7.2) $mol\cdot kg^{-1}$ were performed for quaternary aqueous solutions $NaCl-KCl-NH_4Cl-H_2O$ of different ionic strength fractions y of NaCl(aq) (where $y = I_{NaCl}/I_{tot}$) ranging from 1/3, 1/2, and 2/3 with the constant molal ratio r of KCl(aq) on NH_4Cl(aq) of unity (where $r = m_{KCl}/m_{NH_4Cl}$) at $T = 298.15$ K. The osmotic coefficients were also determined from these water activities measurements.

The ECA rule proposed by Dinane et al. in our previous paper[4] is used to predict water activities of this system from those of the aqueous solutions of the individual component salts. The results are compared with values from Pitzer's model. The experimental data are used for the determination of the newly ionic mixing parameters of the proposed modified equation of Pitzer. The calculation of solute activity coefficients in this system is made using Pitzer's model. The main objectives of this work are to determine thermodynamic properties for the quaternary aqueous solutions $NaCl-KCl-NH_4Cl-H_2O$ using the hygrometric method and to compare these results with those fitted by our models and Pitzer's model.

Experimental Section

The water activity was determined by the hygrometric method previously described in our earlier work.[2] It is based on the measurement of the relative humidity over aqueous solutions containing nonvolatile electrolytes.

A droplet of a reference salt solution of NaCl(aq) or LiCl(aq) was suspended by a spider-thin thread over a cup containing the solution to be studied. The humidity of air surrounding the droplet could be varied. Because of the small size of the droplet, the droplet solution rapidly equilibrates with the vapor-phase water. By changing the relative humidity of the vapor, the droplet can be made to absorb or evaporate water and thereby change the concentration of solution and cause an increase or decrease in its diameter. This diameter is measured by a microscope with an ocular equipped with a micrometric screw.

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* Tel: +212 64 27 21 99. E-mail: dinaneab @yahoo.fr.

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Table 1. Growth Ratios *K* of the NaCl(aq) Droplets, Water Activities a_w, and Osmotic Coefficients ϕ of NaCl−KCl−NH_4Cl(aq) at Total Ionic strength *I* for Different Ionic Strength Fractions *y* of NaCl

m_{NaCl}	m_{KCl}	m_{NH_4Cl}	I	K	a_w	ϕ
			$y = 1/3$			
0.20	0.20	0.20	0.60	1.008[a]	0.9805	0.911
0.40	0.40	0.40	1.20	1.509	0.961	0.920
0.50	0.50	0.50	1.50	1.399	0.951	0.930
0.60	0.60	0.60	1.80	1.322	0.941	0.938
0.80	0.80	0.80	2.40	1.211	0.921	0.952
1.00	1.00	1.00	3.00	1.132	0.900	0.975
1.20	1.20	1.20	3.60	1.078	0.880	0.986
1.40	1.40	1.40	4.20	1.032	0.858	1.012
1.50	1.50	1.50	4.50	1.016	0.849	1.010
1.60	1.60	1.60	4.80	0.996	0.837	1.029
1.80	1.80	1.80	5.40	0.969	0.818	1.033
2.00	2.00	2.00	6.00	0.939	0.794	1.067
2.20	2.20	2.20	6.60	0.918	0.774	1.077
2.40	2.40	2.40	7.20	0.914[b]	0.754	1.088
			$y = 1/2$			
0.20	0.10	0.10	0.40	1.160[a]	0.987	0.908
0.40	0.20	0.20	0.80	1.717	0.974	0.914
0.60	0.30	0.30	1.20	1.509	0.961	0.920
0.80	0.40	0.40	1.60	1.375	0.948	0.926
1.00	0.50	0.50	2.00	1.278	0.934	0.948
1.20	0.60	0.60	2.40	1.211	0.921	0.952
1.40	0.70	0.70	2.80	1.154	0.906	0.979
1.60	0.80	0.80	3.20	1.107	0.891	1.001
1.80	0.90	0.90	3.60	1.073	0.878	1.003
2.00	1.00	1.00	4.00	1.042	0.863	1.022
2.20	1.10	1.10	4.40	1.012	0.847	1.047
2.40	1.20	1.20	4.80	0.990	0.833	1.057
2.60	1.30	1.30	5.20	0.972	0.820	1.059
2.80	1.40	1.40	5.60	0.949	0.802	1.094
3.00	1.50	1.50	6.00	0.935	0.790	1.090
3.20	1.60	1.60	6.40	0.916	0.772	1.122
3.60	1.80	1.80	7.20	0.908[b]	0.745	1.135
			$y = 2/3$			
0.40	0.10	0.10	0.60	1.006[a]	0.9804	0.916
0.80	0.20	0.20	1.20	1.509	0.961	0.920
1.20	0.30	0.30	1.80	1.316	0.940	0.954
1.60	0.40	0.40	2.40	1.204	0.919	0.977
2.00	0.50	0.50	3.00	1.123	0.897	1.006
2.40	0.60	0.60	3.60	1.066	0.875	1.029
2.80	0.70	0.70	4.20	1.019	0.851	1.066
3.20	0.80	0.80	4.80	0.984	0.829	1.084
3.60	0.90	0.90	5.40	0.950	0.803	1.128
4.00	1.00	1.00	6.00	0.927	0.782	1.137
4.40	1.10	1.10	6.60	0.913[b]	0.753	1.193
4.80	1.20	1.20	7.20	0.899[b]	0.733	1.197

[a] Reference water activity is 0.98. [b] Reference solution is LiCl(aq). Numbers without exponents are for the reference water activity of 0.84 and the reference solution of NaCl(aq). $\phi = -1000 \ln a_w/18.015\ (2m)$.

