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Thermodynamic Properties of Aqueous Mixtures of Magnesium and Ammonium Sulfates

Mohamed El Guendouzi,* Abdelfetah Mounir, and Abderrahim Dinane

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

The mixture $\{y\mathrm{MgSO_4} + (1 - y)(\mathrm{NH_4})_2\mathrm{SO_4}\}(\mathrm{aq})$ has been studied with the hygrometric method at the temperature 298.15 K. The relative humidities of this system are measured at total molalities from 0.2 $\mathrm{mol \cdot kg^{-1}}$ to about saturation for different ionic-strength fractions of $\mathrm{MgSO_4}$ with $y = 0.2$, 0.5, and 0.8. The results allow the deduction of new water activities and osmotic coefficients. The experimental results are compared with the predictions of the ECA law (extended composed additivity) and the Zdanovskii−Stokes−Robinson (ZSR), Pitzer, and LS II 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

Activity and osmotic coefficient data of aqueous mixed electrolyte solutions are of great interest in fields such as desalination, oceanography, biology, geochemistry, atmospheric processes, and environment.

Several methods are used for the determination of thermodynamic properties in mixed electrolyte solutions.[1−6] In this work, we use the hygrometric method described in the previous paper,[7] which yields the water activity in aqueous solutions containing electrolytes directly. This method has been used for determining thermodynamic properties of binary aqueous chlorides,[8] sulfate[9] solutions, and mixed electrolytes.[10−13] This paper is the continuation of the research on ternary aqueous mixtures of electrolytes. The main objectives are to determine thermodynamic properties for the ternary solutions of $\mathrm{MgSO_4} + (\mathrm{NH_4})_2\mathrm{SO_4} + \mathrm{H_2O}$ by the hygrometric method. The measurements of relative humidities for the total molality range from 0.2 $\mathrm{mol \cdot kg^{-1}}$ until the saturation of one of the solutes were performed for ternary aqueous solutions, for different ionic-strength fractions y of $\mathrm{MgSO_4}$ ranging from 0.2 to 0.5 to 0.8 at the temperature 298.15 K. The osmotic coefficients are also evaluated for these solutions from the water activities.

We have used the extended composed additivity (ECA) rule proposed in our previous paper [11] to predict water activities of this system. The results are compared with calculated values from three commonly used thermodynamic 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.[7] It is based on the measurement of the relative humidity over aqueous solution containing nonvolatile electrolytes.

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 is then placed in a thermostated box. 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 of 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,[1,14−16] the dependence of the relative humidity on the 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.

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,

$$\mathrm{rh} = P_\mathrm{w}/P_\mathrm{w}^\circ = a_\mathrm{w} \tag{1}$$

where P_w is the partial pressure of the water vapor over the salt solution at the temperature T and P_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 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

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* E-mail: elguendouzi@yahoo.fr. Telephone: (212) (22) 70-46-71/74. Fax: (212) (22) 70-46-75.

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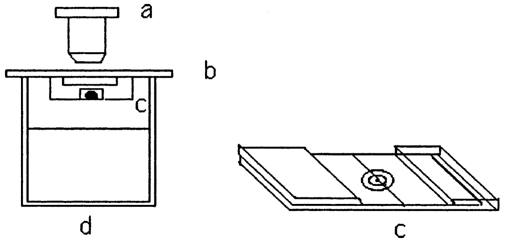

Figure 1. Description of materials used in the hygrometric apparatus: (a) microscope; (b) lid; (c) support of the drops; (d) cup.

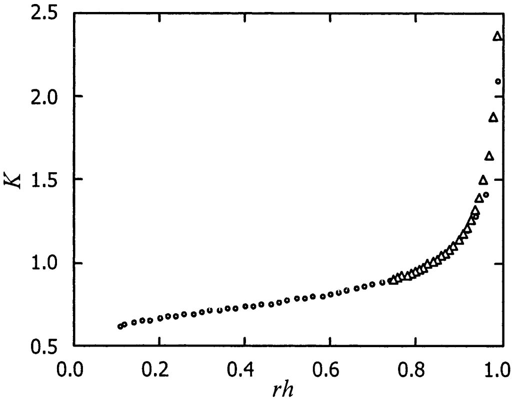

Figure 2. Variation of the ratio K of diameters of the droplets as a function of the relative humidity a_w for LiCl (○) and NaCl (△).

