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Thermodynamic Properties of Ternary Aqueous Solutions with the Common Magnesium Cation $\{Mg/Cl/NO_3/SO_4\}(aq)$ at $T = 298.15$ K

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In this investigation, ternary aqueous electrolytes of chloride, nitrate, and sulfate with the common magnesium cation have been studied using the hygrometric method at 298.15 K. The water activities of the ternary systems $\{yMgCl_2 + (1 - y)MgSO_4\}(aq)$ and $\{yMg(NO_3)_2 + (1 - y)MgSO_4\}(aq)$ are measured at total molalities from 0.35 $mol\cdot kg^{-1}$ to saturation for different ionic strength fractions (y) of $MgCl_2$ or $Mg(NO_3)_2$, respectively, with $y = 0.20$, 0.50, and 0.80. The obtained data allow the deduction of osmotic coefficients of the solvent. From these measurements, mixing ionic parameters are determined and used to predict the solute activity coefficients in the mixture, using Pitzer's model. The parameters θ_{MN} and ψ_{MNX} are evaluated for these systems. The thermodynamic properties of the ternary aqueous systems nitrate, chloride, or sulfate with magnesium, $\{Mg/Cl/NO_3/SO_4\}(aq)$, are compared with the data obtained for the system $[MgCl_2 + Mg(NO_3)_2](aq)$ already published in a previous work.[4] The comparison shows that the hydration is affected by the nature of the solute, $MgSO_4$, $MgCl_2$, or $Mg(NO_3)_2$, in the mixed aqueous solutions. These effects might be influenced by ion pairing, with no contact in $Mg(NO_3)_2(aq)$ and with ion association in $MgSO_4(aq)$.

1. Introduction

Knowledge of thermodynamic properties for aqueous solutions with magnesium is of great interest from both theoretical and practical viewpoints. Aqueous solutions of Mg^{2+} combined with Cl^-, SO_4^{2-}, and NO_3^- are important components in many natural and industrial processes.[1−3] Various chemical processes and industrial problems require thorough knowledge of the properties of aqueous solutions including those of the Mg^{2+} cation. The study of electrolytes is fundamentally important to understand the properties and behavior of aqueous multicomponent systems.

Much attention has been paid to chloride, sulfate, nitrate, magnesium, and their mixtures. The mixed aqueous electrolytes with common cations or anions continue to be interesting. This paper presents research on ternary aqueous mixtures of magnesium chloride, sulfate, and nitrate, $\{Mg^{2+}/Cl^-/NO_3^-/SO_4^{2-}\}(aq)$, that are a continuation of our previous work on the ternary aqueous system $[MgCl_2 + Mg(NO_3)_2](aq)$.[4] In the present work, the thermodynamic properties of the aqueous systems $[MgCl_2 + MgSO_4](aq)$ and $[Mg(NO_3)_2 + MgSO_4](aq)$ were determined using the hygrometric method at 298.15 K. These systems have not been extensively studied in this way. Wu et al.[5] measured the osmotic coefficients of the solvent of the system $[MgCl_2 + MgSO_4](aq)$ by the isopiestic method at 298.15 K in the range of ionic strengths 0.8 to 6.8. Also, Ha and Chan[6] evaluated the water activities of the systems $[MgCl_2 + MgSO_4](aq)$ and $[Mg(NO_3)_2 + MgSO_4](aq)$ using an electrodynamic balance (EDB) method at ambient temperature 293.95 K, for the molar ratio 1:1 in the range of water activity from 0.80 to 0.42.

We report the results of measurements of water activities for the total molality range from 0.35 $mol\cdot kg^{-1}$ to saturation for mixed electrolytes $\{yMgCl_2 + (1 - y)MgSO_4\}(aq)$ and $\{yMg(NO_3)_2 + (1 - y)MgSO_4\}(aq)$ at different ionic strength fractions (y) of $MgCl_2$ ($y = I_{MgCl_2}/(I_{MgCl_2} + I_{MgSO_4})$) or $Mg(NO_3)_2$ ($y = I_{Mg(NO_3)_2}/(I_{Mg(NO_3)_2} + I_{MgSO_4})$), respectively, with $y = 0.20$, 0.50, and 0.80 at 298.15 K. The osmotic coefficients are evaluated for these solutions from the water activities. The experimental data are used for the calculation of solute activity coefficients using the Pitzer model with our ionic mixing parameters. A comparison of the behavior of aqueous electrolyte solutions with magnesium is reported and shows that the hydration in these solutions is affected by the nature of the solute, $MgSO_4$, $MgCl_2$, or $Mg(NO_3)_2$.

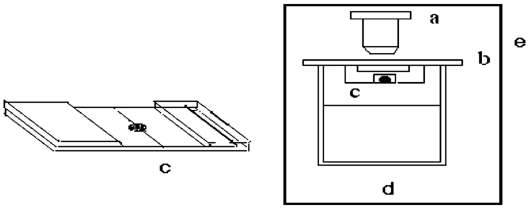

Figure 1. Description of materials used in the hygrometric apparatus: a, microscope; b, lid; c, support of the drops; d, cup; e, wooden box.

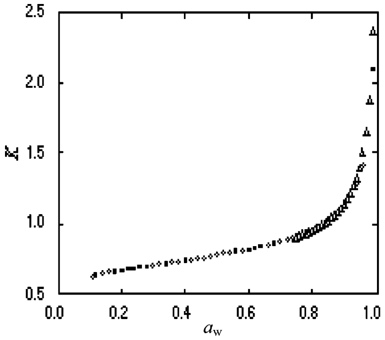

Figure 2. Variation of the ratio K of diameter droplets as a function of the water activity a_w.

