Articles

Thermodynamic Properties of the Mixed Electrolytes $\{(y)NH_4Cl + (1 - y)(NH_4)_2SO_4\}(aq)$ at the Temperature 298.15 K

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The thermodynamic properties of unsymmetrical mixed electrolytes $\{(y)NH_4Cl + (1 - y)(NH_4)_2SO_4\}(aq)$ have been measured. The water activities of the mixtures have been measured by the hygrometric method at the total molalities from 0.4 mol·kg^{-1} to saturation for different ionic-strength fractions of NH_4Cl with $y = 0.2$, 0.5, and 0.8 at the temperature 298.15 K. The results allow the deduction of osmotic coefficients. The experimental results are compared with the predictions of the Pitzer, Zdanovskii−Stokes−Robinson (ZSR), Lietzke and Stoughton (LS II), and Kusik and Meissner (KM) models. From these measurements, the new Pitzer mixing ionic parameters are determined and used to predict the solute activity coefficients in the mixture.

1. Introduction

Investigation of the thermodynamic properties of aqueous mixed electrolyte solutions presents a great interest in both experimental and theorical studies.

In this work, we use the hygrometric method, described in our previous paper,[1] that yields the water activity in aqueous solution containing electrolytes directly. This method has been used for determining thermodynamic properties of binary aqueous solutions[2,3] and ternary mixed electrolytes.[4] This paper is the continuation of the research in ternary aqueous mixtures with a common cation. The main objectives are to determine thermodynamic properties for the ternary solutions of $NH_4Cl + (NH_4)_2SO_4 + H_2O$ by this method. The thermodynamic properties of this system have not been extensively studied. Recently, the measurements of water activities were determined by electrodynamic balance by Ha et al.[5] for the mole ratio 1:1 in the range of water activity from 0.80 to 0.28 at 298.15 K. In this work, the measurements of water activities for the total molality range from 0.4 mol·kg^{-1} to saturation were performed for ternary aqueous solutions $\{(y)NH_4Cl + (1 - y)(NH_4)_2SO_4\}(aq)$ of different ionic-strength fractions $y = 0.2$, 0.5, and 0.8 at the temperature 298.15 K. The osmotic coefficients are also evaluated for these solutions from the water activities.

The experimental results are compared with the predictions made using the Pitzer, ZSR, LSII, and KM models. The experimental data are used for the calculation of solute activity coefficients using the Pitzer model with our ionic mixing parameters.

2. Experimental Section

The water activity was determined by a hygrometric method previously described.[1] It is based on the measurement of the relative humidity over aqueous solution containing nonvolatile electrolytes.

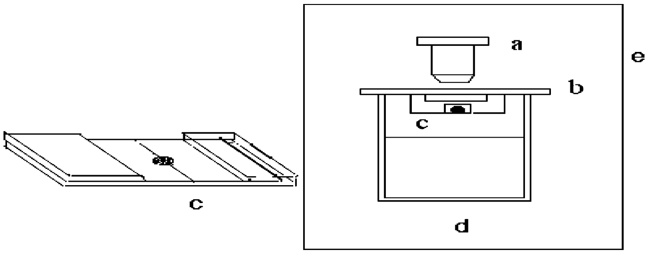

Figure 1. Description of materials used in the hygrometric apparatus: (a) microscope; (b) lid; (c) support of the drops; (d) cup; (e) wooden box.

The apparatus used is a hygrometer in which a droplet of salt solution is maintained on a thin thread.

The droplets of a reference solution of NaCl(aq) or LiCl(aq) are deposited on the spider thin thread by pulverization. This thread is kept tense over a Perspex support, which is fixed to a cup containing the selected studied solution (Figure 1). The cup containing the solution was placed in a wooden box whose temperature was regulated by a precision thermostat. The thermostated wooden box was placed in a regulated chest freezer. The constant temperature inside the wooden box was maintained by circulating air with the help of two fans. Two electrical resistances were used for heating the circulated air. The fluctuation of temperature inside the wooden box was kept within ±0.02 K. The droplet diameter is measured with a microscope with an ocular equipped with a micrometric screw.

The drops are composed of sodium or lithium chloride solutions. These chlorides permit the coverage a large domain of relative humidity. From available literature data of the vapor pressures or the water activities and the densities of these reference solutions,[1] the dependence of the relative humidity on molar concentration of the solution is obtained. This dependence allows the variation of the diameter of the drops composed by these reference solutions with the surrounding relative humidity.