the 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

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

where $c(a_{ref})$ and $c(a_w)$ 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 the vapor phase of 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 of the relative humidity can therefore be determined from measurement of the drop equilibrium diameter $D(a_w)$ at this humidity. Knowing the diameter $D(a_{ref})$ 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 the 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, $MgSO_4$, and $(NH_4)_2SO_4$ were prepared from crystalline material (Extrapur-grade chemicals, NaCl 99.50%, $MgSO_4$ 99.00%, and $(NH_4)_2SO_4$ 99.00%) and deionized distilled water. The reference solution is NaCl(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 less than $\pm$ 0.01 $mol{\cdot}kg^{-1}$. 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 is therefore less than $\pm 0.02\%$ for $a_w > 0.97$, $\approx \pm 0.05\%$ for $a_w > 0.95$, $\approx \pm 0.09\%$ for $a_w > 0.90$, and $\approx \pm 0.2\%$ for $a_w > 0.85$.

3. Theory and Models

3.1. Zdanovskii–Stokes–Robinson (ZSR) Rule. The Zdanovskii–Stokes–Robinson (ZSR) rule[17,18] 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 a water activity of a_w and $m_{0,i}(a_w)$ is the molality of the single-component solution at the same a_w.

3.2. Extended Composed Additivity (ECA) Rule. The application of the theory to the calculation of thermodynamic properties often involves equations highly complex in form and containing interaction parameters, which are not always readily available for mixed electrolytes at concentrations of practical interest. We have proposed in our earlier work[11] a simple mixing rule which allows the properties of mixed electrolyte solutions to be predicted from those of the aqueous solutions of the individual component salts. This ECA "extended composed additivity" rule predicts the water activity in mixed electrolyte solutions by

$$a_w = -1 + a_{w(MX)} + a_{w(NX)} - m_{MX}m_{NX}\lambda - m_{MX}m_{NX}m_{tot}\delta \tag{7}$$

where the parameters λ and δ, determined experimentally for each system, characterize the deviation from ideality in the mixture of MX and NX for a concentrated solution. In general, these quantities depend on the composition and the water activity. In most cases, however, these parameters are fairly constant and arithmetical mean values over a water activity range are used. For electrolytes of higher valence,[12] we have replaced the molality by the ionic strength, and this equation becomes

$$a_w = -1 + a_{w(MX)} + a_{w(NX)} - I_{MX}I_{NX}\lambda - I_{MX}I_{NX}I\delta \tag{8}$$

The unknowns λ and δ may be estimated by a graphical procedure using the modified expression of eq 8

$$\frac{\Delta a_w}{I_{MX}I_{NX}} = -\lambda - I\delta \tag{9}$$

where Δa_w is the difference between the experimental values of water activity a_w and that calculated from eq 8 with $\lambda = 0$ and $\delta = 0$. The quantity on the left was plotted against the total ionic strength I to obtain a linear plot with intercept λ and slope δ.

3.3. Lietzke and Stoughton Model. The Lietzke and Stoughton model (LS II)[19,20] predicts the osmotic coefficient of a multicomponent solution by

$$(\nu_{MX}m_{MX} + \nu_{NX}\mathrm{m}_{NX})\phi = \nu_{MX}m_{MX}\phi_{MX} + \nu_{NX}m_{NX}\phi_{NX} \quad (10)$$

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.

3.4. Ion Interaction Model. The Pitzer model[21−24] 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 $MgSO_4$ and $(NH_4)_2SO_4$ with a common anion is given by Pitzer's model as

$$\phi - 1 = (2 - y)^{-1}[4f^{\phi} + {}^{1}/_{12}(4 - y)yI\{B^{\phi} + {}^{1}/_{12}C^{\phi}_{MgSO_4}(4 - y)\} + {}^{2}/_{9}(4 - y)(1 - y)I\{B^{\phi}_{(NH_4)_2SO_4} + (2^{-1/2}/6)C^{\phi}_{(NH_4)_2SO_4}(4 - y)I\} + {}^{2}/_{3}y(1 - y)I\{\theta_{Mg^{2+}NH_4^+} + {}^{1}/_{12}\psi_{Mg^{2+}NH_4^+SO_4^{2-}}(4 - y)I\}] \quad (11)$$

where f^{ϕ} is the long-range electrostatic term, I is the ionic strength of the common ion, $\theta_{Mg^{2+}NH_4^+}$ is a binary mixing parameter involving unlike ions of the same sign, and $\psi_{Mg^{2+}NH_4^+SO_4^{2-}}$ 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} for electrolyte 1−2 is defined as

$$B^{\phi} = \beta^{(0)} + \beta^{(1)} \exp(-\alpha I^{1/2}) \quad (12)$$

and that for electrolyte 2−2 is defined as

$$B^{\phi} = \beta^{(0)} + \beta^{(1)} \exp(-\alpha_1 I^{1/2}) + \beta^{(2)} \exp(-\alpha_2 I^{1/2}) \quad (13)$$

