334 *J. Chem. Eng. Data* **2005,** *50,* 334−339

Thermodynamic Properties of Aqueous Mixed Electrolyte $\{y\mathrm{NH_4NO_3} + (1 - y)\mathrm{NaNO_3}\}$(aq) at T = 298.15 K

Mohamed El Guendouzi* and Mohamed Marouani

Laboratoire de Chimie Physique, Département de Chimie, Faculté des Sciences Ben M'sik, Université Hassan II
Mohammedia, B.P 7955, Casablanca, Morocco

The mixed aqueous electrolyte system with ammonium and sodium nitrate $\{y\mathrm{NH_4NO_3} + (1 - y)\mathrm{NaNO_3}\}$(aq) has been studied by the hygrometric method at a temperature of 298.15 K. The water activity of this system has been measured at total molalities from 0.4 mol·kg^{-1} to about saturation for different ionic-strength fractions, y, of $\mathrm{NH_4NO_3}$ of 0.20, 0.50, and 0.80. The experimental results are compared with the Zdanovskii−Stokes−Robinson (ZSR), Lietzke and Stoughton (LSII), Kusik and Meissner (KM), and Pitzer models. From these measurements, the Pitzer mixing ionic parameters were determined and used to calculate the solute activity coefficients in the mixture. The obtained results were used to calculate the excess Gibbs energy.

1. Introduction

The thermodynamics of aqueous electrolyte solutions continues to be an area of experimental and theorical interest. Knowledge of solution properties is required for understanding many important industrial,[1] biological,[2] environmental,[3] atmospheric,[4−7] and chemistry[8,9] phenomena.

The thermodynamic properties of binary aqueous nitrate[10] solutions and ternary mixed electrolytes were[11−14] determined by the hygrometric method in our previous work. This paper is a continuation of the research of these mixtures. However, very limited data on $\mathrm{Na^+}$ and $\mathrm{NH_4^+}$ mixtures of nitrate are available. Ha et al.[15] studied the water activities from dilute concentration to high supersaturation (0.40 to 0.80) of $\mathrm{NH_4NO_3 + NaNO_3 + H_2O}$ mixtures of mole ratios 1:1 and 3:1 at a temperature of 297.05 K.

In this work, the water activities of the ternary solution $\{y\mathrm{NH_4NO_3} + (1 - y)\mathrm{NaNO_3} + \mathrm{H_2O}\}$ for total molalities in the range from 0.4 mol·kg^{-1} to saturation were performed for different ionic-strength fractions, y ($y = I_{\mathrm{NH_4NO_3}}/(I_{\mathrm{NH_4NO_3}} + I_{\mathrm{NaNO_3}})$, of $\mathrm{NH_4NO_3}$ of 0.20, 0.50, and 0.80 at a temperature of 298.15 K by the hygrometric method. The osmotic coefficients were also evaluated for these solutions from the water activities. The experimental results are compared with the calculations of the Zdanovskii−Stokes−Robinson (ZSR), Kusik and Meissner (KM), Lietzke and Stoughton (LSII), and Pitzer models.

The experimental data are used for the calculation of solute activity coefficients using the Pitzer model with our obtained ionic mixing parameters. From the data obtained for the osmotic and activity coefficients, the excess Gibbs energy was also determined.

2. Experimental Section

The water activity was determined by a hygrometric method described previously.[11] The apparatus consisted of a thread that was suspended over a cup. A droplet of solution was placed on the thread above the cap. The diameter of the droplet was determined with a microscope, fitted with a micrometer scale. The temperature of the hygrometer was maintained to within ±0.02 K. 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) in the vapor phase 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 solutions. In the subsequent experiments, the solution under test was placed in the cap 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 equilibrium diameter, $D(a_\mathrm{w}{=}0.84)$, at this humidity. Knowing the diameter, $D(a_\mathrm{w}{=}0.84)$, of this droplet at a reference relative humidity of 0.84, we can then calculate K and determine graphically the value of a_w (Figure 1). The values of the ratio of growth, K, can be calculated from the equation $K = D(a_\mathrm{w})/D(a_{\mathrm{w(ref)}})$ for reference NaCl(aq) and LiCl(aq). Generally, the reference relative humidity is 0.84. For middle dilute solution, the reference is 0.98.

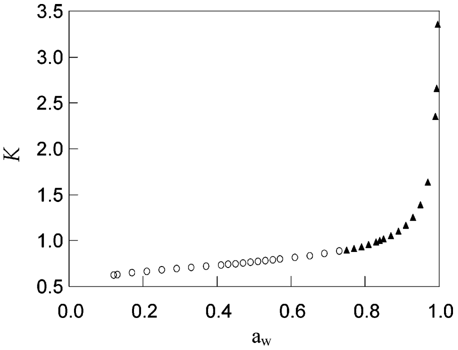

Figure 1. Variation of the ratio K of diameters of the droplets as a function of the water activity, a_w, at h = 0.84: ○, LiCl; ▲, NaCl.