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The relative humidity of a salt solution is related to the water activity of the solution. By considering the equality of the chemical potential of water in the solution and the surrounding vapor, the following relation is obtained

$$\mathrm{rh} = P_{\mathrm{w}}/P°_{\mathrm{w}} = a_{\mathrm{w}} \tag{1}$$

where P_{w} is the partial pressure of the water vapor over the salt solution at the temperature T and $P°_{\mathrm{w}}$ is the saturation vapor pressure of pure water at the same temperature T.

The volume of this droplet of a reference solution with a spherical diameter D is given by

$$V = {}^{4}/_{3}\pi(D/2)^{3} \tag{2}$$

The volume of this droplet containing a constant number of moles of solute varies during water condensation or evaporation, causing an increase or decrease in its diameter. Taking as reference relative humidity the value of 0.84, we can establish a relation between the ratio of growth K of the droplets and their diameters. This ratio is given by

$$K = D(a_{\mathrm{w}})/D(a_{\mathrm{ref}}) \tag{3}$$

where $D(a_{\mathrm{ref}})$ and $D(a_{\mathrm{w}})$ are respectively the diameter of the droplet at the reference relative humidity a_{ref} and at an unknown relative humidity a_{w}. Equation 2 enables us to relate K with the molar concentration using the relation

$$c = n/V \tag{4}$$

where c is the molar concentration of the solution constituting the droplet and n is the number of moles of solute, which remains constant in this droplet. Thus, we obtain

$$K = \{c(a_{\mathrm{ref}})/c(a_{\mathrm{w}})\}^{1/3} \tag{5}$$

where $c(a_{\mathrm{ref}})$ and $c(a_{\mathrm{w}})$ are respectively the molar concentration at reference humidity a_{ref} and the molar concentration at relative humidity a_{w}.

The functional relation between the diameter of the droplet and the relative humidity was determined by calibration experiments in which a suspended droplet of NaCl(aq) was equilibrated with a solution of NaCl(aq) contained in the cup under the same vapor pressure. Similar calibration experiments were performed with LiCl(aq) drops and solution. In the subsequent experiments, the solution under test was placed in the cup and then equilibrated with a suspended drop of NaCl(aq) or LiCl(aq) which served as a standard. The unknown relative humidity can therefore be determined from measurement of the drop equilibrium diameter $D(a_{\mathrm{w}})$ at this humidity. Knowing the diameter $D(a_{\mathrm{ref}})$ of this droplet at the reference relative humidity 0.84, we can calculate K and determine graphically the value of a_{w}. The values of the ratio of growth K calculated from eq 5 for the reference solutions NaCl(aq) and LiCl(aq) are presented in Figure 2. Generally, the reference relative humidity is 0.84. For a middle dilute solution, the water activity reference is 0.98. For water activities greater than 0.75 a solution of NaCl or LiCl is used, while for water activities less than 0.75 a solution of LiCl is used.

The solutions of NaCl, NH_4Cl, and $(NH_4)_2SO_4$ were prepared from crystalline material (Extrapur-grade chemicals: NaCl, 99.50; NH_4Cl, 99.00%; $(NH_4)_2SO_4$, 99.00%) and deionized distilled water. The reference solution is NaCl(aq).

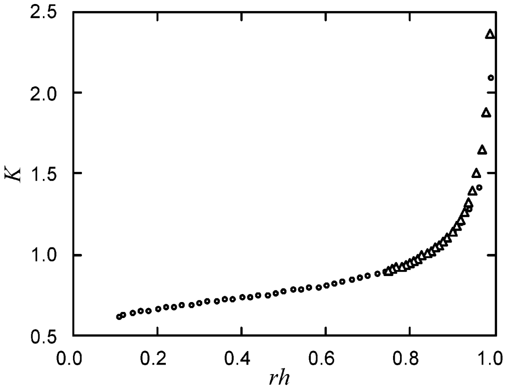

Figure 2. Variation of the ratio K of diameters of the droplets as a function of the relative humidity a_{w} for (○) LiCl and (△) NaCl.