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Table 1. Ratios of Growth K of the NaCl(aq) Droplets, Water Activities a_w, and Osmotic Coefficients ϕ of the Solvent to the Mixture $\{y\mathrm{MgCl_2} + (1 - y)\mathrm{MgSO_4}\}$(aq) at Total Molalities m_{tot} for Different Ionic Strength Fractions (y) of $\mathrm{MgCl_2}$[a]

$m_{\mathrm{MgCl_2}}$ / $\mathrm{mol{\cdot}kg^{-1}}$	$M_{\mathrm{MgSO_4}}$ / $\mathrm{mol{\cdot}kg^{-1}}$	m_{tot} / $\mathrm{mol{\cdot}kg^{-1}}$	K	a_w	ϕ
		$y = 0.20$			
0.15	0.45	0.60	1.074[b]	0.983_5	0.684
0.20	0.60	0.80	1.802	0.977_2	0.711
0.25	0.75	1.00	1.642	0.970_6	0.737
0.30	0.90	1.20	1.532	0.963	0.774
0.40	1.20	1.60	1.356	0.946	0.859
0.50	1.50	2.00	1.231	0.925	0.966
0.60	1.80	2.40	1.126	0.898	1.108
0.70	2.10	2.80	1.056	0.870	1.229
0.74	2.22	2.96	1.030	0.857	1.287
		$y = 0.50$			
0.20	0.15	0.35	1.166[b]	0.987_0	0.807
0.40	0.30	0.70	1.676	0.971_9	0.879
0.60	0.45	1.05	1.438	0.955	0.951
0.80	0.60	1.40	1.278	0.934	1.059
1.00	0.75	1.75	1.167	0.910	1.165
1.20	0.90	2.10	1.085	0.882	1.293
1.40	1.05	2.45	1.017	0.850	1.435
1.60	1.20	2.80	0.964	0.816	1.571
1.80	1.35	3.15	0.920	0.777	1.726
2.00	1.50	3.50	0.895[c]	0.738	1.876
		$y = 0.80$			
0.80	0.15	0.95	1.393	0.951	1.033
1.07	0.20	1.27	1.252	0.929	1.132
1.30	0.24	1.54	1.151	0.906	1.251
1.60	0.30	1.90	1.063	0.873	1.396
1.85	0.35	2.20	1.003	0.842	1.527
2.13	0.40	2.53	0.951	0.805	1.675
2.40	0.45	2.85	1.909	0.766	1.827
2.78	0.52	3.30	0.877[c]	0.708	2.043
3.20	0.60	3.80	0.829	0.640	2.294

[a] The reference water activity is 0.84, and the reference solution is NaCl(aq). [b] Reference water activity is 0.98. [c] Reference solution is LiCl(aq).

Table 2. Ratios of Growth K of the NaCl(aq) Droplets, Water Activities a_w, and Osmotic Coefficients ϕ of the Solvent to the Mixture $\{y\mathrm{Mg(NO_3)_2} + (1 - y)\mathrm{MgSO_4}\}$(aq) at Total Molalities m_{tot} for Different Ionic Strength Fractions (y) of $\mathrm{Mg(NO_3)_2}$[a]

$m_{\mathrm{Mg(NO_3)_2}}$ / $\mathrm{mol{\cdot}kg^{-1}}$	$M_{\mathrm{MgSO_4}}$ / $\mathrm{mol{\cdot}kg^{-1}}$	m_{tot} / $\mathrm{mol{\cdot}kg^{-1}}$	K	a_w	ϕ
		$y = 0.20$			
0.10	0.30	0.4	1.234[b]	0.989_3	0.662
0.15	0.45	0.6	1.078[b]	0.983_7	0.675
0.20	0.60	0.8	1.872	0.977_8	0.691
0.25	0.75	1.0	1.666	0.971_4	0.716
0.30	0.90	1.2	1.544	0.964	0.749
0.40	1.20	1.6	1.372	0.948	0.832
0.50	1.50	2.0	1.246	0.928	0.928
0.60	1.80	2.4	1.149	0.905	1.032
0.65	1.95	2.6	1.106	0.891	1.095
0.70	2.10	2.8	1.072	0.877	1.152
		$y = 0.50$			
0.20	0.15	0.35	1.180[b]	0.987_5	0.779
0.40	0.30	0.70	1.708	0.973_3	0.835
0.60	0.45	1.05	1.463	0.957	0.898
0.80	0.60	1.40	1.302	0.938	0.989
1.00	0.75	1.75	1.187	0.915	1.092
1.20	0.90	2.10	1.103	0.890	1.196
1.40	1.05	2.45	1.040	0.862	1.309
1.60	1.20	2.80	0.988	0.832	1.419
		$y = 0.80$			
0.80	0.15	0.95	1.420	0.953	0.990
1.05	0.20	1.25	1.278	0.934	1.068
1.30	0.25	1.55	1.175	0.912	1.162
1.60	0.30	1.90	1.087	0.884	1.267
1.85	0.35	2.20	1.030	0.857	1.371
2.16	0.41	2.57	0.973	0.822	1.491
2.40	0.45	2.85	0.937	0.793	1.589
2.64	0.50	3.14	0.914[c]	0.763	1.683
2.90	0.54	3.44	0.890[c]	0.729	1.794
3.20	0.60	3.80	0.863[c]	0.688	1.922

[a] The reference water activity is 0.84, and the reference solution is NaCl(aq). [b] Reference water activity is 0.98. [c] Reference solution is LiCl(aq).

2. Experimental Section

The water activity was determined using the hygrometric method described in a previous work.[7] The apparatus used in this study for mixed electrolyte solutions is essentially the same as that used for the investigation of aqueous single electrolyte solutions. It is based on the measurement of the relative humidity over an 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 diameter measurement of the previously calibrated droplet therefore permits knowledge of the relative humidity of the aqueous solution.

The drops are composed of sodium or lithium chloride solutions. The droplets of a reference solution of NaCl(aq) or LiCl(aq) are deposited on the spider-thin thread by pulverisation. 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 by a microscope with an ocular equipped with a micrometric screw.

The relative humidity is equivalent to the water activity a_w in our experiments. 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, we calculate the ratio of growth K ($K = (D(a_w))/(D(a_{w(ref)}))$) and determine graphically the water activity using the variation of the ratio K (Figure 2) as a function of the water activity of reference solution NaCl(aq) or LiCl(aq).

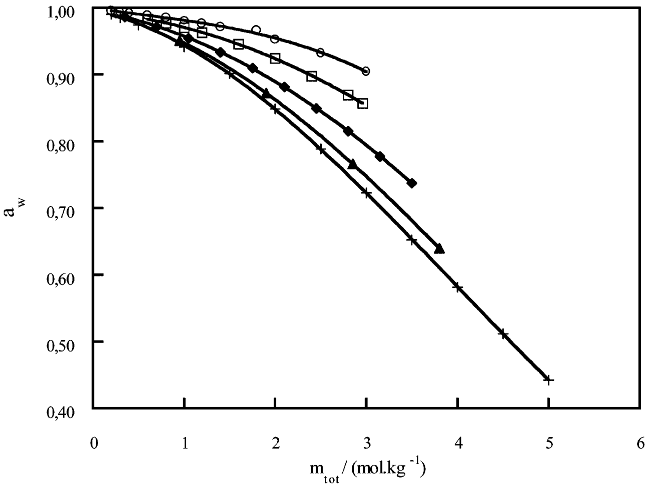

Figure 3. Water activities a_w of $\{y\mathrm{MgCl_2} + (1 - y)\mathrm{MgSO_4}\}$(aq) at total molalities m_{tot}, for different ionic strength fractions (y). ○, $y = 0.00$ ($\mathrm{MgSO_4}$(aq)); □, $y = 0.20$; ◆, $y = 0.50$; ▲, $y = 0.80$; +, $y = 1.00$ ($\mathrm{MgCl_2}$(aq)).