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 $K = D(a_w)/D\{a_{w(ref)}\}$ is calculated, and the relative humidity based upon the variation of the ratio *K* as a function of the water activity of these reference solutions is determined. At equilibrium, the activity of water of solution exactly equals the relative humidity of the surrounding vapor. Generally, the reference relative humidity is 0.84. For moderately dilute solution, the reference value is 0.98.

A reference solution of NaCl(aq) or LiCl(aq) was prepared by mass from reagent grade crystals dried at 453.15 K. The concentration was controlled by conductivity measurements. The uncertainties of molality data for 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.

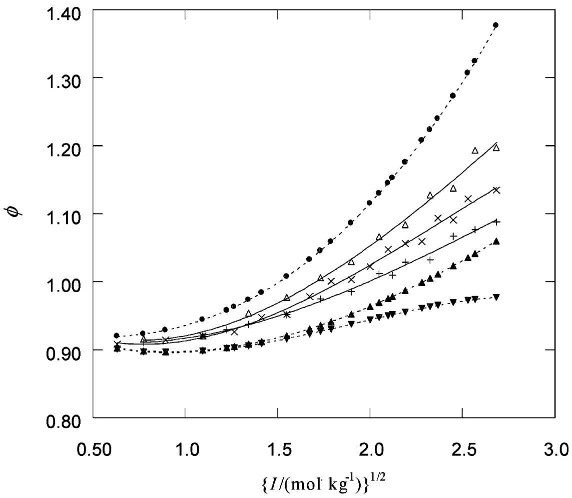

Figure 1. Osmotic coefficient ϕ of NaCl−KCl−NH_4Cl(aq) plotted against square root of total ionic strength $I^{1/2}$ at different ionic strength fractions *y* of NaCl(aq): ●, [NaCl(aq)]; ▲, [KCl(aq)]; ▼, [NH_4(aq)]; +, $y = 1/3$; ×, $y = 1/2$; △, $y = 2/3$.

Hygrometric Equilibrations. A series of measurements of the water activity were made for the mixture NaCl−KCl−NH_4Cl(aq) as a function of total molality ranging from (0.4 to 7.2) mol·kg^{-1}, for different ionic strength fractions *y* of NaCl(aq) (where $y = I_{NaCl}/I_{tot}$) of 1/3, 1/2, and 2/3 with the constant molal ratio *r* of KCl(aq) on NH_4Cl(aq) of unity (where $r = m_{KCl}/m_{NH_4Cl}$) at $T = 298.15$ K. The reference solutions are NaCl(aq) and LiCl(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 accuracy 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.[3]

On the basis of the experimental water activities, we evaluated the osmotic coefficients for different ionic strength fractions. The obtained osmotic coefficients are listed in Table 1 and plotted against $I^{1/2}$ in Figure 1. There are no studies of the present system which are available for comparison with our results.

Treatment of the Thermodynamic Data. As mentioned previously, two different models were used in the current work in modified form. The first is the extended composed additivity (ECA) rule from Dinane, and the second is the ion-interaction model from Pitzer.

(1) ECA Rule. Dinane et al.[4] have proposed the ECA rule, which calculates the water activity in mixed electrolyte solutions from those of the aqueous solutions of the individual component salts. The general ECA equation for mixed electrolytes with the same anion is given by

$$a_w = (2 - n) + \sum_c \sum_a a_{w(ca)} - \sum_c \sum_{c'} I_{ca} I_{c'a} \lambda_{cc'} - \sum_c \sum_{c'} \sum_a I_{ca} I_{c'a} I \delta_{cc'a} \quad (1)$$

where *n* is the number of components in the solution, *c* indicates the cation, *a* indicates the anion, a_w is the water activity, *I* is

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

	a_w(NaCl(aq))	a_w(KCl(aq))	a_w(NH$_4$Cl(aq))
a_0	9.9948 (−1)	9.9953(−1)	9.9996(−1)
a_1	−3.0974 (−2)	−3.0855 (−2)	−3.0993 (−2)
a_2	−1.5048 (−3)	−3.711 (−4)	−3.8250 (−4)
a_3	0	0	5.1788 (−5)
σ	0.00089	0.0006	0.00137
m	0.2 to 6	0.1 to 4.8	0.1 to 6
source	refs 3 and 7	refs 3 and 7	refs 3 and 7

[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	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	σ	source
NaCl−H$_2$O	6.0	0.765	0.2664	0.00127	0.001	ref 9
KCl−H$_2$O	4.8	0.04835	0.2122	−0.00084	0.0005	ref 9
NH$_4$Cl−H$_2$O	7.06	0.0521	0.1916	−0.003		ref 12

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

system	θ	ψ	source
NaCl−KCl−H$_2$O	−0.012	−0.0018	ref 10
NaCl−NH$_4$Cl−H$_2$O	−0.012	−0.0018	refs 13 and 14
KCl− NH$_4$Cl−H$_2$O	0.0516	−0.000847	ref 6

the ionic strength, and the parameters λ and δ, determined experimentally for each system, characterize the binary and ternary deviation from ideality for the mixture in a concentrated solution. The ECA equation applied for quaternary system studied in the present work is given by

$$a_w = -2 + a_{w(NaCl)} + a_{w(KCl)} + a_{w(NH_4Cl)} - I_{NaCl}I_{KCl}\lambda_{NaK} - I_{NaCl}I_{NH_4Cl}\lambda_{NaNH_4} - I_{KCl}I_{NH_4Cl}\lambda_{KNH_4} - I_{NaCl}I_{KCl}I\delta_{NaKCl} - I_{NaCl}I_{NH_4Cl}I\delta_{NaNH_4Cl} - I_{KCl}I_{NH_4Cl}I\delta_{KNH_4Cl} \quad (2)$$