The molality of the sample solution held in the cup was determined by measuring its refractive index. The uncertainties of refractive index measurements are ±0.0002, and those of molality data for solutes are less than ±0.01 $\mathrm{mol{\cdot}kg^{-1}}$. We made several measurements of the spherical drops' diameters, and we take the mean of results which are repeats. For one composition we take five or more cups. For each cup we made five or six measurements adequately. The average diameter $(\mathrm{aq})_{\mathrm{sol}}$ and the corresponding reference diameter $(\mathrm{aq})_{\mathrm{ref}}$ for each cup are used to calculate the ratio K. The average ratio K is calculated for these cups. This ratio is represented at four significants digits, and the determined $\Delta K/K$ is (0.1 at 0.05%). For calculated water activities, we use the graph of the variation of the ratio growth of droplets as a function of water activity for the reference solution (NaCl or LiCl). The data are given, for each cup, with four digits at low molalities and three digits at high molalities, but in the tables we have not considered these digits. Also, the average water activity a_{w} is given as are the determined a_{w} and $\Delta a_{\mathrm{w}}/a_{\mathrm{w}}$. The uncertainty in the water activity depends on the accuracy of the diameter measurements and is therefore less than ±0.02% for $a_{\mathrm{w}} > 0.97$, $\approx \pm 0.05\%$ for $a_{\mathrm{w}} > 0.95$, $\approx \pm 0.09\%$ for $a_{\mathrm{w}} > 0.90$, and $\approx \pm 0.2\%$ for $a_{\mathrm{w}} > 0.85$. Also, the overall uncertainty of the osmotic coefficient is estimated to be at most $\pm 6 \times 10^{-3}$.

3. Theory and Models

3.1. The Zdanovskii−Stokes−Robinson (ZSR) Rule. The Zdanovskii−Stokes−Robinson (ZSR) rule[6,7] has been used to predict the water activity in mixture solutions. The ZSR equation is expressed as

$$\sum_i \frac{m_i}{m_{0,i}(a_w)} = 1 \tag{6}$$

where m_i is the molality of species i in a multicomponent solution with water activity a_{w} and $m_{0,i}(a_{\mathrm{w}})$ is the molality of the single-component solution at the same a_{w}.

3.2. The Lietzke and Stoughton (LS II) Model. The Lietzke and Stoughton model (LS II)[8,9] predicts the osmotic coefficient of a multicomponent solution by

$$(\nu_{\mathrm{MX}} m_{\mathrm{MX}} + \nu_{\mathrm{NX}} m_{\mathrm{NX}})\phi = \nu_{\mathrm{MX}} m_{\mathrm{MX}} \phi_{\mathrm{MX}} + \nu_{\mathrm{NX}} m_{\mathrm{NX}} \phi_{\mathrm{NX}} \tag{7}$$

where ν_{MX} is the number of ions released by the complete dissociation of one molecule of component MX, m_{MX} is its molality, and ϕ_{MX} is the osmotic coefficient of the binary solution of component MX at the total ionic strength of the multicomponent solution.

3.3. The Ion-Interaction Model. The Pitzer model[10−12] is used for calculating the thermodynamic properties of mixed electrolyte solutions. This model requires parameters estimated from common-ion solution in order to characterize binary interactions among different ions of the same sign and ternary interactions between different ions not all of the same sign in a mixed electrolyte solution. The osmotic coefficient of a mixed solution of two salts NH_4Cl and $(NH_4)_2SO_4$ with a common cation is given by Pitzer's model as

$$\phi = 1 + \frac{1}{1+y}\left\{-0.784\frac{I^{1/2}}{1+1.2I^{1/2}} + {}^{2}/_{3}\,y(2+y)I[B^{\phi}_{NH_4Cl} + {}^{1}/_{3}(2+y)IC^{\phi}_{NH_4Cl}] + {}^{2}/_{9}(2+y)(1-y)I[B^{\phi}_{(NH_4)_2SO_4} + 0.2357(2+y)IC^{\phi}_{(NH_4)_2SO_4}] + {}^{2}/_{3}\,y(1-y)[\theta_{ClSO_4} + {}^{1}/_{3}(2+y)I\psi_{NH_4ClSO_4}]\right\} \quad (8)$$

where f^{ϕ} is the long-range electrostatic term, I is the ionic strength of the common ion, θ_{ClSO_4} is a binary mixing parameter involving unlike ions of the same sign, and $\psi_{NH_4ClSO_4}$ is a ternary mixing parameter for two unlike ions of the same sign with a third ion of the opposite sign.

The second virial coefficient B^{ϕ} of the subscribed ions is defined as

$$B^{\phi} = \beta^{(0)} + \beta^{(1)}\exp(-\alpha I^{1/2}) \quad (9)$$

where $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} are ion interaction parameters which are functions of temperature and pressure, where $\alpha = 2$ $(mol \cdot kg^{-1})^{-1}$.