Generally, the reference relative humidity is 0.84. For dilute solutions, the water activity reference is 0.98. For water activities of greater than 0.75, a solution of NaCl or LiCl is used, whereas for water activities of less than 0.75, a solution of LiCl is used.

The uncertainty in the water activity depends on the precision of the diameter measurements and is less than ± 0.02 % for $a_w > 0.97$, ± 0.05 % for $a_w > 0.95$, ± 0.09 % for $a_w > 0.90$, and ± 0.2 % for $a_w > 0.85$. Also the overall uncertainty of the osmotic coefficient is estimated to be, at most, $\pm 6{\cdot}10^{-3}$.

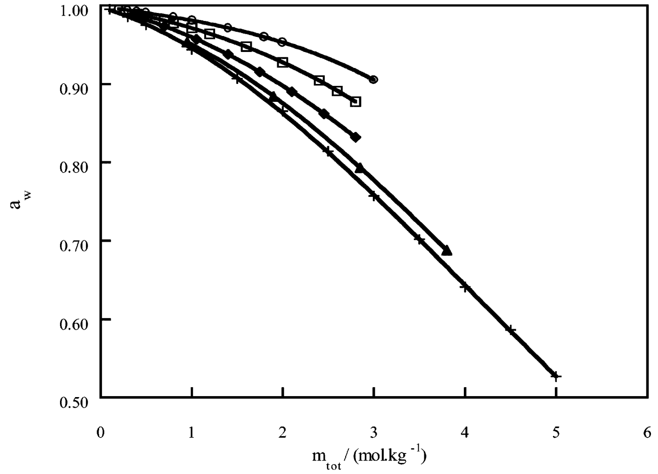

Figure 4. Water activities a_w of {y Mg$(NO_3)_2$ + $(1-y)$MgSO$_4$}(aq) at total molalities m_{tot}, for different ionic-strength fractions (y). ○, y = 0.00 (MgSO$_4$(aq)); □, y = 0.20; ♦, y = 0.50; ▲, y = 0.80; +, y = 1.00 (Mg$(NO_3)_2$(aq)).

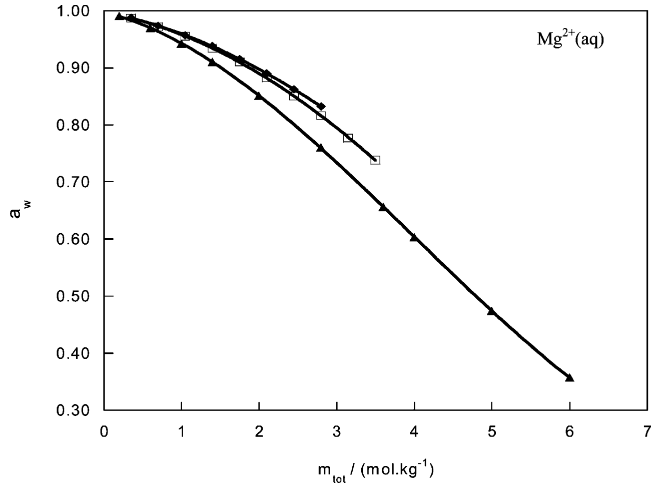

Figure 5. Water activities a_w of magnesium ternary systems at total molalities m_{tot} at an ionic strength fraction of $y = 0.50$. □, MgCl$_2$−MgSO$_4$(aq); ♦, Mg$(NO_3)_2$−MgSO$_4$(aq); ▲, MgCl$_2$−Mg$(NO_3)_2$(aq).[4]

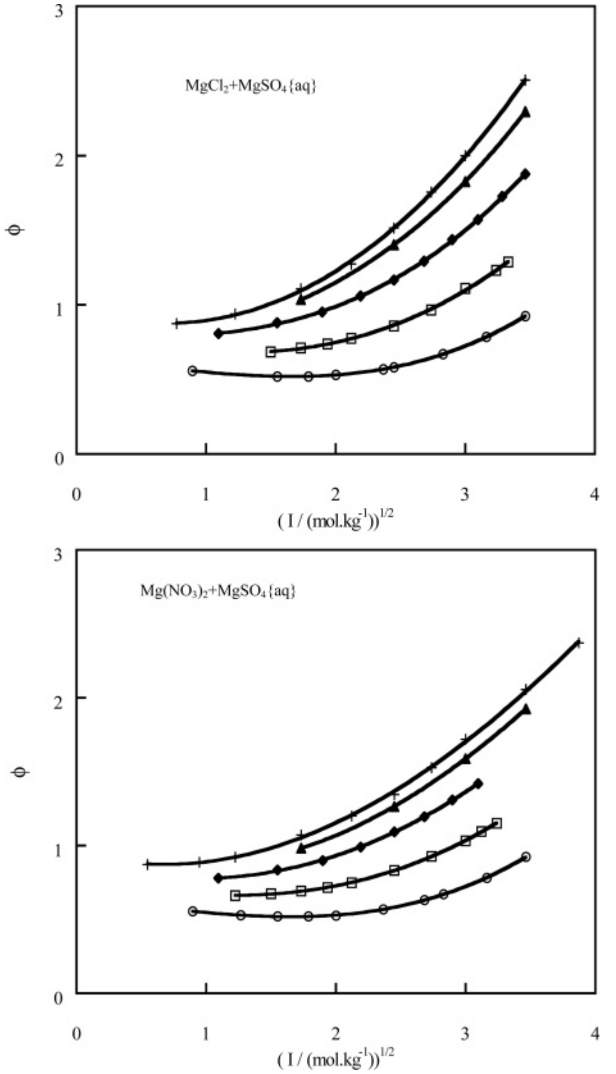

Figure 6. Osmotic coefficient ϕ of water for the ternary systems with magnesium Mg^{2+}/Cl$^-$/NO$_3^-$/SO$_4^{2-}$ against the square root of total ionic strength $I^{1/2}$ at different ionic strength fractions (y). ○, y = 0.00; □, y = 0.20; ♦, y = 0.50; ▲, y = 0.80; +, y = 1.00.