The solutions of NaCl(aq), LiCl(aq), $\mathrm{NH_4NO_3}$(aq), and $\mathrm{NaNO_3}$(aq) were prepared from crystalline material (extrapur-grade chemicals, mass fraction >0.99) and deionized

---

* Corresponding author. E-mail: elguendouzi@yahoo.fr. Fax: (212) (2) 70/46/75.

10.1021/je049884i CCC: $30.25

distilled water. The reference solutions are NaCl(aq) and LiCl(aq).

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 $< \pm 0.01$ mol·kg^{-1}. Several measurements were made of the spherical drops' diameters, and we took the mean of results which are repeats. For one composition, five or more cups were taken. For each cup, five or six measurements adequately were made. 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. The ratio is represented at four significants digits, and the determined $\Delta K/\mathrm{K}$ is (0.1 to 0.05)%. For calculated water activities, the graphs of the variation of the ratio growth of droplets were used as a function of water activity for the reference solution (NaCl or LiCl). Generally, in our study, the data are given, for each cup, with four digits at low molalities and three digits at high molalities. Also, the average water activity is given and determined as 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 $a_{\mathrm{w}} > 0.97$, ±0.05% for $0.97 > a_{\mathrm{w}} > 0.95$, ±0.09% for $0.95 > a_{\mathrm{w}} > 0.90$, and ±0.2% for $0.90 > a_{\mathrm{w}}$. Also, the overall uncertainty of the osmotic coefficient is estimated to be at most ±0.006.

3. Theory and Models

3.1. The Zdanovskii−Stokes−Robinson (ZSR) Rule. The Zdanovskii−Stokes−Robinson (ZSR)[16,17] rule has been used to predict the water activity in mixed electrolyte solutions. The ZSR equation is expressed as

$$\sum_i \frac{m_i}{m_{0,i}(a_{\mathrm{w}})} = 1 \tag{1}$$

where m_i is the molality of species i in a multicomponent solution with a water activity of 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 Kusik and Meissner (KM) Model. The Kusik and Meissner (KM) model[18,19] is based on the Brϕnsted principle of specific interaction, which asserts that electrolyte solution properties are determined primarily by interactions between pairs of oppositely charged ions. For the mixed electrolytes $\{y\mathrm{MX} + (1-y)\mathrm{NX}\}(\mathrm{aq})$, the corresponding KM model water activity equation is

$$\ln a_{\mathrm{w}} = y \ln a^{\circ}_{\mathrm{w,MX}} + (1-y) \ln a^{\circ}_{\mathrm{w,NX}} \tag{2}$$

where y is the ionic-strength fraction and $a^{\circ}_{\mathrm{w,MX}}$ and $a^{\circ}_{\mathrm{w,NX}}$ are the single-component water activities at the same ionic strength as the mixture.

3.3. The Lietzke and Stoughton (LSII) Model. The Lietzke and Stoughton model (LS II)[20,21] predicts the osmotic coefficient of a multicomponent solution by

$$(\nu_{\mathrm{MX}} m_{\mathrm{MX}} + \nu_{\mathrm{NX}} m_{\mathrm{NX}})\phi = \nu_{\mathrm{MX}} m_{\mathrm{MX}} \phi_{\mathrm{MX}} + \nu_{\mathrm{NX}} m_{\mathrm{NX}} \phi_{\mathrm{NX}} \tag{3}$$

where ν_{MX} is the number of ions formed 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.

3.4. The Ion-Interaction Model. The Pitzer model[22−24] is used for calculating the thermodynamic properties of mixed electrolyte solutions. This model requires parameters estimated from common-ion solutions in order to characterize binary interactions among different ions of the same sign and ternary interactions between different ions with equal or unequal signs in a mixed electrolyte solution. The osmotic coefficient of a mixed solution of the two salts $\mathrm{NH_4NO_3}$ and $\mathrm{NaNO_3}$ with the common anion $\mathrm{NO_3}^-$ is given by the Pitzer model as

$$\phi - 1 = z^2 f^{\phi} + m\{(1-y)B^{\phi}_{\mathrm{MX}} + yB^{\phi}_{\mathrm{NX}} + y(1-y)(\theta_{\mathrm{MN}} + I\theta'_{\mathrm{MN}})\} + m^2\{(1-y)C^{\phi}_{\mathrm{MX}} + C^{\phi}_{\mathrm{NX}} + y(1-y)\psi_{\mathrm{MNX}}\} \tag{4}$$

where f^{ϕ} is the long-range electrostatic term, m is the molality of the common ion, which equals the ionic strength of the mixed solution, θ_{MN} is a binary mixing parameter involving unlike ions of the same sign, and ψ_{MNX} is a ternary mixing parameter for two unlike ions of the same sign with a third ion of the opposite sign. This equation can be written as a function of the osmotic coefficient of a single electrolyte as

$$\phi = (1-y)\phi_{\mathrm{MX}} + y\phi_{\mathrm{NX}} + y(1-y)m\theta_{\mathrm{MN}} + y(1-y)m^2\psi_{\mathrm{MNX}} \tag{5}$$

where ϕ_{MX} and ϕ_{NX} are the osmotic coefficients of pure solutions of $\mathrm{NH_4NO_3}$:MX and $\mathrm{NaNO_3}$:NX, respectively, at the same ionic strength as that of the mixed solution. According to the ion-interaction model, these osmotic coefficients of electrolytes of the 1−1 charge type are given by

$$\phi = 1 + f^{\phi} + mB^{\phi} + m^2C^{\phi} \tag{6}$$

The second virial coefficient, B^{ϕ}, is defined as

$$B^{\phi} = \beta^{(0)} + \beta^{(1)} \exp(-\alpha I^{1/2}) \tag{7}$$

$\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} are ion-interaction parameters which are functions of temperature and pressure.