The activity coefficients γ_1 of NH_4Cl and γ_2 of $(NH_4)_2SO_4$ in a common-cation mixture of $NH_4Cl-(NH_4)_2SO_4(aq)$ are given by Pitzer's model as

$$\ln \gamma_{NH_4Cl} = f^{\gamma} + {}^{2}/_{3}(1+2y)I[B_{NH_4Cl} + {}^{1}/_{3}(2+y)IC_{NH_4Cl}] + {}^{1}/_{3}(1-y)I[B_{(NH_4)_2SO_4} + {}^{1}/_{3}(2+y)IC_{(NH_4)_2SO_4} + \theta_{ClSO_4}] + {}^{1}/_{3}\,y(2+y)I^2[B'_{NH_4Cl} + C_{NH_4Cl}] + {}^{1}/_{9}(1-y)(2+y)I^2 \times [B'_{(NH_4)_2SO_4} + C_{(NH_4)_2SO_4}] + {}^{1}/_{9}(1-y)(1+2y)I^2\psi_{NH_4ClSO_4} \quad (10)$$

and

$$\ln \gamma_{(NH_4)_2SO_4} = 2f^{\gamma} + {}^{4}/_{3}\,yI[B_{NH_4Cl} + {}^{1}/_{3}(2+y)C_{NH_4Cl} + {}^{1}/_{2}\theta_{ClSO_4}] + {}^{2}/_{9}(4-y)I[B_{(NH_4)_2SO_4} + {}^{1}/_{3}(2+y)IC_{(NH_4)_2SO_4}] + {}^{1}/_{3}\,y(2+y)I^2[2B'_{NH_4Cl} + {}^{4}/_{3}C_{NH_4Cl}] + {}^{1}/_{9}(1-y)(2+y)I^2 \times [2B'_{(NH_4)_2SO_4} + {}^{4}/_{3}C_{(NH_4)_2SO_4}] + {}^{1}/_{9}\,y(4-y)I^2\psi_{NH_4ClSO_4} \quad (11)$$

The coefficients B_{MX} and B'_{MX} for the electrolytes 1−1 and 1−2 are defined as

$$B_{MX} = \beta^{(0)}_{MX} + (2\beta^{(1)}_{MX}/\alpha^2 I)[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})] \quad (12)$$

$$B'_{MX} = (2\beta^{(1)}_{MX}/\alpha^2 I^2)[-1 + (1 + \alpha I^{1/2} + {}^{1}/_{2}\alpha^2 I)\exp(-\alpha I^{1/2})] \quad (13)$$

$$C_{MX} = \frac{C^{\phi}_{MX}}{2|Z_M Z_X|^{1/2}} \quad (14)$$

Table 1. Ratios of Growth K of the NaCl(aq) Droplets, Water Activities a_w, and Osmotic Coefficients of NH_4Cl + $(NH_4)_2SO_4(aq)$ at Total Molalities m_{tot} for Different Ionic-Strength Fractions y of NH_4Cl at 298.15 K[a]