The solutions of NaCl, LiCl, MgCl$_2$, MgSO$_4$, and Mg$(NO_3)_2$ were prepared from crystalline material (Extrapur-grade chemicals, NaCl 99.50 %, LiCl, MgCl$_2$·6H$_2$O 99.00 %, Mg$(NO_3)_2$·6H$_2$O 99.00 %, and MgSO$_4$ 99.00 %) and deionized distilled water. The reference solutions are NaCl(aq) or LiCl(aq).

3. Results and Discussion

3.1 Water Activity and Osmotic Coefficient. In this work, the water activity was measured for the ternary systems{yMgCl$_2$ + $(1 - y)$MgSO$_4$}(aq) and {yMg$(NO_3)_2$ + $(1 - y)$MgSO$_4$}(aq), at a total molality range from 0.35 mol·kg^{-1} to saturation at 298.15 K. We report the results of measurements of water activities at different ionic strength fractions (y) of MgCl$_2$ ($y = I_{MgCl_2}/(I_{MgCl_2} + I_{MgSO_4})$) or of Mg$(NO_3)_2$ ($y = I_{Mg(NO_3)_2}/(I_{Mg(NO_3)_2} + I_{MgSO_4})$), respectively, with y = 0.20, 0.50, and 0.80. The experimental values of water activity are listed in Tables 1 and 2 and presented in Figures 3 and 4. The ranges of water activity are presented, for each ternary system: $0.9752 > a_w > 0.504$ for [MgCl$_2$ + MgSO$_4$](aq); $0.9906 > a_w > 0.357$ for [Mg$(NO_3)_2$ + MgSO$_4$](aq); and we report also for [MgCl$_2$ + Mg$(NO_3)_2$](aq),[4] $0.9906 > a_w > 0.269$.

These figures show that the water activity decreases with increases of concentration. It is noted that the curves for the ternary systems are between those for the corresponding binary systems in the following order: $a_{w(MgSO_4(aq))} > a_{w(y = 0.20)} > a_{w(y = 0.50)} > a_{w(y = 0.80)} > a_{w(Mg(NO_3)_2)}$ or $a_{w(MgCl_2(aq))}$.

For comparison of the behavior of these systems with magnesium, we have presented in Figure 5 the water activity curves for the studied ternary systems Mg^{2+}/Cl$^-$/NO$_3^-$/SO$_4^{2-}$ at an ionic strength fraction of $y = 0.50$.

The plots are practically identical for [MgCl$_2$ + MgSO$_4$](aq) and [Mg$(NO_3)_2$ + MgSO$_4$](aq) in the studied range of molality, but the electrolyte [MgCl$_2$ + Mg$(NO_3)_2$](aq) presents a lower water activity than the systems containing magnesium sulfate. The variation of water activities shows that the hydration of the magnesium electrolytes Mg^{2+}/Cl$^-$/NO$_3^-$/SO$_4^{2-}$ decreases in the following order: hyd$_{(Cl/NO_3)}$ > hyd$_{(Cl/SO_4)}$ ~ hyd$_{(NO_3/SO_4)}$. This behavior was observed in binary aqueous solutions[8] and is explained by the hydration phenomenon. The amount of water molecules required to hydrate the ions increases, and the amount of free solvent decreases. Therefore, the quantity of solvent which can pass into the vapor phase diminishes, and the most extensively hydrated salt results in a relatively low water activity. This order of hydration is influenced by the presence

Table 3. Ionic Interaction Parameters θ_{MN} and ψ_{MNX} in Ternary Systems $\{Mg^{2+}/Cl^-/NO_3^-/SO_4^{2-}\}$(aq) and Their Binary $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ at 298.15 K

electrolyte	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^ϕ	ref
$MgCl_2$	0.3492	1.6653		0.0060	23
$Mg(NO_3)_2$	0.3216	1.7578		−0.0051	24
$MgSO_4$	0.2305	3.267	−47.93	0.0232	8
ternary system with common cation $\{Mg^{2+}/Cl^-/NO_3^-/SO_4^{2-}\}$(aq)	θ_{MN}	ψ_{MNX}	σ_ϕ		
$MgCl_2 + Mg(NO_3)_2 + H_2O$	0.0528	−0.0082	0.0083		4
$MgCl_2 + MgSO_4 + H_2O$	0.0383	−0.0094	0.0088		this work
$Mg(NO_3)_2 + MgSO_4 + H_2O$	0.0447	−0.0046	0.0058		this work

of magnesium sulfate in solution. This behavior can be explained by the presence of ionic association in the solution of magnesium sulfate. This phenomenon of ionic association was observed in aqueous binary solutions of sulfates.[8] Indeed, many studies of the ion association in aqueous solutions in the $MgSO_4$ system have been reported.[9−12] In general, there are two types of ion association in aqueous electrolyte solutions. The first type is strong association of cations and anions by ionic or covalent bonds. The second type is the weak association complex in the form of solvent-separated ion pairs, associated by predominantly electrostatic forces. Zhang and Chan[13] have observed, using Raman spectra, the characteristics of contact ion pairs between Mg^{2+} and SO_4^{2-} and proposed a chain structure composed of the contact biden tate ion pairs in highly supersaturated $MgSO_4$ solutions. But for the solute $Mg(NO_3)_2$(aq) in aqueous solutions, several studies[14−19] with some techniques have concluded that contact ion pairs do not form up to saturation. These studies confirmed that NO_3^- does not bind directly to Mg^{2+} within the experimental concentration range and imply that complex formation between Mg^{2+} and NO_3^- in aqueous solutions is unlikely. Consequently, the most dominating phenomenon which results from these interactions is the hydration of the ions. The interactions between ions and water molecules dominate. For these mixed electrolytes $Mg^{2+}/Cl^-/NO_3^-/SO_4^{2-}$, the presence of $MgSO_4$ in the ternary systems influences the interaction type in the solution $[MgCl_2 + MgSO_4]$(aq). But for $[Mg(NO_3)_2 + MgSO_4]$(aq), the effect of ionic association in aqueous solutions of $MgSO_4$ is dominated by the effect of $Mg(NO_3)_2$(aq) in aqueous solution, which is the hydration of ions by water molecules.

3.2 Osmotic Coefficient. Using the obtained experimental results of the water activity, the osmotic coefficients of water were evaluated for the ternary systems of magnesium $Mg^{2+}/Cl^-/NO_3^-/SO_4^{2-}$ at different ionic strength fractions (y) by

$$\phi = -\left(\frac{1000}{M_w \sum_i \nu_i m_i}\right) \cdot \ln a_w \tag{1}$$

where ν_i is the number of ions released by dissociation; m_i is the molality of solute i; and M_w is the molar mass of water. The obtained osmotic coefficients are listed in Tables 1 and 2 and are shown in Figure 6.