where I_{NaCl}, I_{KCl}, I_{NH_4Cl}, and I are respectively the ionic strengths of the electrolytes NaCl(aq), KCl(aq), and NH$_4$Cl(aq) in the mixture and the total ionic strength. Here, $a_{w(NaCl)}$, $a_{w(KCl)}$, $a_{w(NH_4Cl)}$, and a_w are the water activities of binary solution of NaCl(aq) at the ionic strength I_{NaCl}, the water activities of binary solution of KCl(aq) at the ionic strength I_{KCl}, the water activities of binary solution of NH$_4$Cl(aq) at the ionic strength I_{NH_4Cl}, and the water activity of ternary solution at the total ionic strength I, respectively. 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_{NaKCl}, λ_{NaNH_4}, λ_{KNH_4} , δ_{NaKCl}, δ $_{NaNH_4Cl}$, and δ $_{KNH_4Cl}$ are given in our previous work.[4−6]

The water activities for the binary solutions were calculated using polynomial fits of water activity data obtained in our previous work[3] and those from Robinson and Stokes.[7] The general equation of these polynomial fits is $a_w = a_0 + a_1m + a_2m^2 + a_3m^3 + a_4m^4 + ...$. The coefficients (a_i) for each electrolyte are listed in Table 2. The mean values determined for different ternary solutions, derived from combination of electrolytes studied in this work NaCl−KCl(aq),[4] NaCl−NH$_4$Cl(aq),[5] and KCl−NH$_4$Cl(aq)[6] are respectively $\lambda_{NaK} = 0.00125$ (mol·kg^{-1})$^{-2}$, $\lambda_{NaNH_4} = 0.001107$ (mol·kg^{-1})$^{-2}$, $\lambda_{KNH_4} = 0.0001757$ (mol·kg^{-1})$^{-2}$, and $\delta_{NaKCl} = -0.000015$ (mol·kg^{-1})$^{-3}$, $\delta_{NaNH_4Cl} = -0.00007$ (mol·kg^{-1})$^{-3}$, $\delta_{KNH_4Cl} = -0.000016$ (mol·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 $\sigma_{aw} = 0.0013$.

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

$$a_w = -2 + a_{w(NaCl)} + a_{w(KCl)} + a_{w(NH_4Cl)} - I_{NaCl}I_{KCl}I_{NH_4Cl}\lambda_{NaKNH_4Cl} - I_{NaCl}I_{KCl}I_{NH_4Cl}I\delta_{NaKNH_4Cl} \quad (3)$$

where the parameters λ_{NaKNH_4} and δ_{NaKNH_4Cl}, determined experimentally for each system, characterize ternary interactions among different ions of the same sign and quaternary interactions between different ions not all of the same sign in the concentrated solution mixture. The unknowns λ and δ may be estimated by a graphical procedure using the modified expression of eq 3. This yields

$$\Delta a_w/I_{NaCl}I_{KCl}I_{NH_4Cl} = -\lambda_{NaKNH_4} - I\delta_{NaKNH_4Cl} \quad (4)$$

where Δa_w is the difference between the experimental values of water activity $a_{w(exp)}$ and the calculated water activities $a_{w(calc)}$ from eq 3 with $\lambda = 0$ and $\delta = 0$. The quantity Δa_w on the left was plotted against the total ionic strength I to obtain a linear plot with intercept λ and slope δ.

The mean values determined for NaCl−KCl−NH$_4$Cl(aq) are $\lambda_{NaKNH_4} = 0.0035$ (mol·kg^{-1})$^{-3}$ and $\delta_{NaKNH_4Cl} = -0.00038$ (mol·kg^{-1})$^{-4}$. The standard deviation for the fit is $\sigma_{aw} = 0.0016$.

(2) Pitzer's Model. Pitzer's model[8−11] for the calculation of water activity of the mixtures has been used to treat the results from experiments and to compare with the data obtained using the ECA rule. Calculations of thermodynamic properties for mixed electrolyte systems generally require relevant data for the pure components. In case of NaCl(aq), KCl(aq), and NH$_4$Cl(aq), the required quantities were calculated from data obtained in our previous work.[3]

The osmotic coefficient is given by the Pitzer model as

$$\phi - 1 = \frac{2}{\sum_i m_i}\left\{-\frac{A_\phi I^{3/2}}{1 + 1.2\sqrt{I}} + m_{Na}m[B^\phi_{NaCl} + mC^\phi_{NaCl}] + m_K m[B^\phi_{KCl} + mC^\phi_{KCl}] + m_{NH_4}m[B^\phi_{NH_4Cl} + mC^\phi_{NH_4Cl}] + m_{Na}m_K[\theta_{NaK} + m\psi_{NaKCl}] + m_{Na}m_{NH_4}[\theta_{NaNH_4} + m\psi_{NaNH_4Cl}] + m_K m_{NH_4}[\theta_{KNH_4} + m\psi_{KNH_4Cl}]\right\} \quad (5)$$

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

$$B^\phi = \beta^{(0)} + \beta^{(1)}\exp(-2\sqrt{I}) \quad (6)$$

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[9] for NaCl(aq) and KCl(aq) and by Christov et al. for NH$_4$Cl(aq).[12] The values