$\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} are ion interaction parameters which are functions of temperature and pressure; $\alpha = 2\ (\mathrm{mol{\cdot}kg^{-1}})^{-1}$, $\alpha_1 = 1.4\ (\mathrm{mol{\cdot}kg^{-1}})^{-1}$, and $\alpha_1 = 12\ (\mathrm{mol{\cdot}kg^{-1}})^{-1}$.

The activity coefficients γ_{MgSO_4} of $MgSO_4$ and $\gamma_{(NH_4)_2SO_4}$ of $(NH4)_2SO_4$ in a common-ion mixture of $MgSO_4-(NH_4)_2SO_4(aq)$ are given by Pitzer's model as

$$\ln \gamma_{MgSO_4} = 4f^{\gamma} + {}^{1}/_{6}(2 + y)I\{B^{\gamma}_{MgSO_4} + {}^{1}/_{3}(1 - \mathrm{y})I\psi_{Mg^{2+}NH_4^+SO_4^{2-}}\} + {}^{1}/_{12}(4 - y)I^2\{{}^{1}/_{6}(4 + 5y)C_{MgSO4} + yB'_{MgSO_4} + {}^{8}/_{3}(1 - y)(C_{(NH_4)_2SO_4} + B'_{(NH_4)_2SO_4})\} + {}^{2}/_{3}(1 - y)I(B^{\gamma}_{(NH_4)_2SO_4} + \theta_{Mg^{2+}NH_4^+}) \quad (14)$$

and

$$\ln \gamma_{(NH_4)_2SO_4} = 2f^{\gamma} + {}^{1}/_{9}(8 - 5y)I\{B^{\gamma}_{(NH_4)_2SO_4} + {}^{1}/_{8}y\mathrm{I}\psi_{Mg^{2+}NH_4^+SO_4^{2-}}\} + {}^{1}/_{18}(4 - y)I^2\{(4 - 3y)C_{(NH_4)2SO_4} + yC_{MgSO_4} + 2(1 - y)B'_{(NH_4)_2SO_4} + {}^{3}/_{4}yB'_{MgSO_4}\} + {}^{1}/_{6}yI(B^{\gamma}_{MgSO_4} + 2\theta_{Mg^{2+}NH_4^+}) \quad (15)$$

Table 1. Ratios of Growth K of the NaCl(aq) Droplets, Water Activities a_w, and Osmotic Coefficients of $MgSO_4-(NH_4)_2SO_4(aq)$ at Total Molalities m_{tot} for Different Ionic-Strength Fractions y of $MgSO_4$ at 298.15 K[a]