The activity coefficients of $\mathrm{NH_4NO_3}$:MX and $\mathrm{NaNO_3}$:NX, $\gamma_{\mathrm{NH_4NO_3}}$ and $\gamma_{\mathrm{NaNO_3}}$, respectively, in the mixture $\mathrm{NH_4NO_3} + \mathrm{NaNO_3(aq)}$ are given by the Pitzer model as

$$\ln \gamma_{\mathrm{MX}} = \ln \gamma_{\mathrm{MX}}{}^{*} + y\Delta\phi^{*} + ym\{\theta_{\mathrm{MN}} + m(1-y/2)\psi_{\mathrm{MNX}}\} \tag{8}$$

where $\Delta\phi^{*}$ is $(\phi_{\mathrm{NX}}{}^{*} - \phi_{\mathrm{MX}}{}^{*})$ and the asterisk denotes pure components at the same molality as the total molality of the mixture. $\Delta\phi^{*}$ can be expressed as

$$\Delta\phi^{*} = m\{\beta^{(0)}_{\mathrm{NX}} - \beta^{(0)}_{\mathrm{MX}} + h^{\phi}_{1}(\beta^{(1)}_{\mathrm{NX}} - \beta^{(1)}_{\mathrm{MX}}) + m^2(C_{\mathrm{NX}} - C_{\mathrm{MX}})\} \tag{9}$$

where γ^{*} is the solution activity coefficient determined by the ion-interaction model.

For component NX, γ_{NX} is given by the similar equation

$$\ln \gamma_{\mathrm{NX}} = \ln \gamma_{\mathrm{NX}}{}^{*} + (1-y)\Delta\phi^{*} + (1-y)m\{\theta_{\mathrm{MN}} + m(1+y/2)\psi_{\mathrm{MNX}}\} \tag{10}$$

The quantities f, B, and C were calculated from ref 24.

4. Results and Discussion

4.1. Water Activity and Osmotic Coefficient. Measurements of the water activity as a function of molality were performed for the system $\{y\mathrm{NH_4NO_3} + (1-y)\mathrm{NaNO_3}\}(\mathrm{aq})$ for 0.4 mol·kg^{-1} to about saturation at $T =$

Table 1. Ratios of Growth, *K*, of the NaCl(aq) Droplets, Water Activities, a_w, and Osmotic Coefficients of $\{y\mathrm{NH_4NO_3} + (1 - y)\mathrm{NaNO_3}\}$(aq) at Total Molalities, $m_{tot}/(\mathrm{mol \cdot kg^{-1}})$, for Different Ionic-Strength Fractions, *y*, of NH_4NO_3 at T = 298.15 K[a]

m_{NaNO_3}	K	a_w	ϕ	$m_{NH_4NO_3}$	K	a_w	ϕ
	y = 0.00				y = 1.00		
0.1	1.792	(0.9967)	0.917	0.1	1.792	(0.9967)	0.913
0.2	1.426	(0.9935)	0.905	0.2	1.430	(0.9934)	0.892
0.3	1.276	(0.9905)	0.883	0.3	1.282	(0.9907)	0.875
0.4	1.180	(0.9875)	0.873	0.4	1.186	(0.9876)	0.863
0.5	1.099	(0.9845)	0.867	0.5	1.104	(0.9847)	0.854
1.0	1.638	0.9700	0.845	1.0	1.654	0.9703	0.821
1.5	1.450	0.9559	0.835	1.5	1.472	0.9578	0.797
2.0	1.329	0.9420	0.829	2.0	1.346	0.9445	0.778
2.5	1.250	0.9288	0.820	2.5	1.288	0.9348	0.761
3.0	1.191	0.9161	0.811	3.0	1.214	0.9215	0.745
3.5	1.142	0.9033	0.806	3.5	1.178	0.9129	0.730
4.0	1.105	0.8910	0.801	4.0	1.142	0.9030	0.716
4.5	1.077	0.8795	0.792	4.5	1.108	0.8918	0.702
5.0	1.027	0.8560	0.786	5.0	1.087	0.8841	0.687
5.5	1.027	0.8560	0.785	5.5	1.067	0.8749	0.673
6.0	0.901	0.8430	0.790	6.0	1.050	0.8667	0.659