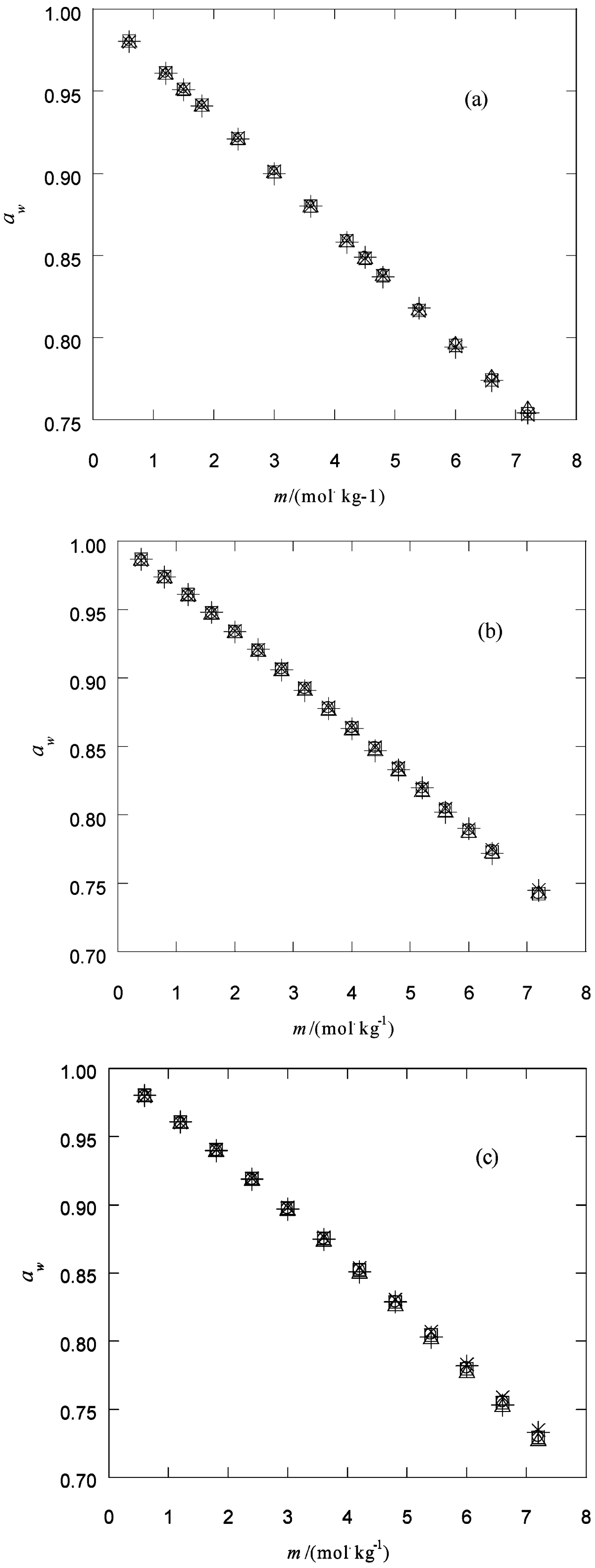

Figure 2. Water activity a_w of NaCl−KCl−NH$_4$Cl(aq) plotted against total molality m at different ionic strength fractions y of NaCl(aq). (a) $y = 1/3$; (b) $y = 1/2$; (c) $y = 2/3$: +, experimental points; ○, ECA I rule; ×, ECA II rule; □, Pitzer; △, Dinane−Pitzer.

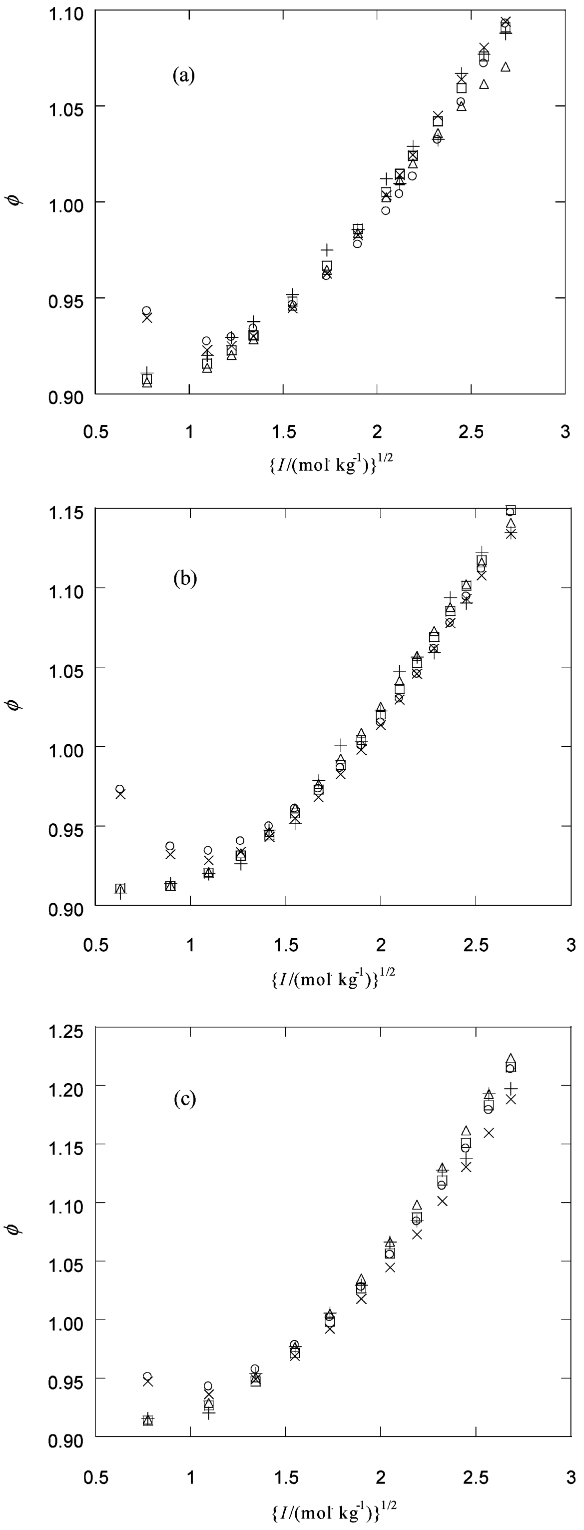

Figure 3. Osmotic coefficient ϕ of NaCl−KCl−NH$_4$Cl(aq) plotted against square root of total ionic strength $I^{1/2}$ at different ionic strength fractions y of NaCl(aq). (a) $y = 1/3$; (b) $y = 1/2$; (c) $y = 2/3$: +, experimental points; ○, ECA I rule; ×, ECA II rule; □, Pitzer; △, Dinane−Pitzer.

