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# Solubility in the Ternary Aqueous Systems Containing M, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$ with M = $NH_4^+$, $Li^+$, or $Mg^{2+}$ at $T = 298.15$ K[†]

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The component solubilities of the ternary aqueous systems containing M, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$ with M = $NH_4^+$, $Li^+$, or $Mg^{2+}$ at $T = 298.15$ K were calculated using an ion-interaction model. In previous works, water activities at total molality from dilution to saturation for binary and mixed ternary electrolytes are used to evaluate the osmotic coefficients of the solvent for the solutions. From the experimental data, the activity coefficients of the solute were calculated using our ionic mixing parameters. In this paper, these parameters in the range of molality from dilution to saturation are used to predict the solubility in these systems. Also, we have completed measurements of water activities from 6 $mol \cdot kg^{-1}$ to saturation of the pure electrolyte solutions for LiCl(aq), $LiNO_3$(aq), and $NH_4NO_3$(aq) using the hygrometric method. The values of the pure electrolyte and mixing ion interaction parameters, which give the best fit of the activity data in binary and ternary solutions, and solubility data are tabulated. Thermodynamic characteristics, solubility products $K°_{sp}$, and the standard molar Gibbs energy of formation $\Delta G_{f\ m}^{\ 0}$ of the crystallizing solids are given. The predicted solubility isotherms are compared with the experimental data.

## Introduction

The prediction of the solubility in aqueous electrolyte solutions is important for a variety of applications in the chemical and geochemical processes, seawater systems, and evaporation as well as desalination.[1−4]

Thermodynamic properties of aqueous electrolytes solutions with a common cation are of great interest from theoretical and practical applications. Various chemical processes require a knowledge of the properties of aqueous solutions including those with a common cation. The study of solubility diagrams of ternary electrolyte solutions allows a better understanding of the properties and behavior of multicomponent aqueous systems.[5−10] The amount of solubility data available in the literature is limited.

The prediction of the various species in an aqueous mixed-electrolyte solution is directly involved in a manufacturing process. Studies of solubility diagrams of ternary and multicomponent solutions with participation chloride, nitrate, or sulfate with a common cation are of importance for many applications.

Experimental measurements of water activity and osmotic coefficient of the solvent for these aqueous mixed electrolytes have been made in our laboratory, for the binary[11−13] {MCl(aq), $MSO_4$(aq), $MNO_3$(aq)} and ternary systems[14−19] $\{y\text{MCl} + (1-y)\text{MSO}_4\}$(aq), $\{y\text{MNO}_3 + (1-y)\text{MSO}_4\}$(aq), and $\{y\text{MCl} + (1-y)\text{MNO}_3\}$(aq) with M = $NH_4^+$, $Li^+$, or $Mg^{2+}$. Prediction of activity coefficients using the ion-interaction model was also evaluated in unsatured and satured aqueous electrolyte solutions.[14−19]

This paper emphasizes the prediction and evaluation of solubility data in the above systems. The development of the ion interaction equation by Pitzer and co-workers provided a practical framework for a thermodynamic treatment of multicompound electrolyte solution with high ionic strengths. Harvie and Weare[20,21] showed that the Pitzer approach could be expanded to calculate accurately solubility in complex brines, and the basic theory for calculations of the component solubility of complicated systems was also presented by Pabalan and Pitzer.[22,23]

Previously, we measured water activities from dilution to saturation of the mixed electrolyte solutions, and the osmotic coefficients of the solvent are evaluated. In this paper, we have completed measurements of water activities from 6 $mol \cdot kg^{-1}$ to saturation of the pure electrolyte solutions for LiCl(aq), $LiNO_3$(aq), and $NH_4NO_3$(aq) using the hygrometric method. The osmotic coefficients of the solvent are evaluated, and the parameters for these binary systems are also determined. These results are used to calculate solute activity coefficients using the ion interaction model with our ionic binary and ternary mixing parameters.

The parameters for binary and ternary aqueous electrolytes at the range of molality from dilution to the saturation are used for the prediction of solubility in the studied systems. The prediction of mineral solubility is determined for the ternary aqueous systems $MCl + M_2SO_4 + H_2O$, $MCl + MNO_3 + H_2O$, and $M_2SO_4 + MNO_3 + H_2O$ with M = $NH_4^+$, $Li^+$, and $MgCl_2 + MgSO_4 + H_2O$, $MgCl_2 + Mg(NO_3)_2 + H_2O$, and $MgSO_4 + Mg(NO_3)_2 + H_2O$, at $T = 298.15$ K using the ion interaction model with our ionic mixing parameters. The results are compared with solubility experimental data given in the literature.