m_{NaNO_3}	$m_{NH_4NO_3}$	m_{tot}	K	a_w	ϕ
		y = 0.20			
0.1	0.4	0.5	1.104	0.9847[b]	0.854
0.2	0.8	1.0	1.652	0.9706	0.828
0.4	1.6	2.0	1.342	0.9437	0.804
0.5	2.0	2.5	1.262	0.9313	0.790
0.6	2.4	3.0	1.201	0.9186	0.785
0.9	3.6	4.5	1.083	0.8831	0.767
1.0	4.0	5.0	1.061	0.8716	0.763
1.3	5.2	6.5	0.999	0.8409	0.740
1.5	6.0	7.5	0.970	0.8207	0.731
1.7	6.8	8.5	0.945	0.8021	0.720
2.0	8.0	10.0	0.920	0.7762	0.703
2.5	10.0	12.5	0.898	0.7362[c]	0.680
3.0	12.0	15.0	0.867	0.7049[c]	0.647
		y = 0.50			
0.2	0.2	0.4	1.166	0.9877[b]	0.860
0.3	0.3	0.6	1.038	0.9819[b]	0.843
0.4	0.4	0.8	1.778	0.9763	0.832
0.5	0.5	1.0	1.658	0.9709	0.821
1.0	1.0	2.0	1.347	0.9447	0.790
2.0	2.0	4.0	1.125	0.8978	0.748
3.0	3.0	6.0	1.031	0.8573	0.712
4.0	4.0	8.0	0.975	0.8237	0.673
5.0	5.0	10.0	0.932	0.7884	0.660
6.0	6.0	12.0	0.904	0.7616	0.630
8.0	8.0	16.0	0.884	0.7199[c]	0.570
		y = 0.80			
0.4	0.1	0.5	1.109	0.9849[b]	0.847
0.8	0.2	1.0	1.660	0.9711	0.815
1.2	0.3	1.5	1.472	0.9580	0.794
2.0	0.5	2.5	1.276	0.9338	0.760
3.2	0.8	4.0	1.137	0.9016	0.700
4.0	1.0	5.0	1.081	0.8815	0.719
6.0	1.5	7.5	1.003	0.8416	0.638
6.8	1.7	8.5	0.981	0.8276	0.618
8.0	2.0	10.0	0.952	0.8059	0.599
10.0	2.5	12.5	0.916	0.7736	0.570
12.0	3.0	15.0	0.896	0.7521	0.527

[a] The reference water activity is 0.84. [b] The values are for a reference water activity of 0.98 (NaCl). [c] The values are for a reference water activity of 0.84 (LiCl).

298.15 K. The experimental values of water activity are listed in Table 1 and shown in Figure 2. Also, the ZSR, LSII, KM, and Pitzer models for the calculations of the water activity of the mixture were used to compare with experimental data.