of these ion interaction parameters are listed in Table 3. The mixing parameters θ and ψ that were evaluated by different authors and that give excellent agreement with experimental data in the quaternary system are given in Table 4.

(3) Dinane−Pitzer Model. The Pitzer equation contains several mixing ionic parameters. To simplify this equation, we propose a modified Pitzer's equation containing only the reduced parameters corresponding to the all ionic interactions in the mixed electrolyte solution. This equation, used for calculating the osmotic coefficients of mixed electrolyte solutions, requires parameters estimated from common-ion solutions to characterize ternary interactions among different ions of the same sign and quaternary interactions between different ions not all of the same sign in a mixed electrolyte solution. Starting from the equation

Table 5. Activity Coefficients Calculated by Pitzer's Model γ_{NaCl} of NaCl(aq), γ_{KCl} of KCl(aq), and γ_{NH_4Cl} of NH_4Cl(aq) in NaCl−KCl−NH_4Cl(aq) at Total Ionic Strength I for Different Ionic Strength Fractions y of NaCl(aq)

$y = 1/3$				$y = 1/2$				$y = 2/3$			
I	γ_{NaCl}	γ_{KCl}	γ_{NH_4Cl}	I	γ_{NaCl}	γ_{KCl}	γ_{NH_4Cl}	I	γ_{NaCl}	γ_{KCl}	γ_{NH_4Cl}
0.60	0.598	0.605	0.604	0.40	0.631	0.637	0.636	0.60	0.597	0.600	0.599
1.20	0.548	0.550	0.549	0.80	0.576	0.579	0.578	1.20	0.550	0.545	0.545
1.50	0.535	0.535	0.534	1.20	0.549	0.548	0.547	1.80	0.532	0.520	0.519
1.80	0.526	0.524	0.523	1.60	0.534	0.529	0.528	2.40	0.527	0.506	0.506
2.40	0.517	0.510	0.509	2.00	0.526	0.516	0.516	3.00	0.528	0.499	0.499
3.00	0.513	0.501	0.501	2.40	0.522	0.508	0.507	3.60	0.533	0.496	0.496
3.60	0.514	0.497	0.497	2.80	0.520	0.502	0.502	4.20	0.542	0.496	0.496
4.20	0.517	0.495	0.495	3.20	0.521	0.499	0.498	4.80	0.554	0.498	0.497
4.50	0.520	0.495	0.494	3.60	0.524	0.497	0.496	5.40	0.568	0.502	0.501
4.80	0.523	0.495	0.494	4.00	0.527	0.496	0.495	6.00	0.584	0.506	0.505
5.40	0.530	0.496	0.495	4.40	0.532	0.496	0.495	6.60	0.601	0.512	0.510
6.00	0.538	0.498	0.496	4.80	0.538	0.497	0.496	7.20	0.620	0.519	0.516
6.60	0.547	0.500	0.498	5.20	0.545	0.498	0.497				
7.20	0.558	0.503	0.500	5.60	0.552	0.500	0.499				
				6.00	0.560	0.502	0.501				
				6.40	0.569	0.505	0.503				
				7.20	0.588	0.511	0.508				

as defined and discussed by Pitzer and Kim,[10] a working expression may be obtained for the osmotic coefficient of a mixed electrolytes involving, in addition to the quantities characterizing pure electrolytes, only two terms that define all the interactions of different ions present in the solution of the same sign and those with different sign. Then, the Dinane−Pitzer equation is given by

$$\phi - 1 = \frac{2}{\sum_i m_i}\Bigg\{-\frac{A_\phi I^{3/2}}{1 + 1.2\sqrt{I}} + 2\sum_c \sum_a m_c m_a\left[B^\phi_{ca} + \frac{(\sum mz)}{z_c z_a}C^\phi_{ca}\right] + \sum_c \sum_{c'} \sum_{c''} \sum_{c'''} m_c m_{c'} m_{c''} m_{c'''} \ldots [\eta_{cc'c''c'''} \ldots + \sum_a m_a \chi_{cc'c''c'''\ldots a}] + \sum_a \sum_{a'} \sum_{a''} \sum_{a'''} m_a m_{a'} m_{a''} m_{a'''} \ldots [\eta_{aa'a''a'''\ldots} + \sum_c m_a \chi_{caa'a''a'''\ldots}]\Bigg\} \tag{7}$$

where $(\Sigma mz) = (\Sigma m_c z_c) = (\Sigma m_a|z_a|)$ and c, c′, c″, and c‴ are indices covering all cations while a, a′, a″, and a‴ cover all anions, the second term comprises a multiple sum over molalities and the second and third virial coefficients for pure electrolytes. The final two terms include interaction parameters involving all cations and all anions present in the mixture.