$m_1/mol \cdot kg^{-1}$	$m_2/mol \cdot kg^{-1}$	$m_{tot}/mol \cdot kg^{-1}$	K	a_w	ϕ
		$y = 0.2$			
0.30	0.40	0.70	1.789	0.976_3	0.740
0.45	0.60	1.05	1.562	0.965_3	0.726
0.60	0.80	1.40	1.434	0.954_3	0.721
0.75	1.00	1.75	1.335	0.943	0.724
0.90	1.20	2.10	1.267	0.932	0.724
1.05	1.40	2.45	1.211	0.921	0.725
1.20	1.60	2.80	1.167	0.910	0.727
1.35	1.80	3.15	1.126	0.898	0.737
1.50	2.00	3.50	1.095	0.887	0.740
1.65	2.20	3.85	1.074	0.876	0.742
1.80	2.40	4.20	1.044	0.864	0.751
1.95	2.60	4.55	1.023	0.853	0.754
2.10	2.80	4.90	1.003	0.842	0.758
2.25	3.00	5.25	0.986	0.831	0.761
2.40	3.20	5.60	0.970	0.820	0.765
2.55	3.40	5.95	0.956	0.809	0.769
2.70	3.60	6.30	0.943	0.798	0.773
3.00	4.00	7.00	0.920	0.777	0.778
		$y = 0.5$			
0.30	0.10	0.4	1.152[b]	0.986_5	0.838
0.45	0.15	0.6	1.002[b]	0.980_1	0.826
0.60	0.20	0.8	1.672	0.973_7	0.822
0.90	0.30	1.2	1.497	0.961_0	0.818
1.20	0.40	1.6	1.373	0.948	0.823
1.50	0.50	2.0	1.302	0.936	0.816
1.80	0.60	2.4	1.216	0.923	0.824
2.10	0.70	2.8	1.167	0.910	0.831
2.40	0.80	3.2	1.123	0.897	0.838
2.70	0.90	3.6	1.087	0.884	0.845
3.00	1.00	4.0	1.061	0.872	0.845
3.30	1.10	4.4	1.034	0.859	0.852
3.60	1.20	4.8	1.011	0.846	0.860
3.90	1.30	5.2	0.990	0.834	0.861
4.20	1.40	5.6	0.973	0.822	0.864
4.50	1.50	6.0	0.957	0.810	0.866
5.10	1.70	6.8	0.932	0.788	0.864
5.70	1.90	7.6	0.916[c]	0.766	0.865
		$y = 0.8$			
1.20	0.10	1.30	1.475	0.958_2	0.878
1.80	0.15	1.95	1.302	0.938	0.877
2.16	0.18	2.34	1.236	0.926	0.878
2.40	0.20	2.60	1.199	0.918	0.879
3.00	0.25	3.25	1.123	0.897	0.894
3.36	0.28	3.64	1.090	0.885	0.897
3.60	0.30	3.90	1.069	0.876	0.907
4.20	0.35	4.55	1.028	0.856	0.913
4.56	0.38	4.94	1.003	0.843	0.924
4.80	0.40	5.20	0.992	0.835	0.927
5.40	0.45	5.85	0.963	0.815	0.935
5.76	0.48	6.24	0.950	0.804	0.934
6.00	0.50	6.50	0.940	0.796	0.938
6.60	0.55	7.15	0.921	0.778	0.938
6.96	0.58	7.54	0.917[b]	0.767	0.940

[a] The reference water activity is 0.84, and the reference solution is NaCl(aq). [b] The reference water activity is 0.98. [c] Index 1 denotes NH_4Cl, and 2 denotes $(NH_4)_2SO_4$.

3.4. The Kusik and Meissner (KM) Model. The Kusik and Meissner (KM) model is based on the Bronsted principle of specific interaction, which asserts that electrolyte solution properties are determined primarily by interactions between pairs of oppositely charged ions. For unsymmetrical mixed electrolytes $\{(y)NH_4Cl + (1-y)(NH_4)_2SO_4\}(aq)$ with a common cation of ammonium, the corresponding KM model water activity equation[13,14] is

$$\ln a_w = \left(\frac{2+y}{3}\right) y \ln a^{\circ}_{w,NH_4Cl} + \left(\frac{2+y}{2}\right)(1-y)\ln a^{\circ}_{w,(NH_4)_2SO_4} - 0.003y(1-y)I \quad (15)$$

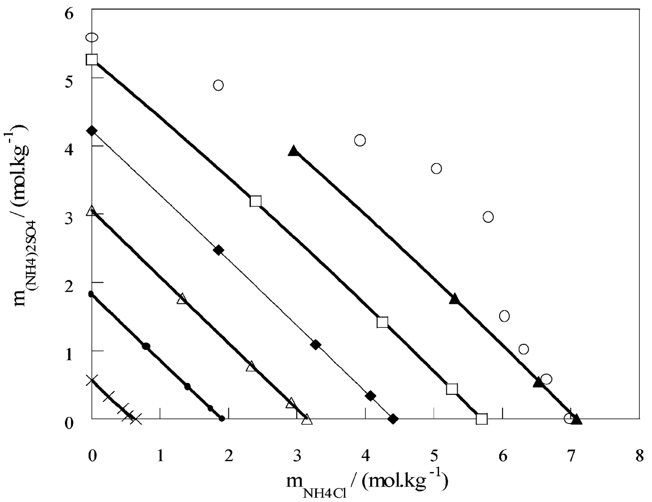

Figure 3. Dependence of molality of $(NH_4)_2SO_4$ versus molality of NH_4Cl in mixed $NH_4Cl-(NH_4)_2SO_4(aq)$ at constant water activity: ×, $a_w = 0.98$; ●, $a_w = 0.94$; △, $a_w = 0.90$; ◆, $a_w = 0.86$; □, $a_w = 0.82$; ▲, $a_w = 0.78$; ○, experimental solubilities data from Linke and Seidell.[15]