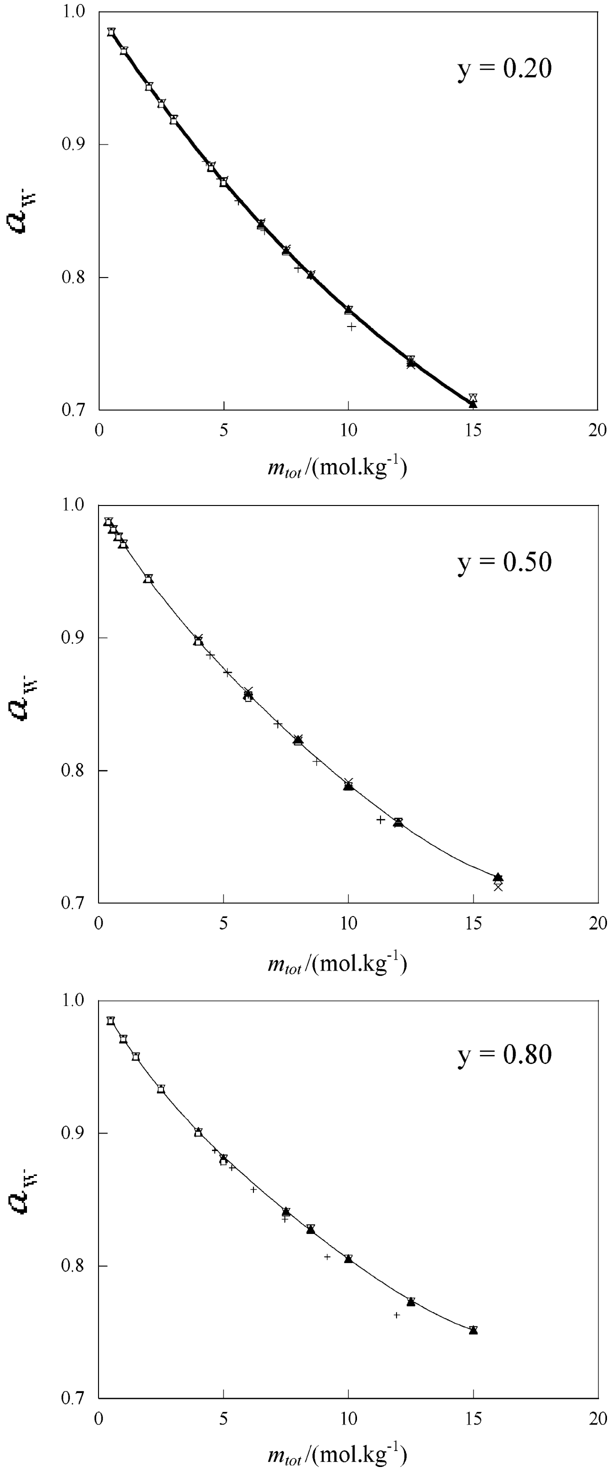

Figure 2. Water activity, a_w, of $\{y\mathrm{NH_4NO_3} + (1 - y)\mathrm{NaNO_3}\}$(aq) against the total molality, m_{tot}, at different ionic-strength fractions, *y*, of NH_4NO_3 (0.20, 0.50, and 0.80): ▲, experimental point; ▽, LSII; △, KM; □, ZSR; ×, Pitzer; +, ref 26.

The plot of NH_4NO_3 molality, $m_{NH_4NO_3}$, as a function of $NaNO_3$ molality, m_{NaNO_3}, is represented in Figure 3. The ZSR rule agrees well with the experimental data for the whole range of a_w studied with a standard deviation of σ_{a_w} = 0.0031.

Using the obtained experimental data for the water activity, we evaluated the osmotic coefficients for different ionic-strength fractions, *y*, of NH_4NO_3. The osmotic coefficients are listed in Table 1 and represented in Figure 4.

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

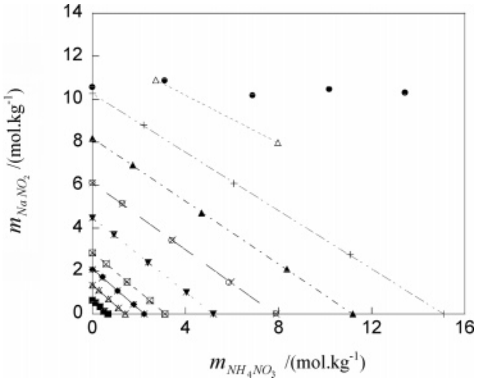

Figure 3. Dependence of the molality of NH_4NO_3, $m_{NH_4NO_3}$, against the molality of $NaNO_3$, m_{NaNO_3}, in mixed $NH_4NO_3-NaNO_3$(aq) at constant water activity, a_w: ■, $a_w = 0.98$; △, $a_w = 0.96$; ◆, $a_w = 0.94$; □, $a_w = 0.92$; ▼, $a_w = 0.88$; ○, $a_w = 0.86$; ×, ZSR model; ●, experimental solubilities data.[25]

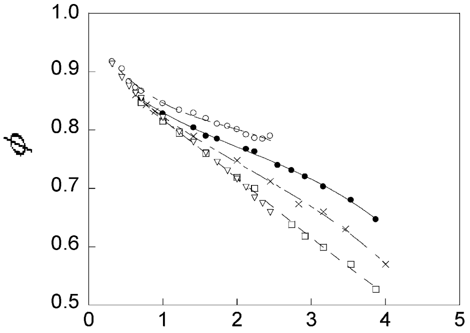

Figure 4. Osmotic coefficient, ϕ, of $\{yNH_4NO_3 + (1 - y)NaNO_3\}$(aq) against the square root of total ionic strength, $I^{1/2}$, at different ionic-strength fractions, y, of NH_4NO_3: ○, $y = 0$; ●, $y = 0.20$; ×, $y = 0.50$; □, $y = 0.80$; ▽, $y = 1$.

Table 2. Ion-Interaction Parameters at $T = 298.15$ K

electrolyte	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	ref
NH_4NO_3	−0.0109	0.07821	−0.0010	10
$NaNO_3$	0.0095	0.1247	−0.0010	10

electrolyte	θ_{MN}	ψ_{MNX}	I_{max}	ref
$NH_4NO_3 + NaNO_3$	−0.0474	0.0053	16	this study

possible to determine the unknown mixed Pitzer parameters θ_{MX} and ψ_{MNX}. These parameters are used to calculate the solute activity coefficients in the mixture. θ_{MX} and ψ_{MNX} are estimated by a graphical procedure. This procedure defines the quantity $\Delta\phi$ as the difference between the experimental values, ϕ_{exptl}, and that calculated from eq 4, ϕ_{calcd}. This yields

$$(m_{tot}/m_{MX}m_{NX})\Delta\phi = \theta_{MN} + \psi_{MNX}m_X \qquad (11)$$

so that a plot of $\Delta\phi$ versus total molality, m_{tot}, should give a straight line with intercept ϕ_{MX} and ψ_{MNX}. The standard deviation is $\sigma_\phi = 0.0084$. The corresponding values of the ionic parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} of the pure electrolytes NH_4NO_3(aq) and $NaNO_3$(aq)[10] and the values of the binary solutions in this range of saturation are extrapolated; the Pitzer mixing ionic parameters θ_{MX} and ψ_{MNX} are listed in Table 2. The comparison of the calculated parameters' thermodynamics and that of the parameters obtained experimentally shows that the Pitzer model permits activity coefficients to be obtained for these ternary solutions and gives good agreement with experimental data because these ion-interaction parameters (θ and ψ) are adjustable to fitting.