m_1/mol·kg^{-1}	m_2/mol·kg^{-1}	m_{tot}/mol·kg^{-1}	K	a_w	ϕ
		$y = 0.2$			
0.10	0.53	0.63	1.850	0.9791	0.651
0.12	0.64	0.76	1.758	0.9754	0.641
0.15	0.80	0.95	1.636	0.9699	0.628
0.17	0.96	1.13	1.548	0.9643	0.626
0.20	1.07	1.27	1.499	0.9603	0.625
0.22	1.17	1.39	1.458	0.9565	0.625
0.25	1.33	1.58	1.396	0.9505	0.626
0.27	1.44	1.71	1.360	0.9464	0.629
0.30	1.60	1.90	1.319	0.9405	0.631
		$y = 0.5$			
0.15	0.20	0.30	(1.508)	0.9895	0.651
0.18	0.24	0.42	(1.180)	0.9875	0.645
0.23	0.30	0.53	(1.104)	0.9847	0.634
0.27	0.36	0.63	(1.028)	0.9818	0.628
0.30	0.40	0.70	(1.000)	0.9800	0.623
0.33	0.44	0.77	1.826	0.9782	0.619
0.38	0.50	1.75	1.761	0.9755	0.612
0.42	0.56	0.98	1.690	0.9725	0.614
0.45	0.60	1.05	1.648	0.9705	0.616
0.48	0.64	1.12	1.614	0.9687	0.614
0.53	0.70	1.23	1.560	0.9658	0.613
0.57	0.76	1.33	1.528	0.9628	0.615
0.60	0.80	1.40	1.505	0.9608	0.617
		$y = 0.8$			
0.30	0.10	0.40	(1.694)	0.9905	0.589
0.36	0.12	0.48	(1.218)	0.9887	0.586
0.45	0.15	0.60	(1.137)	0.9860	0.580
0.54	0.18	0.72	(1.070)	0.9833	0.577
0.60	0.20	0.80	(1.030)	0.9816	0.573
0.66	0.22	0.88	1.864	0.9797	0.576
0.75	0.25	1.00	1.793	0.9768	0.579
0.84	0.28	1.12	1.705	0.9739	0.583
0.90	0.30	1.20	1.674	0.9718	0.588
0.96	0.32	1.28	1.633	0.9697	0.593
1.05	0.35	1.40	1.580	0.9664	0.602
1.14	0.38	1.52	1.530	0.9629	0.613
1.20	0.40	1.60	1.500	0.9606	0.620
1.26	0.42	1.68	1.473	0.9580	0.630
1.35	0.45	1.80	1.432	0.9541	0.644

[a] The reference water activity is 0.84; the numbers in parentheses are for a reference water activity of 0.98 (the index 1 denotes $MgSO_4$, and 2 denotes $(NH_4)_2SO_4$).

The coefficient B'_{MX} for electrolyte 1−2 is defined as

$$B'_{MX} = (\beta^{(1)}/\alpha^2 I^2)[(-1 + (1 + \alpha I^{1/2} + {}^{1}/_{2}\alpha^2 I)) \exp(-\alpha I^{1/2})] \quad (16)$$

and that for electrolyte 2−2 is defined as

$$B'_{MX} = (\beta^{(1)}/\alpha_1{}^2 I^2)[(-1 + (1 + \alpha_1 I^{1/2} + {}^{1}/_{2}\alpha_1{}^2 I)) \times \exp(-\alpha_1 I^{1/2})] + (\beta^{(2)}/\alpha_2{}^2 I^2)[(-1 + (1 + \alpha_2 I^{1/2} + {}^{1}/_{2}\alpha_2{}^2 I)) \exp(-\alpha_2 I^{1/2})] \quad (17)$$

4. Results and Discussion

4.1. Water Activity and Osmotic Coefficient. The thermodynamics of the mixture of magnesium and ammonium sulfates has not been extensively studied. In this work, a series of measurements of the water activity were made for the mixture $\{yMgSO_4 + (1 - y)(NH_4)_2SO_4\}(aq)$ as a function of total molality ranging from 0.2 mol·kg^{-1} to about saturation of one of the solutes, with different ionic-strength fractions y of $MgSO_4$ ranging from 0.2 to 0.5

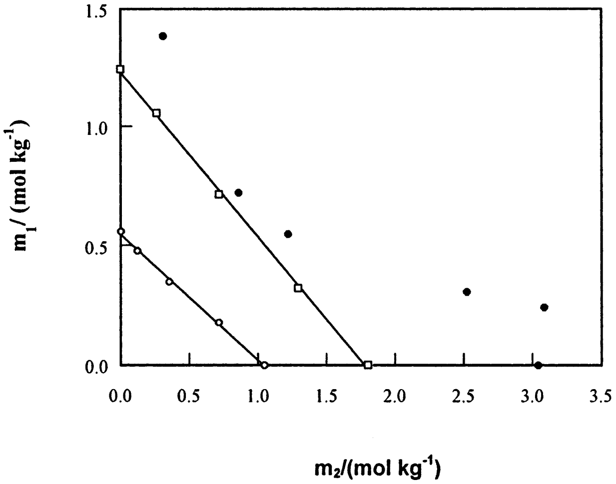

Figure 3. Dependence of molality of $MgSO_4$ m_2 versus molality of $(NH_4)_2SO_4$ m_1 in mixed $MgSO_4-(NH_4)_2SO_4(aq)$ at constant water activity a_w at 298.15 K: ▽, 0.98; ○, $a_w = 0.96$; ×, ZSR model; ●, experimental solubility data.[25]