For a mixture of just three symmetrical electrolytes of charge $z = 1$ and with a common anion, the expression is considerably simplified. The osmotic coefficient of a mixed solution of three salts NaCl(aq), KCl(aq), and NH_4Cl(aq) is given by the Dinane−Pitzer equation as

$$\phi - 1 = \frac{2}{\sum_i m_i}\Bigg\{-\frac{A_\phi I^{3/2}}{1 + 1.2\sqrt{I}} + m_{NaCl}m[B^\phi_{NaCl} + mC^\phi_{NaCl}] + m_{KCl}m[B^\phi_{KCl} + mC^\phi_{KCl}] + m_{NH_4Cl}m[B^\phi_{NH_4Cl} + mC^\phi_{NH_4Cl}] + m_{NaCl}m_{KCl}m_{NH_4Cl}[\eta_{NaKNH_4} + m\chi_{NaKNH_4Cl}]\Bigg\} \tag{8}$$

where η_{NaKNH_4} is a ternary mixing parameter involving unlike ions of the same sign and χ_{NaKNH_4Cl} is a quaternary mixing parameter for the three unlike ions of the same sign with a fourth ion of the opposite sign.

From the osmotic coefficients determined from the experimental water activities of the studied mixture at different ionic strength fractions, it is possible to determine the unknown mixing ionic parameters η_{NaKNH_4} and χ_{NaKNH_4Cl}. These quantities are evaluated by a graphical procedure that defines the quantity $\Delta\phi$ as the difference between the experimental value ϕ_{exp} and that calculated from eq 8 ϕ_{calc} without mixing ionic parameters. This yields

$$\frac{m}{m_{NaCl}m_{KCl}m_{NH_4Cl}}\Delta\phi = \eta_{NaKNH_4} + \chi_{NaKNH_4Cl}m_{Cl} \tag{9}$$

so that a plot of $\Delta\phi$ versus total molality m should give a straight line with intercept η_{NaKNH_4} and slope χ_{NaKNH_4Cl}.

We have evaluated the unknown mixing ionic parameters for the Dinane−Pitzer equation. The values are $\eta_{NaKNH_4} = 0.001$, $\chi_{NaKNH_4Cl} = -0.005$, and the standard deviation is $\sigma_\phi = 0.009$.

The comparison of the water activities shows that the values calculated with ECA I and ECA II rules and those predicted by the Pitzer and Dinane−Pitzer models are relatively close over the molality range (Figure 2). The standard deviation is $\sigma_{aw} = 0.001$ for Pitzer's model; $\sigma_{aw} = 0.0015$ for Dinane−Pitzer's model. The average difference is less than ± 0.0015 between our ECA II rule and the Dinane−Pitzer model.

The calculations of the osmotic coefficients by ECA rules have been generalized for different mixtures. The standard deviation for osmotic coefficient is $\sigma_\phi = 0.007$ for Pitzer's model and $\sigma_\phi = 0.01$ for ECA II and ECA I.

The comparison of our results with those of Pitzer's model is shown in Figure 3. The predictions by the ECA rules are very similar to those of Pitzer's model at concentrations above 1 mol·kg^{-1}. The deviation of the ECA becomes quite large at very low molality less than 1 mol·kg^{-1}. This is due to the $a_w\phi$ relationship by the term $1000/\Sigma_i\nu_i\, m_i M_w$, which becomes greater for $m < 1$ mol·kg^{-1} and yields large deviations for the water activities.

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 3). The average difference is less than ± 0.01 between our ECA II rule and Dinane−Pitzer's model.

The activity coefficient γ_{NaCl} of NaCl(aq) in mixtures with KCl(aq) and NH_4Cl(aq) is given by the Pitzer model as

$$\begin{aligned}\ln \gamma_{\mathrm{NaCl}} = {} & f^{\gamma} + \frac{m_{\mathrm{Cl}}}{3}[2B_{\mathrm{NaCl}} + mC_{\mathrm{NaCl}}] + \\ & \frac{m_{\mathrm{Na}}}{3}[2B_{\mathrm{NaCl}} + mC_{\mathrm{NaCl}}] + \frac{m_{\mathrm{K}}}{3}[2B_{\mathrm{KCl}} + mC_{\mathrm{KCl}} + 2\theta_{\mathrm{NaK}}] + \\ & \frac{m_{\mathrm{Li}}}{3}[2B_{\mathrm{NH_4Cl}} + mC_{\mathrm{NH_4Cl}} + 2\theta_{\mathrm{NaNH_4}}] + \\ & m_{\mathrm{Na}}m_{\mathrm{Cl}}\left[B'_{\mathrm{NaCl}} + \frac{2C_{\mathrm{NaCl}}}{3}\right] + m_{\mathrm{K}}m_{\mathrm{Cl}}\left[B'_{\mathrm{KCl}} + \frac{2C_{\mathrm{KCl}}}{3} + \frac{\psi_{\mathrm{NaKCl}}}{3}\right] + \\ & m_{\mathrm{NH_4}}m_{\mathrm{Cl}}\left[B'_{\mathrm{NH_4Cl}} + \frac{2C_{\mathrm{NH_4Cl}}}{3} + \frac{\psi_{\mathrm{NaNH_4Cl}}}{3}\right] + \\ & \frac{1}{3}m_{\mathrm{Na}}m_{\mathrm{K}}\psi_{\mathrm{NaKCl}} + \frac{1}{3}m_{\mathrm{Na}}m_{\mathrm{NH_4}}\psi_{\mathrm{NaNH_4Cl}} + \frac{1}{3}m_{\mathrm{K}}m_{\mathrm{NH_4}}\psi_{\mathrm{KNH_4Cl}}\end{aligned} \tag{10}$$

where f^{γ} is the term of Debye−Hückel for the activity coefficient; the quantities *B*, *B′*, and *C* were calculated from ref 8.