The plots of osmotic coefficients of ternary systems of magnesium $Mg^{2+}/Cl^-/NO_3^-/SO_4^{2-}$ against the square root of total ionic strength $I^{1/2}$ (Figure 6) are between those for the correspondent binary systems. The order is $\phi_{((Mg(NO_3)_2)}$ or $\phi_{(MgCl_2)} > \phi_{(y\,=\,0.80)} > \phi_{(y\,=\,0.50)} > \phi_{(y\,=\,0.20)} > \phi_{(MgSO_4)}$. We can observe that when we added the electrolyte $MgSO_4$(aq) to a binary solution of $Mg(NO_3)_2$(aq) or $MgCl_2$(aq) for $[Mg(NO_3)_2 + MgSO_4]$(aq) and $[MgCl_2 + MgSO_4]$(aq), respectively, the solution approached the properties of the added salt $MgSO_4$(aq).

3.3 Activity Coefficient. The osmotic coefficient of the mixed electrolyte solution of salts $Mg^{2+}/Cl^-/$ $NO_3^-/SO_4^{2-}$with a

Table 4. Activity Coefficients γ_{MgCl_2} (γ_1) and γ_{MgSO_4} (γ_2) in $\{yMgCl_2 + (1 - y)MgSO_4\}$(aq) against Total Ionic Strength I for Different Ionic Strength Fractions (y) of $MgCl_2$

$y = 0.00$			$y = 0.20$			$y = 0.50$			$y = 0.80$			$y = 1.00$		
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
0.80	0.406	0.1440	2.25	0.390	0.0747	1.20	0.428	0.105	3.00	0.518	0.0937	0.60	0.485	0.144
2.40	0.363	0.0661	3.00	0.398	0.0670	2.40	0.436	0.0834	4.01	0.620	0.101	1.50	0.475	0.108
3.20	0.365	0.0576	3.75	0.415	0.0625	3.60	0.481	0.0780	4.90	0.716	0.109	3.00	0.563	0.104
4.00	0.374	0.0523	4.50	0.438	0.0600	4.80	0.556	0.0793	6.00	0.866	0.123	4.50	0.742	0.122
5.60	0.410	0.0466	6.00	0.505	0.0588	6.00	0.661	0.0851	6.95	1.048	0.142	6.00	1.039	0.157
6.00	0.423	0.0459	7.50	0.602	0.0612	7.20	0.804	0.0949	8.12	1.369	0.176	7.50	1.513	0.216
8.00	0.505	0.0449	9.00	0.735	0.0667	8.40	0.995	0.109	9.00	1.703	0.211	9.00	2.272	0.311
10.00	0.626	0.0474	10.50	0.915	0.0754	9.60	1.250	0.129	9.92	2.157	0.259	12.00	3.494	0.464
12.00	0.801	0.0530	11.10	1.001	0.0798	10.80	1.590	0.155	10.86	2.749	0.321			
						12.00	2.043	0.190	12.00	3.671	0.417			

Table 5. Activity Coefficients $\gamma_{Mg(NO_3)_2}$ (γ_1) and γ_{MgSO_4} (γ_2) in $\{yMg(NO_3)_2 + (1 - y)MgSO_4\}$(aq) against Total Ionic Strength I at Different Ionic Strength Fractions (y) of $Mg(NO_3)_2$

$y = 0.00$			$y = 0.20$			$y = 0.50$			$y = 0.80$			$y = 1.00$		
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
0.80	0.407	0.1140	1.50	0.390	0.0879	1.20	0.423	0.1030	3.00	0.450	0.0780	0.30	0.530	0.191
1.60	0.371	0.0809	2.25	0.381	0.0729	2.40	0.410	0.0774	3.95	0.483	0.0759	0.90	0.466	0.123
2.40	0.359	0.0661	3.00	0.382	0.0644	3.60	0.429	0.0681	4.90	0.526	0.0760	1.50	0.451	0.101
3.20	0.359	0.0576	3.75	0.391	0.0593	4.80	0.466	0.0652	6.00	0.593	0.0790	3.00	0.471	0.0817
4.00	0.365	0.0523	4.50	0.405	0.0561	6.00	0.520	0.0660	6.95	0.667	0.0844	4.50	0.537	0.0803
5.60	0.393	0.0466	6.00	0.449	0.0535	7.20	0.592	0.0696	8.12	0.781	0.0950	6.00	0.642	0.0878
7.20	0.440	0.0448	7.50	0.513	0.0544	8.40	0.683	0.0757	9.00	0.886	0.106	7.50	0.790	0.103
8.00	0.470	0.0449	9.00	0.598	0.0578	9.60	0.796	0.0846	9.92	1.015	0.121	9.00	0.989	0.126
10.00	0.568	0.0474	9.75	0.650	0.0605				10.86	1.169	0.139	12.00	1.590	0.210
12.00	0.705	0.0530	10.50	0.710	0.0638				12.00	1.389	0.166	15.00	2.567	0.378