The activity coefficients of NH_4NO_3(aq) and $NaNO_3$(aq) in the mixture, listed in Table 3, were calculated by the Pitzer equation using obtained ionic mixing parameters.

The plots of activity coefficients in the mixture divided by the activity coefficient of that same solute in its binary solution at the same ionic strength ($\gamma_{NH_4NO_3}/\gamma^{\circ}_{NH_4NO_3}$ and $\gamma_{NaNO_3}/\gamma^{\circ}_{NaNO_3}$) as a function of the square root of the ionic strength, $I^{1/2}$, are shown in Figures 5 and 6.

4.3. Excess Gibbs Energy. From obtained osmotic coefficient and activity coefficient data, we determined the excess Gibbs energy of $\{yNH_4NO_3 + (1 - y)NaNO_3\}$(aq) using the following expression

$$G^{E} = RT\{\nu_{MX}m_{MX}(1 - \phi + \ln \gamma_{MX}) + \nu_{NX}m_{NX}(1 - \phi + \ln \gamma_{NX})\} \qquad (12)$$

Figure 7 is a plot of the variation of G^{E} against the total molality of the studied system at different ionic-strength fractions, y. The plots are similar and are near.

5. Conclusion

The water activities and osmotic coefficients of the mixture $\{yNH_4NO_3 + (1 - y)NaNO_3\}$(aq) have been determined for total molalites at 298.15 K by the hygrometric method. The obtained water activities are compared with data from the commonly used ZSR, LSII, KM, and

Table 3. Activity Coefficients $\gamma_{NH_4NO_3}$ and γ_{NaNO_3} in $\{yNH_4NO_3 + (1 - y)NaNO_3\}$(aq) at Total Ionic Strength, I, for Different Ionic-Strength Fractions, y, of NH_4NO_3

$y = 0.0$			$y = 20.0$			$y = 50.0$			$y = 80.0$			$y = 1$		
I / mol·kg^{-1}	$\gamma_{NH_4NO_3}$	γ_{NaNO_3}	I / mol·kg^{-1}	$\gamma_{NH_4NO_3}$	γ_{NaNO_3}	I / mol·kg^{-1}	$\gamma_{NH_4NO_3}$	γ_{NaNO_3}	I / mol·kg^{-1}	$\gamma_{NH_4NO_3}$	γ_{NaNO_3}	I / mol·kg^{-1}	$\gamma_{NH_4NO_3}$	γ_{NaNO_3}
0.1	0.746	0.753	0.5	0.581	0.601	0.4	0.608	0.618	0.5	0.584	0.587	0.1	0.746	0.746
0.2	0.680	0.693	1.0	0.498	0.530	0.6	0.562	0.575	1.0	0.504	0.507	0.2	0.681	0.681
0.3	0.638	0.655	2.0	0.410	0.457	0.8	0.529	0.543	1.5	0.455	0.458	0.3	0.640	0.639
0.4	0.606	0.628	2.5	0.380	0.434	1.0	0.501	0.518	2.5	0.391	0.395	0.4	0.609	0.608
0.5	0.580	0.606	3.0	0.356	0.415	2.0	0.415	0.440	4.0	0.331	0.336	0.5	0.585	0.583
1.0	0.496	0.537	4.5	0.304	0.374	4.0	0.326	0.361	5.0	0.302	0.308	1.0	0.505	0.499
1.5	0.444	0.497	5.0	0.290	0.364	6.0	0.275	0.318	7.5	0.248	0.261	1.5	0.457	0.449
2.0	0.406	0.468	6.5	0.257	0.338	8.0	0.239	0.288	8.5	0.231	0.247	2.0	0.422	0.411
2.5	0.376	0.446	7.5	0.240	0.324	10.0	0.213	0.267	10.0	0.208	0.230	2.5	0.394	0.381
3.0	0.351	0.429	8.5	0.226	0.312	12.0	0.192	0.251	12.5	0.177	0.210	3.0	0.371	0.357
3.5	0.331	0.414	10.0	0.208	0.295	16.0	0.162	0.230	15.0	0.151	0.196	3.5	0.351	0.336
4.0	0.313	0.402	12.5	0.185	0.272							4.0	0.333	0.318
4.5	0.297	0.390	15.0	0.169	0.252							4.5	0.317	0.302
5.0	0.284	0.380										5.0	0.303	0.289
5.5	0.271	0.371										5.5	0.290	0.276
6.0	0.260	0.363										6.0	0.277	0.265