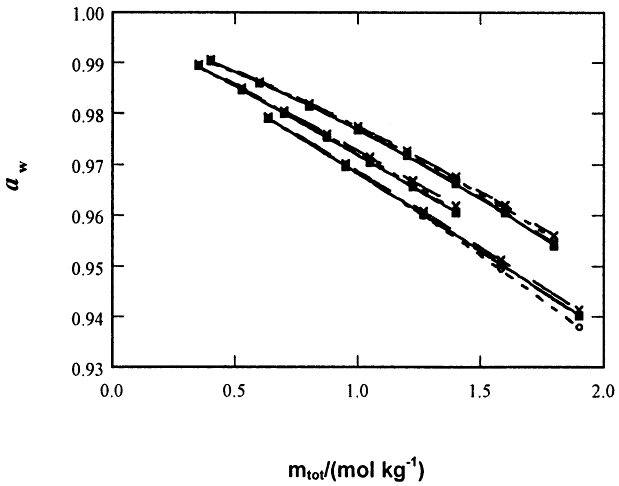

Figure 4. Water activity a_w of $MgSO_4-(NH_4)_2SO_4(aq)$ against total molality m_{tot} at different ionic-strength fractions y of $MgSO_4$ of 0.2, 0.5, and 0.8 at 298.15 K: △ (—), experimental points; ○ (- - -), ECA rule; × (- —), LS; □ (· · ·), Pitzer.

to 0.8 at the temperature 298.15 K. The experimental values of water activity are listed in Table 1.

The molalities of $MgSO_4$ 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, as the dependence of m_2 of $(NH)_2SO_4$ versus m_1 of $MgSO_4$, are represented in Figure 3. The ZSR rule has been used to compare the measurements. The ZSR predictions agree well with the experimental data for the whole range of a_w studied with a standard deviation of 0.032.

We used the ECA rule for the system $MgSO_4-(NH_4)_2SO_4(aq)$, and the suggested values of associated parameters are $\delta = -0.001\,22$ $(mol{\cdot}kg^{-1})^{-2}$ and $\lambda = 0.000\,261$ $(mol{\cdot}kg^{-1})^{-3}$. The standard deviation for the fit is $\sigma_{aw} = 0.0005$. Extensive tests on the validity of eq 8 have been carried out, and it is shown that a_w values calculated by employing the assigned values of δ and λ are in good agreement (±0.04% error on the average) with experimental values (Figure 4).

Two models for the predictions of water activities of the mixtures were used to compare with our ECA rule. 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 $MgSO_4(aq)$ and $(NH_4)_2SO_4(aq)$, the required quantities were calculated from data obtained in our previous work.[12] The comparison of the water activities shows that the experimental values and those calculated with the ECA rule (eq 8) are very close to the values calculated from the two models up to the values of the molality range as shown in Figure 4. The average difference is less than ±0.001 between our ECA rule and the two models.

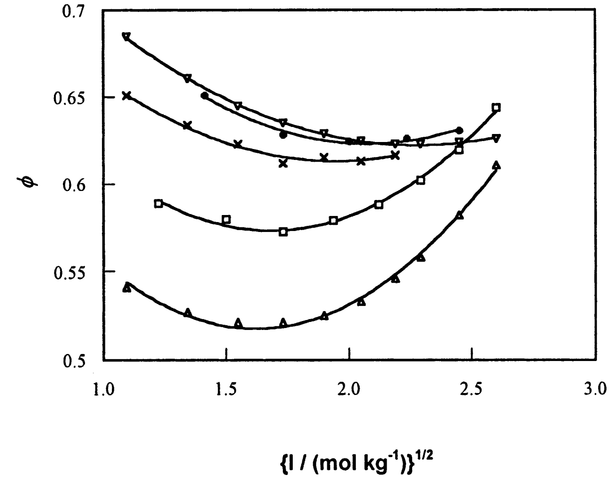

Figure 5. Osmotic coefficient ϕ of $MgSO_4-(NH_4)_2SO_4(aq)$ against square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions y of $MgSO_4$ at 298.15 K: ▽, $y = 0$; ●, $y = 0.2$; ×, $y = 0.5$; □, $y = 0.8$; △, $y = 1$.