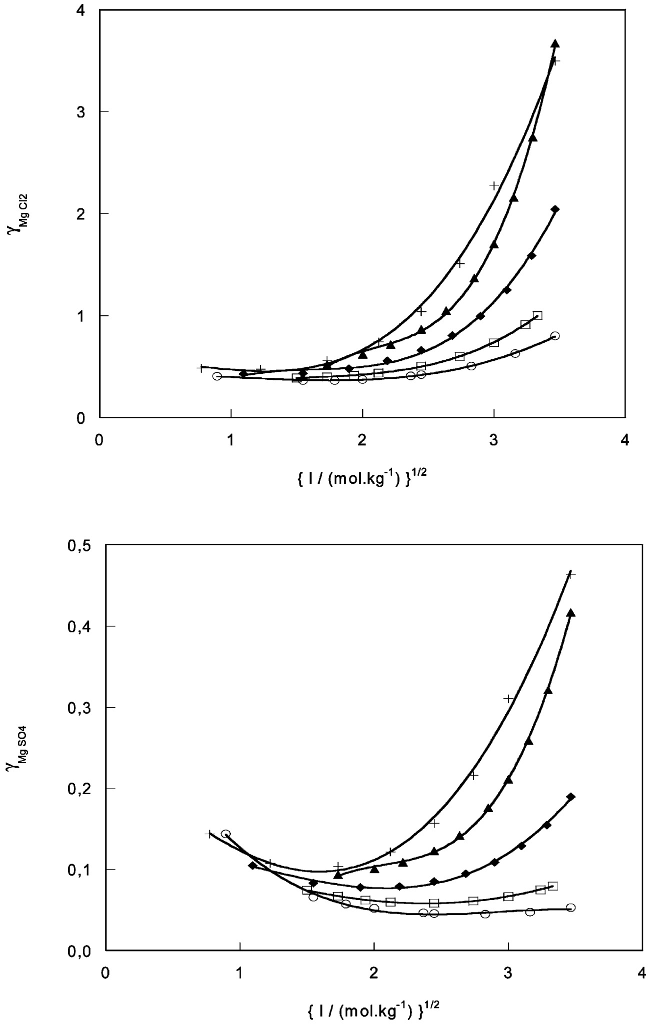

Figure 7. Activity coefficients γ_{MgCl_2} and γ_{MgSO_4} in $\{y\text{MgCl}_2 + (1 - y)\text{MgSO}_4\}$(aq) as a function of the square root of the ionic strength $I^{1/2}$ at different ionic strength fractions (y) of $MgCl_2$. ○, $y = 0.00$; □, $y = 0.20$; ◆, $y = 0.50$; ▲, $y = 0.80$; +, $y = 1.00$.

common cation Mg^{2+} is given by eq 2 based on the Pitzer ion interaction model[20−22]

$$\phi - 1 = \left(\sum_i m_i\right)^{-1}\left\{2If^{\phi} + 2\sum_c\sum_a m_c m_a\left[B^{\phi}_{ca} + \frac{(\sum m_z)}{(z_c z_a)^{1/2}}C^{\phi}_{ca}\right] + \sum_c\sum_{c'} m_c m_{c'}\left[\theta_{cc'} + I\theta'_{cc'} + \sum_a m_a\psi_{cc'a}\right] + \sum_a\sum_{a'} m_a m_{a'}\left[\theta_{aa'} + I\theta'_{aa'} + \sum_c m_c\psi_{caa'}\right]\right\} \quad (2)$$

where f^{ϕ} is a function of ionic strength expressing the effect of long-range electrostatic forces; I is the total ionic strength of the solution; θ and θ' are binary mixing parameters involving unlike ions of the same sign; and ψ is a ternary mixing parameter for two different ions of the same sign with a third ion of the opposite sign. The second virial coefficient B^{ϕ} of the ions is defined as

$$B^{\phi} = \beta^{(0)} + \beta^{(1)}\exp(-\alpha I^{1/2}) \quad (3)$$

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

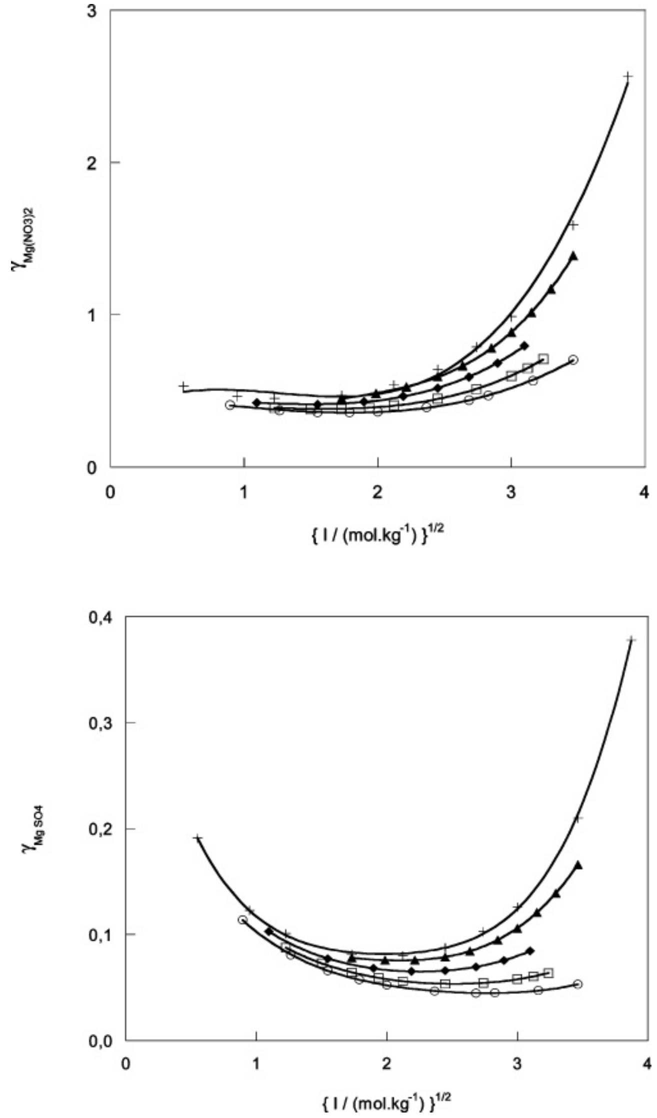

Figure 8. Activity coefficients $\gamma_{Mg(NO_3)_2}$ and γ_{MgSO_4} in $\{y\text{Mg(NO}_3)_2 + (1 - y)\text{MgSO}_4\}$(aq) as a function of the square root of the ionic strength $I^{1/2}$ at different ionic strength fractions (y) of $Mg(NO_3)_2$. ○, $y = 0.00$; □, $y = 0.20$; ◆, $y = 0.50$; ▲, $y = 0.80$; +, $y = 1.00$.

The activity coefficient γ_{MX} of MX in a common cation mixture is given by Pitzer's model as

$$\ln\gamma_{MX} = |z_M z_X|f^{\gamma} + \left(2\frac{\upsilon_M}{\upsilon}\right)\sum_a m_a\left[B_{Ma} + \left(\sum m_z\right)C_{Ma} + \left(\frac{\upsilon_X}{\upsilon_M}\right)\theta_{Xa}\right] + \left(2\frac{\upsilon_X}{\upsilon}\right)\sum_c m_c\left[B_{cX} + \left(\sum m_z\right)C_{cX} + \left(\frac{\upsilon_M}{\upsilon_X}\right)\theta_{Mc}\right] + \sum_c\sum_a m_c m_a\{|z_M z_X|B'_{ca} + \upsilon^{-1}[2\upsilon_M z_M C_{ca} + \upsilon_M\psi_{Mca} + \upsilon_X\psi_{caX}]\} + \frac{1}{2}\sum_c\sum_c m_c m_{c'}\left[\left(\frac{\upsilon_X}{\upsilon}\right)\psi_{cc'X} + \left|z_M z_X\right|\theta'_{cc'}\right] + \frac{1}{2}\sum_a\sum_{a'} m_a m_{a'}\left[\left(\frac{\upsilon_M}{\upsilon}\right)\psi_{Maa'} + \left|z_M z_X\right|\theta'_{aa'}\right] \quad (4)$$