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

$$\begin{aligned}\ln \gamma_{\mathrm{KCl}} = {} & f^{\gamma} + \frac{m_{\mathrm{Cl}}}{3}[2B_{\mathrm{KCl}} + mC_{\mathrm{KCl}}] + \\ & \frac{m_{\mathrm{K}}}{3}[2B_{\mathrm{KCl}} + mC_{\mathrm{KCl}}] + \frac{m_{\mathrm{Na}}}{3}[2B_{\mathrm{NaCl}} + mC_{\mathrm{NaCl}} + 2\theta_{\mathrm{NaK}}] + \\ & \frac{m_{\mathrm{NH4}}}{3}[2B_{\mathrm{NH_4Cl}} + mC_{\mathrm{NH_4Cl}} + 2\theta_{\mathrm{NaNH_4}}] + \\ & m_{\mathrm{K}}m_{\mathrm{Cl}}\left[B'_{\mathrm{KCl}} + \frac{2C_{\mathrm{KCl}}}{3}\right] + m_{\mathrm{Na}}m_{\mathrm{Cl}}\left[B'_{\mathrm{NaCl}} + \frac{2C_{\mathrm{NaCl}}}{3} + \frac{\psi_{\mathrm{NaKCl}}}{3}\right] + \\ & m_{\mathrm{NH_4}}m_{\mathrm{Cl}}\left[B'_{\mathrm{NH_4Cl}} + \frac{2C_{\mathrm{NH_4Cl}}}{3} + \frac{\psi_{\mathrm{KNH_4Cl}}}{3}\right] + \frac{1}{3}m_{\mathrm{Na}}m_{\mathrm{K}}\psi_{\mathrm{NaKCl}} + \\ & \frac{1}{3}m_{\mathrm{K}}m_{\mathrm{NH_4}}\psi_{\mathrm{KNH_4Cl}} + \frac{1}{3}m_{\mathrm{Na}}m_{\mathrm{NH_4}}\psi_{\mathrm{NaNH_4Cl}}\end{aligned} \tag{11}$$

The activity coefficient $\gamma_{\mathrm{NH_4Cl}}$ of NH_4Cl(aq) in mixtures with NaCl(aq) and KCl(aq) is given by

$$\begin{aligned}\ln \gamma_{\mathrm{NH_4Cl}} = {} & f^{\gamma} + \frac{m_{\mathrm{Cl}}}{3}[2B_{\mathrm{NH_4Cl}} + mC_{\mathrm{NH_4Cl}}] + \\ & \frac{m_{\mathrm{NH_4}}}{3}[2B_{\mathrm{NH_4Cl}} + mC_{\mathrm{NH_4Cl}}] + \frac{m_{\mathrm{K}}}{3}[2B_{\mathrm{KCl}} + mC_{\mathrm{KCl}} + 2\theta_{\mathrm{KNH_4}}] + \\ & \frac{m_{\mathrm{Na}}}{3}[2B_{\mathrm{NaCl}} + mC_{\mathrm{NaCl}} + 2\theta_{\mathrm{NaNH_4}}] + \\ & m_{\mathrm{NH_4}}m_{\mathrm{Cl}}\left[B'_{\mathrm{NH_4Cl}} + \frac{2C_{\mathrm{NH_4Cl}}}{3}\right] + m_{\mathrm{K}}m_{\mathrm{Cl}}\left[B'_{\mathrm{KCl}} + \frac{2C_{\mathrm{KCl}}}{3} + \right. \\ & \left.\frac{\psi_{\mathrm{NH_4KCl}}}{3}\right] + m_{\mathrm{Na}}m_{\mathrm{Cl}}\left[B'_{\mathrm{NaCl}} + \frac{2C_{\mathrm{NaCl}}}{3} + \frac{\psi_{\mathrm{NaNH_4Cl}}}{3}\right] + \\ & \frac{1}{3}m_{\mathrm{NH_4}}m_{\mathrm{Na}}\psi_{\mathrm{NaNH_4Cl}} + \frac{1}{3}m_{\mathrm{K}}m_{\mathrm{NH_4}}\psi_{\mathrm{KNH_4Cl}} + \frac{1}{3}m_{\mathrm{K}}m_{\mathrm{Na}}\psi_{\mathrm{NaKCl}}\end{aligned} \tag{12}$$

The activity coefficients γ_{NaCl}, γ_{KCl}, and $\gamma_{\mathrm{NH_4Cl}}$ in the mixture are listed in Table 5.

Figure 4 is a plot of γ_{NaCl}, γ_{KCl}, and $\gamma_{\mathrm{NH_4Cl}}$ as a function of $I^{1/2}$. The magnitude of the activity coefficients of the solutes in the quaternary solutions is similar to those in the binary solutions. For NH_4Cl(aq), the $\gamma_{\mathrm{NH_4Cl}}$ exhibited relatively low solute activity coefficients in comparison to the two other electrolytes. A cursory comparison of these results shows that the activity coefficients for NaCl(aq) in the mixture decrease with increasing ionic strength fractions *y* from the activity coefficient of pure NaCl(aq) in the following order: $\gamma_{\mathrm{NaCl(bin)}} > \gamma_{\mathrm{NaCl}(y=2/3)} > \gamma_{\mathrm{NaCl}(y=1/2)} > \gamma_{\mathrm{NaCl}(y=1/3)}$. For the KCl(aq), the activity coefficients of KCl(aq) in the mixture decrease with increasing ionic strength fractions *y* from the activity coefficient of pure KCl(aq) in the following order: $\gamma_{\mathrm{KCl(bin)}} > \gamma_{\mathrm{KCl}(y=1/3)} > \gamma_{\mathrm{KCl}(y=1/2)} > \gamma_{\mathrm{KCl}(y=2/3)}$ for total molality less than 3 mol·kg^{-1},