Using the obtained experimental data for the water activity, we had evaluated the osmotic coefficients for different ionic strength fractions y of $MgSO_4$. 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 for different ionic-strength fractions, it is possible to determine the unknowns Pitzer mixing ionic $\theta_{Mg^{2+}NH_4^+}$ and $\psi_{Mg^{2+}NH_4^+SO_4^{2-}}$, which are not given in the literature. These parameters may be used to predict the solute activity coefficients in the mixture. $\theta_{Mg^{2+}NH_4^+}$ and $\psi_{Mg^{2+}NH_4^+SO_4^{2-}}$ 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 11 ϕ_{calc}[23] with $\theta = 0$ and $\psi = 0$. This yields

$$\frac{2m_{MgSO_4} + 3m_{(NH_4)_2SO_4}}{4m_{MgSO_4}m_{(NH_4)_2SO_4}}\Delta\phi = \theta_{Mg^{2+}NH_4^+} + \psi_{Mg^{2+}NH_4^+SO_4^{2-}}m_{SO_4^{2-}} \qquad (18)$$

so that a plot of $\Delta\phi$ versus total molality m_{tot} should give a straight line with intercept $\theta_{Mg^{2+}NH_4^+}$ and slope $\psi_{Mg^{2+}NH_4^+SO_4^{2-}}$. The values of these ionic parameters are given in $\theta_{Mg^{2+}NH_4^+} = -0.000\,33$ and $\psi_{Mg^{2+}NH_4^+SO_4^{2-}} = 0.000\,78$, and the standard error is $s = 6 \times 10^{-5}$ and the standard deviation is $\sigma_{\Delta\phi} = 0.002$. The values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} for $MgSO_4(aq)$[9] and $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} for $(NH_4)_2SO_4$ (aq)[9] are given in Table 2.

The activity coefficients of $MgSO_4(aq)$ 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 γ_{MgSO_4} and $\gamma_{(NH_4)_2SO_4}$ as a function of $I^{1/2}$. The extremes of composition are illustrated

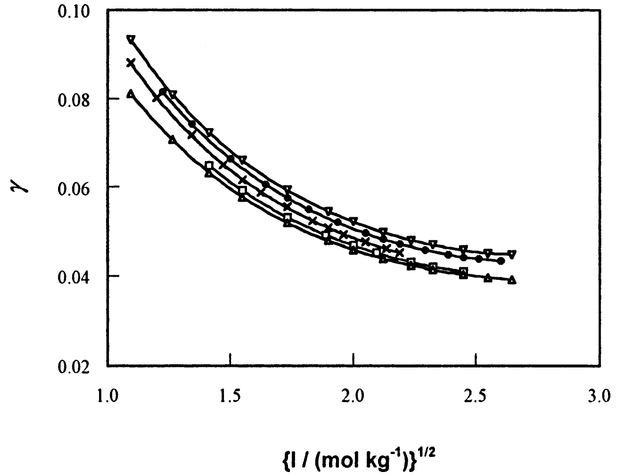

Figure 6. Activity coefficients γ_{MgSO_4} of $MgSO_4(aq)$ in $MgSO_4-(NH_4)_2SO_4(aq)$ against square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions y of $MgSO_4$ at 298.15 K: ▽, $y = 0$; ●, $y = 0.2$; ×, $y = 0.5$; □, $y = 0.8$; △, $y = 1$; —, Pitzer model.

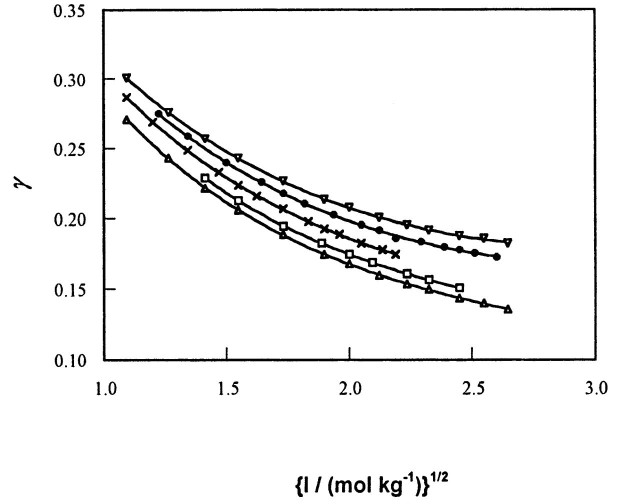

Figure 7. Activity coefficient $\gamma_{(NH_4)_2SO_4}$ of $(NH_4)_2SO_4(aq)$ in $MgSO_4-(NH_4)_2SO_4(aq)$ against square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions y of $MgSO_4$ at 298.15 K: ▽, $y = 0$; ●, $y = 0.2$; ×, $y = 0.5$; □, $y = 0.8$; △, $y = 1$; —, Pitzer model.