with

$$f^{\gamma} = -A_{\phi}\left[\frac{I^{1/2}}{1 + 1.2I^{1/2}} + \left(\frac{2}{1.2}\right)\ln(1 + 1.2I^{1/2})\right] \quad (5)$$

$$B_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + \left(\frac{2\beta^{(1)}_{\mathrm{MX}}}{\alpha^2 I^2}\right)[1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] \quad (6)$$

$$B'_{\mathrm{MX}} = \left(\frac{2\beta^{(1)}_{\mathrm{MX}}}{\alpha^2 I^2}\right)\left[-1 + \left(1 + \alpha I^{1/2} + \frac{1}{2}\alpha^2 I\right) \exp(-\alpha I^{1/2})\right] \quad (7)$$

$$C_{\mathrm{MX}} = \frac{C^{\phi}_{\mathrm{MX}}}{2|z_{\mathrm{M}} z_{\mathrm{X}}|^{1/2}} \quad (8)$$

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 unknowns θ_{MN} and ψ_{MNX}. These parameters were used to predict the solute activity coefficients in the mixture. θ_{MN} and ψ_{MNX} are estimated by a graphical procedure. The quantity $\Delta\phi$ is defined by the difference between the experimental values ϕ_{exptl} and that calculated ϕ_{calcd} from eq 2. This yields

$$\left(\frac{\sum_i m_{\mathrm{i}}}{2m_{\mathrm{M}} m_{\mathrm{N}}}\right)\Delta\phi = \theta_{\mathrm{MN}} + m_{\mathrm{X}}\psi_{\mathrm{MNX}} \quad (9)$$

$$m_{\mathrm{X}} = |z_{\mathrm{M}}/z_{\mathrm{X}}| m_{\mathrm{MX}} + |z_{\mathrm{N}}/z_{\mathrm{X}}| m_{\mathrm{NX}} \quad (10)$$

A plot of $\Delta\phi$ versus total molality m_{tot} should give a straight line from which intercept θ_{MN} and slope ψ_{MNX} can be calculated. The corresponding values of ionic parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} of the pure electrolytes $MgCl_2$(aq), $Mg(NO_3)_2$(aq), and $MgSO_4$(aq) were obtained from Pitzer's expressions by a fit of the experimental osmotic coefficients given in our previous works[8,23−24] and the unknown mixing ionic parameters θ_{MN} and ψ_{MNX} which are listed in Table 3. The standard deviations on ϕ over the entire range of total ionic strengths are between $0.0088 > \sigma_{\phi} > 0.0058$.

The activity coefficients of $MgCl_2$(aq), $Mg(NO_3)_2$(aq), and $MgSO_4$(aq), in their ternary systems [$MgCl_2 + MgSO_4$](aq) and [$Mg(NO_3)_2 + MgSO_4$](aq), listed in Tables 4 and 5, were calculated from eq 9 using the obtained ionic mixing parameters.

The plots of activity coefficients in the mixtures against the square root of the ionic strength $I^{1/2}$ are shown in Figures 7 to 9. From the theoretical point of view, it is suitable to compare and explain the behavior of various ionic solutes, magnesium, in wide ranges of composition.

Activity coefficients in the various mixtures $\{Mg^{2+}/Cl^-/NO_3^-/SO_4^{2-}\}$(aq) as a function at molality show that the behavior for each aqueous solution is similar with that of its corresponding binary solution. It is also noted that these curves for systems [$Mg(NO_3)_2 + MgSO_4$](aq) and [$MgCl_2 + MgSO_4$](aq) are between those of their binary correspondents, but for [$MgCl_2 + Mg(NO_3)_2$](aq), the behavior of the solute activity coefficients is identical, and we can conclude that the structure of solution is not perturbed by addition of the electrolyte solute $MgCl_2$ to $Mg(NO_3)_2$(aq) in all the ranges of composition.

The activity coefficient $\gamma_{\mathrm{MgSO_4}}$ in their systems has lower values ($1 > \gamma$). These values confirmed the presence of the phenomenon of ionic association manifested in these systems, and contrarily for $\gamma_{\mathrm{Mg(NO_3)_2}}$ or $\gamma_{\mathrm{MgCl_2}}$, the higher values than unity reflect the interaction in the solution (Table 6).

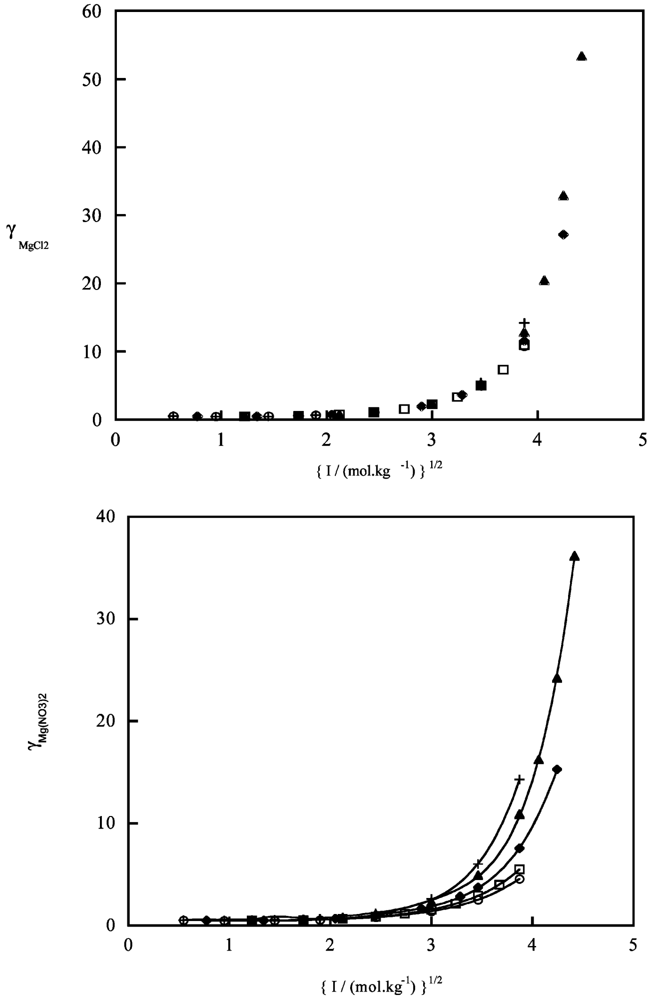

Figure 9. Activity coefficients $\gamma_{\mathrm{MgCl_2}}$ and $\gamma_{\mathrm{Mg(NO_3)_2}}$ in $\{yMgCl_2 + (1 - y)Mg(NO_3)_2\}$(aq)[4] as a function of the square root of the ionic strength $I^{1/2}$ at different ionic strength fractions (y) of $MgCl_2$. ○, $y = 0.00$; □, $y = 0.20$; ♦, $y = 0.50$; ▲, $y = 0.80$; +, $y = 1.00$.