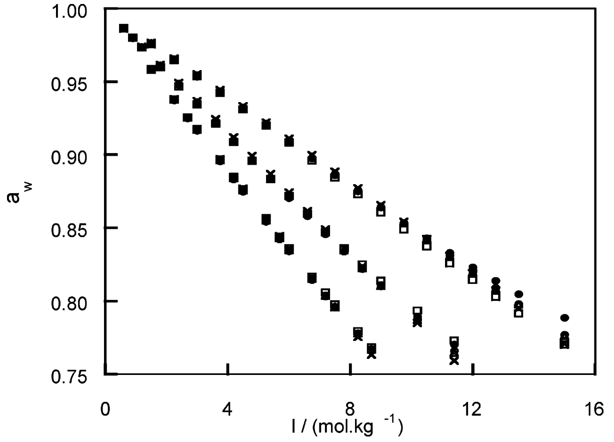

Figure 4. Water activity a_w of $NH_4Cl-(NH_4)_2SO_4(aq)$ against total ionic strength I at different ionic-strength fractions y of 0.2, 0.5, and 0.8; ○, experimental points; ×, KM; ●, LSII; □, Pitzer.

where I is the total ionic strength of the mixture, y is the ionic strength fraction, and $a^{\circ}_{NH_4Cl}$ and $a^{\circ}_{(NH_4)_2SO_4}$ are the single-component water activities at the same ionic strength as that of the mixture.

4. Results and Discussion

4.1. Water Activity and Osmotic Coefficient. The thermodynamics of the mixture of chlorides and sulfates with a common cation of ammonium have not been extensively studied. In this work, a series of measurements of the water activity were made for the mixture $\{(y)NH_4Cl + (1 - y)(NH_4)_2SO_4\}(aq)$ as a function of total molality ranging from 0.4 mol·kg^{-1} to saturation of one of the solutes, with different ionic-strength fractions y of NH_4Cl of 0.2, 0.5, and 0.8 at the temperature 298.15 K. The experimental values of water activity are listed in Table 1.

The molalities of NH_4Cl and $(NH_4)_2SO_4$ at different constant water activities of the ternary mixture were evaluated from experimental data. The plots of water activities and isoactivities on dependence of $m_{(NH_4)_2SO_4}$ of $(NH)_2SO_4$ versus m_{NH_4Cl} of NH_4Cl are represented in Figure 3. The ZSR rule has been used to compare with the measurements. The ZSR predictions agree well with the experimental data for the whole range of a_w studied with a standard deviation of 0.094.

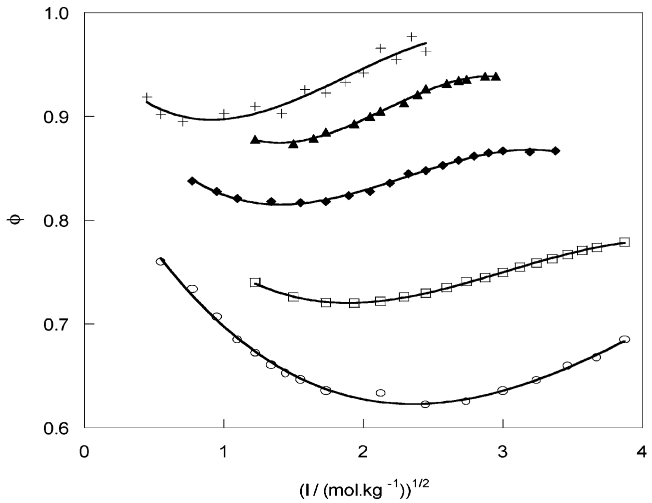

Figure 5. Osmotic coefficient ϕ of $NH_4Cl-(NH_4)_2SO_4(aq)$ against square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions y of $NH_4Cl(aq)$: ○, $y = 0.0$; □, $y = 0.2$; ◆, $y = 0.5$; ▲, $y = 0.8$; +, $y = 1.0$.

Table 2. Pitzer Parameters for NH_4Cl and $(NH_4)_2SO_4$ and Their Mixtures at 298.15 K

electrolyte	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	ref
NH_4Cl	0.0527	0.2011	−0.00306	2
$(NH_4)_2SO_4$	0.04022	0.5911	−0.00106	3

electrolyte	θ_{ClSO_4}	$\psi_{NH_4ClSO_4}$	ref
$NH_4Cl + (NH_4)_2SO_4$	−0.021	0.002	this study

The four models for the predictions of water activity of the mixtures were used to compare with our experimental data (Figure 4). The calculations of thermodynamic properties for mixed electrolyte systems generally require those of the pure component at the same ionic strength I as that of the mixture. In the case of $NH_4Cl(aq)$ and $(NH_4)_2SO_4(aq)$, the required quantities were calculated from data obtained in our previous work.[2,3]

Using the obtained experimental data for the water activity, we had evaluated the osmotic coefficients for different ionic-strength fractions y of NH_4Cl. The obtained osmotic coefficients are listed in Table 1 and are shown in Figure 5.