Table 2. Pitzer Parameters for $MgSO_4$ and $(NH4)_2SO_4$ and Their Mixtures at 298.15 K

electrolyte	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	ref
$MgSO_4$	0.2305	3.267	−47.93	0.0232	9
$(NH_4)_2SO_4$	0.04022	0.5911		−0.00106	9

electrolyte	$\theta_{Mg^{2+}NH_4^+}$	$\psi_{Mg^{2+}NH_4^+SO_4^{2-}}$	ref
$MgSO_4 + (NH_4)_2SO_4$	−0.00033	0.00078	this study

in these figures, that is, the activity coefficients of pure and trace components. The curves of variation of both γ_{MgSO_4} and $\gamma_{(NH_4)_2SO_4}$ at different ionic-strength fractions y are quite similar in their dependence on total ionic strength.

5. Conclusion

We have used a simple hygrometric method to determine the water activities and osmotic coefficients of the mixture $MgSO_4-(NH_4)_2SO_4(aq)$ at 298.15 K. The obtained water activities are compared with data from three commonly used thermodynamic models. The experimental data are used for the calculation of solute activity coefficients, using the Pitzer model with our newly obtained ionic mixing parameters, from obtained data of the osmotic and activity coefficients.

Table 3. Activity Coefficients γ_1 of $MgSO_4$ and γ_2 of $(NH_4)_2SO_4$ in $MgSO_4-(NH_4)_2SO_4(aq)$ at Total Ionic Strength I/mol·kg^{-1} for Different Ionic-Strength Fractions y of $MgSO_4$ at 298.15 K

I	γ_1	γ_2	I	γ_1	γ_2	I	γ_1	γ_2
	y = 0.0			y = 0.2			y = 0.5	
1.20	0.0812	0.271	2.00	0.0649	0.229	1.20	0.0881	0.287
1.60	0.0708	0.243	2.40	0.0593	0.213	1.44	0.0802	0.269
2.00	0.0633	0.222	3.00	0.0533	0.195	1.80	0.0720	0.249
2.40	0.0578	0.206	3.56	0.0493	0.183	2.16	0.0651	0.233
3.00	0.0520	0.189	4.00	0.0470	0.175	2.40	0.0617	0.224
3.60	0.0480	0.175	4.39	0.0453	0.169	2.64	0.0589	0.216
4.00	0.0460	0.168	5.00	0.0432	0.162	3.00	0.0556	0.207
4.50	0.0440	0.160	5.40	0.0422	0.157	3.36	0.0525	0.198
5.00	0.0425	0.154	6.00	0.0411	0.151	3.60	0.0509	0.193
5.40	0.0415	0.150				3.84	0.495	0.189
6.00	0.0404	0.144				4.20	0.0477	0.183
6.50	0.0397	0.140				4.56	0.0462	0.178
7.00	0.0393	0.136				4.80	0.0453	0.175
	$y = 0.8$			$y = 1.0$				
1.50	0.0816	0.275	1.20	0.0934	0.301			
1.80	0.0744	0.259	1.60	0.0809	0.276			
2.25	0.0664	0.240	2.00	0.0724	0.257			
2.70	0.0607	0.226	2.40	0.0661	0.243			
3.00	0.0577	0.218	3.00	0.0594	0.227			
3.30	0.0551	0.211	3.60	0.0546	0.214			
	$y = 0.8$			$y = 1.0$				
3.75	0.0521	0.203	4.00	0.0523	0.208			
4.20	0.0497	0.196	4.50	0.0499	0.201			
4.50	0.0484	0.192	5.00	0.0481	0.196			
4.80	0.0473	0.186	5.40	0.0471	0.192			
5.25	0.0459	0.184	6.00	0.0459	0.188			
5.70	0.0449	0.180	6.50	0.0452	0.186			
6.00	0.0443	0.178	7.00	0.0449	0.185			
6.30	0.0439	0.176						
6.75	0.0435	0.173						

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