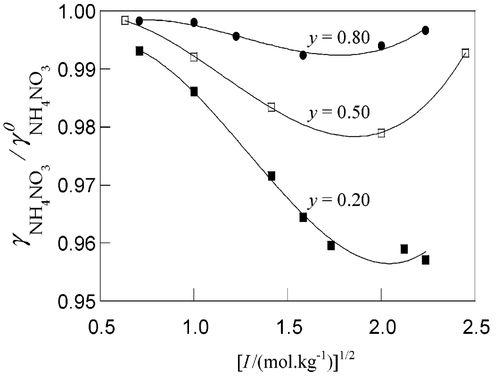

Figure 5. Activity coefficients of NH_4NO_3(aq), $\gamma_{NH_4NO_3}$, in the mixture $\{yNH_4NO_3 + (1 - y)NaNO_3\}$(aq) divided by the activity coefficient in its binary solution, $\gamma^\circ_{NH_4NO_3}$:($\gamma_{NH_4NO_3}/\gamma^\circ_{NH_4NO_3}$), against the square root of total ionic strength, $I^{1/2}$, at different ionic-strength fractions, y, of NH_4NO_3: ■, $y = 0.20$; □, $y = 0.50$; ●, $y = 0.80$.

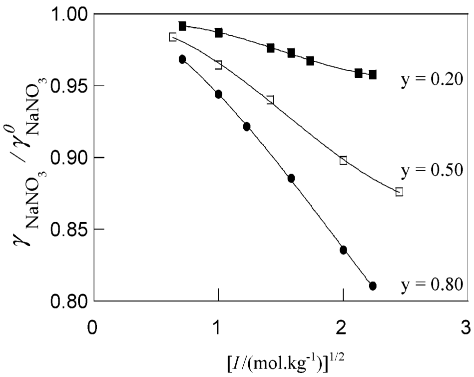

Figure 6. Activity coefficients of $NaNO_3$(aq), γ_{NaNO_3}, in the mixture $\{yNH_4NO_3 + (1 - y)NaNO_3\}$(aq) divided by the activity coefficient in its binary solution, $\gamma_{NH_4NO_3}$:($\gamma_{NaNO_3}/\gamma^\circ_{NaNO_3}$), against the square root of total ionic strength, $I^{1/2}$, at different ionic-strength fractions, y, of NH_4NO_3: ■, $y = 0.20$; □, $y = 0.50$; ●, $y = 0.80$.

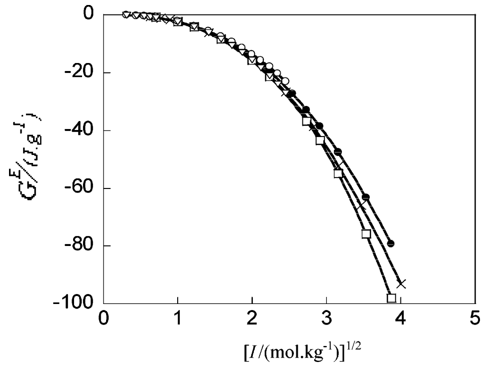

Figure 7. Excess Gibbs energy of $\{yNH_4NO_3 + (1 - y)NaNO_3\}$(aq) against the square root of total ionic strength, $I^{1/2}$, at different ionic-strength fractions, y, of NH_4NO_3: ○, $y = 0$; ●, $y = 0.20$; ×, $y = 0.50$; □, $y = 0.80$; ▽, $y = 1$.

Pitzer thermodynamic models. The comparison of the calculated parameters' thermodynamics and that of the parameters obtained experimentally shows that the Pitzer model permits activity coefficients for these ternary solutions to be obtained and gives good agreement with experimental data because these ion-interaction parameters (θ and ψ) are adjustable to fitting. The experimental data are used for the calculation of solute activity coefficients using the Pitzer model with our obtained ionic mixing parameters. These parameters have been evaluated at $\theta_{MX} = -0.0474$ and $\psi_{MNX} = 0.0053$. From the obtained data of the osmotic and activity coefficients, the excess Gibbs energy is also determined.

Literature Cited

(1) Oakes, C. S.; Femly, A. R.; Sterner, S. M. Thermodynamic proprieties of aqueous calcium nitrate $\{Ca(NO_3)_2\}$ to the temperature 373 K including new enthalpy of dilution data. *J. Chem. Thermodyn.* **2000**, *32*, 29−54.

(2) Khavanninzadeh, A.; Modarress, H.; Taghikhani, V.; Khoshkbarchi, M. K. Activity coefficients of electrolyte and amino acid in the systems (water + potassium chloride + DL-valine) at T = 298.15 K and (water + sodium chloride + L-valine) at T = 308.15 K. *J. Chem. Thermodyn.* **2002**, *34*, 1297−1309.

(3) Peng, C.; Chan, C. K. The water cycles of water-soluble organic salts of atmospheric importance. *Atmos. Environ.* **2001**, *35*, 1183−1192.

(4) Chan, C. K.; Ha, Z.; Choi, Y. M. Study of water activities of aerosols of mixtures of sodium and magnesium salts. *Atmos. Environ.* **2000**, *34*, 4795−4803.

(5) Ansari, A. S.; Pandis, S. N. The effect of metastable equilibrium states on the partitioning of nitrate between the gas and aerosol phases. *Atmos. Environ.* **2000**, *34*, 157−168.