4.2. Activity Coefficient. 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 Pitzer mixing ionic θ_{ClSO_4} and $\psi_{NH_4ClCO_4}$. These parameters may be used to predict the solute activity coefficients in the mixture. θ_{ClSO_4} and $\psi_{NH_4ClSO_4}$ are estimated by a graphical procedure. This procedure defines the quantity $\Delta\phi$ as the difference between the experimental values ϕ_{exp} and that calculated from eq 8, ϕ_{calc}. This yields

$$\frac{2m_1 + 3m_2}{2m_1m_2}\Delta\phi = \theta_{ClSO_4} + m_{NH_4^+}\psi_{NH_4ClSO_4} \qquad (16)$$

so that a plot of $\Delta\phi$ versus total molality m_{tot} should give a straight line with intercept θ_{ClSO_4} and slope $\psi_{NH_4ClSO_4}$, The standard deviation on ϕ over the entire range of total ionic strengths is $\sigma_{\Delta\phi} = 0.004$. The corresponding values of the ionic parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} of the pure electrolytes $NH_4Cl(aq)$ and $(NH_4)_2SO_4(aq)$ and the unknown Pitzer mixing ionic parameters θ_{ClSO_4} and $\psi_{NH_4ClSO_4}$ are listed in Table 2.

Table 3. Activity Coefficients γ_1 of $NH_4Cl(aq)$ and γ_2 of $(NH_4)_2SO_4(aq)$ in NH_4Cl + $(NH_4)_2SO_4(aq)$ at Total Ionic Strength *I* for Different Ionic-Strength Fractions *y* of NH_4Cl

$y = 0.0$			$y = 0.2$			$y = 0.5$			$y = 0.8$			$y = 1.0$		
I/mol·kg^{-1}	γ_1	γ_2	I/mol·kg^{-1}	γ_1	γ_2	I/mol·kg^{-1}	γ_1	γ_2	I/mol·kg^{-1}	γ_1	γ_2	I/mol·kg^{-1}	γ_1	γ_2
0.3	0.676	0.430	1.50	0.539	0.253	0.6	0.621	0.355	1.50	0.572	0.266	0.2	0.716	0.491
0.6	0.607	0.347	2.25	0.512	0.217	0.9	0.590	0.310	2.25	0.554	0.232	0.3	0.685	0.442
0.9	0.572	0.301	3.00	0.495	0.194	1.2	0.570	0.281	2.70	0.548	0.218	0.5	0.648	0.383
1.2	0.547	0.271	3.75	0.485	0.178	1.8	0.545	0.243	3.00	0.546	0.211	1.0	0.603	0.309
1.5	0.529	0.249	4.50	0.478	0.167	2.4	0.530	0.219	3.75	0.543	0.197	1.5	0.582	0.270
1.8	0.514	0.232	5.25	0.473	0.158	3.0	0.521	0.202	4.20	0.542	0.190	2.0	0.571	0.246
2.1	0.503	0.218	6.00	0.471	0.151	3.6	0.515	0.190	4.50	0.543	0.187	2.5	0.566	0.229
2.4	0.493	0.206	6.75	0.469	0.146	4.2	0.512	0.181	5.25	0.544	0.179	3.0	0.563	0.216
3.0	0.478	0.189	7.50	0.469	0.142	4.8	0.510	0.173	5.70	0.544	0.176	3.5	0.562	0.206
4.5	0.456	0.160	8.25	0.469	0.138	5.4	0.509	0.168	6.00	0.545	0.174	4.0	0.562	0.199
6.0	0.444	0.144	9.00	0.469	0.135	6.0	0.509	0.163	6.75	0.546	0.170	4.5	0.563	0.193
7.5	0.439	0.133	9.75	0.470	0.132	6.6	0.509	0.159	7.20	0.547	0.168	5.0	0.565	0.188
9.0	0.437	0.125	10.50	0.471	0.130	7.2	0.510	0.156	7.50	0.547	0.167	5.5	0.566	0.184
10.5	0.437	0.120	11.25	0.471	0.129	7.8	0.511	0.153	8.25	0.548	0.164	6.0	0.567	0.181
12.0	0.438	0.116	12.00	0.472	0.127	8.4	0.512	0.151	8.70	0.547	0.163			
13.5	0.440	0.113	12.75	0.473	0.126	9.0	0.512	0.149						
15.0	0.442	0.110	13.50	0.473	0.125	10.2	0.513	0.146						
			15.00	0.473	0.123	11.4	0.512	0.144						