Table 6. Range of Activity Coefficients in Their Systems

system	γ_1	γ_2
[$Mg(NO_3)_2 + MgSO_4$](aq)	$2.567 > \gamma_{\mathrm{Mg(NO_3)_2}} > 0.359$	$0.378 > \gamma_{\mathrm{MgSO_4}} > 0.046$
[$MgCl_2 + MgSO_4$](aq)	$3.670 > \gamma_{\mathrm{MgCl_2}} > 0.363$	$0.464 > \gamma_{\mathrm{MgSO_4}} > 0.046$
[$MgCl_2 + Mg(NO_3)_2$](aq)	$55 > \gamma_{\mathrm{MgCl_2}} > 0.479$	$38 > \gamma_{\mathrm{Mg(NO_3)_2}} > 0.471$

Literature Cited

(1) 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.

(2) Neumann, J. P.; Gokcen, N. A. *Technical Report;* Inf. Cric. Bureau of Mines: U.S., 1981.

(3) Bourouis, M.; Coronas, A.; Romero, R. J.; Siqueiros, J. Purification of seawater using absorption heat transformers with water−(LiBr+LiI+LiNO3+LiCl) and low temperature heat sources. *Desalination* **2004**, *166*, 209−214.

(4) Errougui, A.; El Guendouzi, M. Thermodynamic properties of ternary aqueous mixtures of $\{yMgCl_2 + (1-y)Mg(NO_3)_2\}$ (aq) at T = 298.15 K. *Calphad* **2006**, *30*, 260−265.

(5) Wu, Y. C.; Rush, R. M.; Scatchard, G. Osmotic and activity coefficients for binary mixtures of sodium chloride, sodium sulfate, magnesium sulfate, and magnesium chloride in water at 25 °C. I. Isopiestic measurements on the four systems with common ions. *J. Phys. Chem.* **1968**, *72*, 4048−4053.

(6) Ha, Z.; Chan, K. C. The Water Activities of $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, and Their Mixtures. *Aerosol Sci. Technol.* **1999**, *31*, 154−169.

(7) El Guendouzi, M.; Errougui, A. Thermodynamics properties of the Mixed Electrolytes $\{(y)NH_4Cl + (1 - y)(NH_4)_2SO_4\}$(aq) at the temperature 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 186−191.

(8) El Guendouzi, M.; Mounir, A.; Dinane, A. Water Activity, Osmotic and Activity coefficients of Aqueous solutions of Li_2SO_4, Na_2SO_4, K_2SO_4, $(NH_4)_2$ SO_4, $MgSO_4$, $MnSO_4$, $NiSO_4$, $CuSO_4$ and $ZnSO_4$ at T=298.15K. *J. Chem. Thermodyn*. **2003**, *35*, 209−220.

(9) Brown, P. G. M.; Prue, J. E. A Study of Ionic Association in Aqueous Solutions of Bi−Bivalent Electrolytes by Freezing−Point Measurements. *Proc. R. Soc. A* **1955**, *232*, 320−336.

(10) Nair, V. S. K.; Nancollas, G. H. Thermodynamics of ion association. Part IV. Magnesium and zinc sulphates. *J. Chem. Soc*. **1958**, 3706−3710.

(11) Atkinson, G.; Petrucci, S. Ion Association of Magnesium Sulfate in Water at 25 °C. *J. Phys. Chem*. **1966**, *70*, 3122−3128.

(12) Marshall, W. L. Aqueous systems at high temperature. XX. Dissociation constant and thermodynamic functions for magnesium sulfate to 200 degree. *J. Phys. Chem*. **1967**, *71*, 3584−3588.

(13) Zhang, Y. H.; Chan, C. K. Study of Contact Ion Pairs of Supersaturated Magnesium Sulfate Solutions Using Raman Scattering of Levitated Single Droplets. *J. Phys. Chem. A* **2000**, *104*, 9191−9196.

(14) Wahab, A.; Mahiuddina, S.; Hefter, G.; Kunz, W.; Minorar, B.; Jungwirth, P. Ultrasonic velocities, densities, viscosities, electrical conductivities, Raman spectra, and molecular dynamics simulations of aqueous solutions of $Mg(OAc)_2$ and $Mg(NO_3)_2$: Hofmeister effects and ion pair formation. *J. Phys. Chem. B* **2005**, *109*, 24108−24120.

(15) Vollmar, P. M. Ionic Interactions in Aqueous Solution: A Raman Spectral Study. *J. Chem. Phys.* **1963**, *39*, 2236−2248.

(16) Zhang, Y. H.; Choi, M. Y.; Chan, C. K. Relating Hygroscopic Properties of Magnesium Nitrate to the Formation of Contact Ion Pairs. *J. Phys. Chem. A* **2004**, *108*, 1712 −1718.

(17) James, D. W.; Carrick, M. T.; Frost, R. L. Structure of aqueous solutions: Fourier transformation and band component analysis in magnesium nitrate solutions. *J. Raman Spectrosc.* **1982**, *13*, 115−119.

(18) Righellato, E. C.; Davies, C. W. The extent of dissociation of salts in water. Part II. Uni−bivalent salts. *Trans. Faraday Soc.* **1930**, *26*, 592−600.

(19) Robinson, R. A.; Wilson, J. M.; Ayling, H. S. The Activity Coefficients of Some Bivalent Metal Nitrates in Aqueous Solution at 25° from Isopiestic Vapor Pressure Measurements. *J. Am. Chem. Soc*. **1942**, *64*, 1469−1471.

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

(21) 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.

(22) Pitzer, K. S.; Kim, J. J. Thermodynamic of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes. *J. Am. Chem. Soc.* **1974**, *96*, 5701−5707.

(23) El Guendouzi, M.; Dinane, A.; Mounir, A. Water activities, osmotic and activity coefficients in aqueous chlorides solutions at 298.15 K by the hygrometric method. *J. Chem. Thermodyn*. **2001**, *33*, 1059−1072.

(24) 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.

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