(6) Zhang, Y.; Seigneur, C.; Seinfeld, J. H.; Jacobson, M.; Clegg, S. L.; Binkowski, F. S. A comparative review of inorganic aerosol thermodynamique equilibrium modules: similarities, differences, and their likely causes. *Atmos. Environ.* **2000**, *34*, 117−137.

(7) Choi, M. Y.; Chan, C. K. Continuous Measurements of the Water Activities of the $Mg^{2+}-Ca^{2+}-Na^+-Cl^--NO_3^--SO_4^{2-}-H_2O$ System. *J. Chem. Eng. Data* **2002**, *47*, 1526−1531.

(8) Ally, M. R.; Clegg, S. L.; Braunstein, J.; Simonson, J. M. A BET model of the thermodynamics of aqueous multicomponent solutions at extreme concentration. *J. Chem. Thermodyn.* **2001**, *33*, 905−915.

(9) Christov, C. Thermodynamics of formations of ammonium, sodium and potassium alums and chromium. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **2002**, *26*, 85−94.

(10) El Guendouzi, M.; Marouani, M. Water Activities and Osmotic and Activity Coefficients of Aqueous Solutions of Nitrates at 25 °C by the Hygrometric Method. *J. Solution Chem.* **2003**, *32*, 535−546.

(11) El Guendouzi, M.; Errougui, A. Thermodynamic Properties of the Mixed Electrolytes $\{yNH_4Cl + (1 - y)(NH_4)_2SO_4\}$(aq) at the Temperature 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 186−191.

(12) El Guendouzi, M.; Benbiyi, A.; Dinane, A.; Azougen, R. Determination of Water Activities, Osmotic and Activity Coefficients of the System $LiCl-KCl-H_2O$ at the Temperature 298.15 K. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **2003**, *27*, 213-219.

(13) El Guendouzi, M.; Azougen, R.; Mounir, A.; Benbiyi, A. Water Activities, Osmotic and Activity Coefficients of the System $(NH_4)_2SO_4-K_2SO_4-H_2O$ at the Temperature 298.15 K. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **2004**, *27*, 409−414.

(14) El Guendouzi, M.; Marouani, M. Thermodynamic Properties of the System $NH_4NO_3-KNO_3-H_2O$ at 298.15 K. *Fluid Phase Equilib.* **2004**, *216*, 249−254.

(15) Ha, Z.; Choy, L.; Chan, C. K. Study of water activities of supersaturated aerosols of sodium and ammonium salts. *J. Geophys. Res.* **2000**, *105*, 11699−11709.

(16) Zdanovskii, A. B. New methods of calculating solubilities of electrolytes in multicomponent systems. *Zh. Fiz. Khim.* **1948**, *22*, 1475−1485.

(17) Robinson, R. A.; Stokes, R. H. *Electrolyte solutions*, 2nd ed.; Butterworth: London, 1970.

(18) Kusik, C. L.; Meissner, H. P. Electrolyte Activity Coefficients in Inorganic Processing.1 *AIChE Symp. Ser.* **1978**, *173*, 14−20.

(19) Stelson, A. W.; Bassett, M. E.; Seinfeld, J. H. Thermodynamic equilibrium Properties of aqueous solutions of Nitrate, sulfate and Ammonium. In *Chemistry of Particles, Fogs and Rain*; Durham, J. L., Ed.; Butterworth: Boston, MA, 1984; pp 1−52.

(20) Lietzke, M. H.; Stoughton, R. W. Simple empirical equation for the prediction of the activity coefficients value of each component in aqueous electrolyte mixtures containing a common ion. *J. Solution Chem.* **1972**, *1*, 299−308.

(21) Lietzke, M. H.; Stoughton, R. W. Model for Electrolyte Solutions to Aqueous Mixed Electrolyte Systems. *J. Inorg. Nucl. Chem.* **1975**, *37*, 2503.

(22) Pitzer, K. S. Thermodynamics of electrolytes. Theoretical Basis and General Equations. *J. Phys. Chem.* **1973**, *77*, 268−277.

(23) Pitzer, K. S.; Mayorga, G. Thermodynamics of Electrolytes. II. Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent. *J. Phys. Chem.* **1973**, *77*, 2300−2307.

(24) Pitzer, K. S.; Kim, J. Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mixed Electrolytes. *J. Am. Chem. Soc.* **1974**, *96*, 5701−5707.

(25) Linke, W. F.; Seidell, A. *Solubilities of Inorganic and Metal-organic Compounds*; American Chemical Society: Washington, DC, 1965.

(26) Kirgintsev, A. N.; Luk'ynov, A. V. Isopiestic investigation of ternary solutions. VI aqueous ternary solutions containing sodium nitrate with the nitrates of lithium, potassium, ammonium, rubidium, and caesium, respectively. *Russ. J. Phys. Chem.* **1965**, *39*, 653−655.

Received for review March 22, 2004. Accepted November 14, 2004.

JE049884I