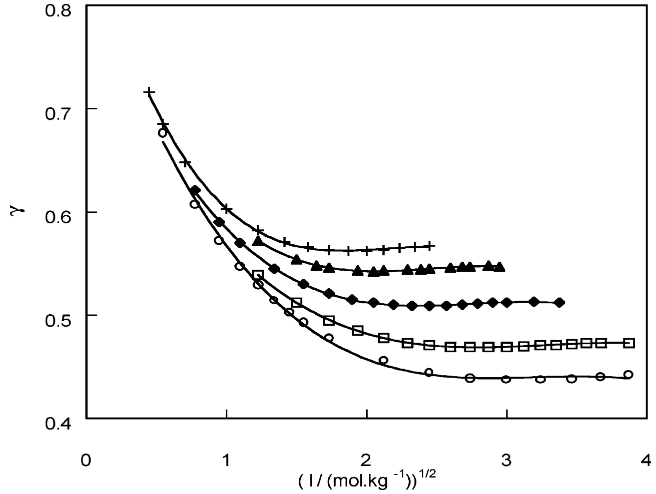

Figure 6. Activity coefficients γ_1 of $NH_4Cl(aq)$ in $NH_4Cl-(NH_4)_2SO_4(aq)$ against square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions *y* of $NH_4Cl(aq)$: ○, $y = 0.0$ (trace of NH_4Cl); □, $y = 0.2$; ◆, $y = 0.5$; ▲, $y = 0.8$; +, $y = 1.0$ (pure NH_4Cl).

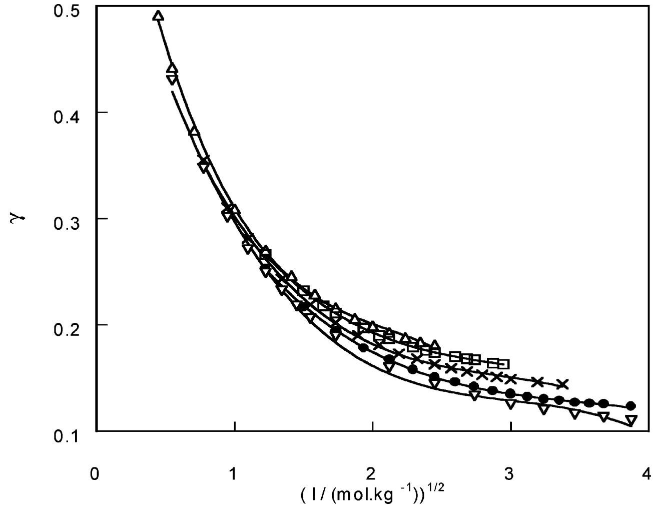

Figure 7. Activity coefficients γ_2 of $(NH_4)_2SO_4(aq)$ in $NH_4Cl-(NH_4)_2SO_4(aq)$ against square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions *y* of $NH_4Cl(aq)$: ▽, $y = 0.0$ (trace of NH_4Cl); ●, $y = 0.2$; ×, $y = 0.5$; □, $y = 0.8$; △, $y = 1.0$ (pure NH_4Cl).

The activity coefficients of $NH_4Cl(aq)$ and $(NH_4)_2SO_4(aq)$ in the mixture, listed in Table 3, were calculated by Pitzer's equation using our newly obtained ionic mixing parameters.

Figures 6 and 7 are plots of $\gamma_1$and γ_2 as a function of $I^{1/2}$. The extremes of composition are illustrated in these figures, that is, the activity coefficients of pure and trace components.

5. Conclusion

The water activities and osmotic coefficients of the NH_4Cl + $(NH_4)_2SO_4(aq)$ system at $T = 298.15$ K from dilute concentration to saturation have been determined for different ionic-strength fractions of NH_4Cl, $y = 0.2$, 0.5, and 0.8, respectively, using the hygrometric method. Good agreement has been obtained for the water activities with the treatment of four commonly thermodynamic models: the Pitzer, Zdanovskii−Stokes−Robinson (ZSR), Lietzke and Stoughton (LS II), and Kusik and Meissner (KM) models. The experimental data are used for the calculation of solute activity coefficients using the ionic-interaction model of Pitzer with our obtained ionic mixing parameters θ_{ClSO_4} and $\psi_{NH_4ClSO_4}$.

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