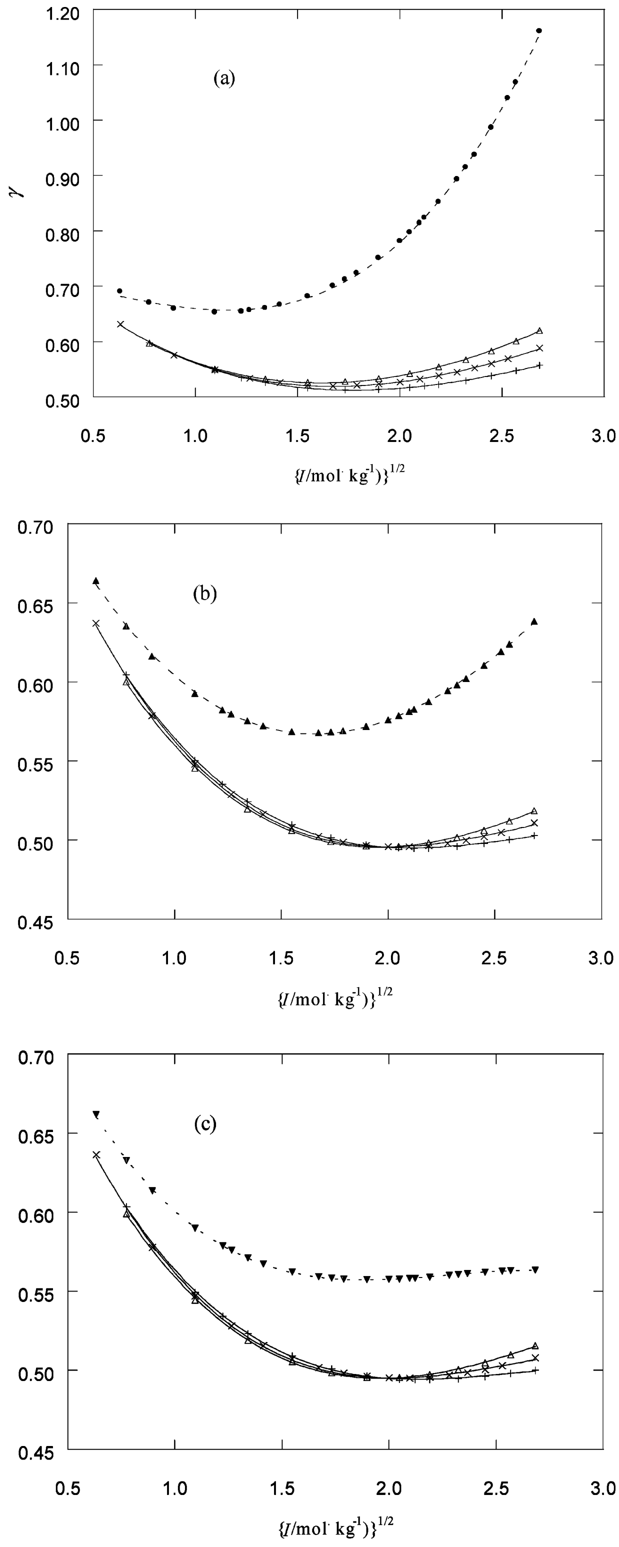

Figure 4. Activity coefficients calculated by Pitzer's model γ_{NaCl} of NaCl(aq), γ_{KCl} of KCl(aq), and $\gamma_{\mathrm{NH_4Cl}}$ of NH_4Cl(aq) in NaCl−KCl−NH_4Cl(aq) and plotted against square root of total ionic strength $I^{1/2}$ at different ionic strength fractions *y* of NaCl(aq). (a) γ_{NaCl}; (b) γ_{KCl}; (c) $\gamma_{\mathrm{NH_4Cl}}$: +, $y = 1/3$; ×, $y = 1/2$; Δ, $y = 2/3$. Curves with dashed line are for pure electrolytes: ●, [NaCl(aq)]; ▲, [KCl(aq)]; ▼, [NH_4(aq)].

and this order is reversed for total molality greater than 3 mol·kg^{-1} in the following order: $\gamma_{\mathrm{KCl(bin)}} > \gamma_{\mathrm{KCl}(y=2/3)} > \gamma_{\mathrm{KCl}(y=1/2)} > \gamma_{\mathrm{KCl}(y=1/3)}$. For the NH_4Cl(aq), the activity coefficients of NH_4Cl(aq) in the mixture decrease with increasing ionic strength fractions y from the activity coefficient of pure NH_4Cl(aq) for molalities greater than 2 mol·kg^{-1} in the following order: $\gamma_{\mathrm{NH_4Cl(bin)}} > \gamma_{\mathrm{NH_4Cl}(y=2/3)} > \gamma_{\mathrm{NH_4Cl}(y=1/2)} > \gamma_{\mathrm{NH_4Cl}(y=1/3)}$; for molalities less than 3 mol·kg^{-1} the order is reversed.

Conclusions

The water activity as a function of solute concentration has been determined at $T = 298.15$ K for aqueous electrolyte mixtures of $NaCl-KCl-NH_4Cl-H_2O$ to total ionic strengths from (0.4 to 7.2) mol·kg^{-1} with the use of an hygrometric method. 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 NaCl(aq).

Four 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 ECA I and the ECA II methods and the Pitzer and the Dinane-Pitzer models, using information from single electrolyte solutions and ionic mixing parameters, were generally able to predict the mixture's water activity and osmotic coefficient to within the uncertainty of the experimental data for $NaCl-KCl-NH_4Cl-H_2O$ system.

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