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**Table 1. Water Activity $a_w$, Osmotic Coefficient $\phi$, and Activity Coefficient $\gamma$ of LiCl(aq) at Different Molalities $m$ and $T$ = 298.15 K**

| $m$/(mol·kg$^{-1}$) | $a_{w(exp)}$ | $\phi_{(exp)}$ | $\phi_{(calc)}$ | $\gamma_{(calc)}$ |
|---|---|---|---|---|
| 0.1 | 0.9954 | 1.280 | 0.913 | 0.741 |
| 0.3 | 0.9898 | 0.948 | 0.899 | 0.657 |
| 0.5 | 0.9827 | 0.969 | 0.912 | 0.634 |
| 1.0 | 0.9640 | 1.018 | 0.981 | 0.651 |
| 1.5 | 0.9440 | 1.066 | 1.066 | 0.715 |
| 2.0 | 0.9210 | 1.142 | 1.156 | 0.807 |
| 2.5 | 0.8970 | 1.207 | 1.247 | 0.924 |
| 3.0 | 0.8710 | 1.278 | 1.337 | 1.067 |
| 4.0 | 0.8110 | 1.454 | 1.514 | 1.437 |
| 5.0 | 0.7480 | 1.612 | 1.683 | 1.943 |
| 6.0 | 0.6800 | 1.784 | 1.843 | 2.621 |
| 7.5 | 0.5820 | 2.003 | 2.068 | 4.060 |
| 9.0 | 0.5085 | 2.086 | 2.273 | 6.169 |
| 10.5 | 0.4344 | 2.204 | 2.459 | 9.170 |
| 12.0 | 0.3613 | 2.355 | 2.626 | 13.308 |
| 14.0 | 0.3014 | 2.378 | 2.818 | 21.023 |
| 16.0 | 0.2500 | 2.405 | 2.975 | 31.699 |
| 18.0 | 0.1941 | 2.528 | 3.098 | 45.567 |
| 19.2 | 0.1734 | 2.530 | 3.156 | 55.520 |

**Table 2. Water Activity $a_w$, Osmotic Coefficient $\phi$, and Activity Coefficient $\gamma$ of $LiNO_3$(aq) at Different Molalities $m$ and $T$ = 298.15 K**

| $m$/(mol·kg$^{-1}$) | $a_{w(exp)}$ | $\phi_{(exp)}$ | $\phi_{(calc)}$ | $\gamma_{(calc)}$ |
|---|---|---|---|---|
| 0.1 | 0.9967 | 0.917 | 0.940 | 0.789 |
| 0.3 | 0.9900 | 0.930 | 0.949 | 0.746 |
| 0.5 | 0.9831 | 0.946 | 0.970 | 0.746 |
| 1.0 | 0.9643 | 1.009 | 1.036 | 0.796 |
| 1.5 | 0.9450 | 1.047 | 1.107 | 0.879 |
| 2.0 | 0.9239 | 1.098 | 1.179 | 0.984 |
| 2.5 | 0.9033 | 1.129 | 1.251 | 1.109 |
| 3.0 | 0.8818 | 1.164 | 1.322 | 1.254 |
| 4.0 | 0.8329 | 1.269 | 1.458 | 1.605 |
| 5.0 | 0.7723 | 1.434 | 1.585 | 2.048 |
| 6.0 | 0.7254 | 1.485 | 1.703 | 2.590 |
| 7.5 | 0.6434 | 1.632 | 1.860 | 3.608 |
| 9.0 | 0.5614 | 1.780 | 1.993 | 4.879 |
| 10.5 | 0.4803 | 1.938 | 2.100 | 6.383 |
| 12.0 | 0.4168 | 2.024 | 2.182 | 8.065 |
| 13.0 | 0.3677 | 2.136 | 2.221 | 9.239 |

**Table 3. Water Activity $a_w$, Osmotic Coefficient $\phi$, and Activity Coefficient $\gamma$ of $NH_4NO_3$(aq) at Different Molalities $m$ and $T$ = 298.15 K**

| $m$/(mol·kg$^{-1}$) | $a_{w(exp)}$ | $\phi_{(exp)}$ | $\phi_{(calc)}$ | $\gamma_{(calc)}$ |
|---|---|---|---|---|
| 0.1 | 0.9967 | 0.917 | 0.917 | 0.753 |
| 0.3 | 0.9907 | 0.864 | 0.878 | 0.648 |
| 0.5 | 0.9847 | 0.856 | 0.852 | 0.589 |
| 1.0 | 0.9703 | 0.837 | 0.803 | 0.498 |
| 1.5 | 0.9578 | 0.798 | 0.762 | 0.438 |
| 2.0 | 0.9445 | 0.792 | 0.727 | 0.393 |
| 2.5 | 0.9348 | 0.749 | 0.695 | 0.357 |
| 3.0 | 0.9215 | 0.756 | 0.665 | 0.327 |
| 4.0 | 0.9030 | 0.708 | 0.614 | 0.280 |
| 5.0 | 0.8941 | 0.621 | 0.571 | 0.245 |
| 6.0 | 0.8767 | 0.609 | 0.535 | 0.218 |
| 7.5 | 0.8572 | 0.570 | 0.491 | 0.187 |
| 9.0 | 0.8393 | 0.540 | 0.460 | 0.165 |
| 10.5 | 0.8215 | 0.520 | 0.440 | 0.148 |
| 12.0 | 0.8032 | 0.507 | 0.431 | 0.136 |
| 14.0 | 0.7804 | 0.492 | 0.434 | 0.125 |
| 16.0 | 0.7550 | 0.487 | 0.456 | 0.119 |
| 18.0 | 0.7174 | 0.512 | 0.496 | 0.116 |
| 20.0 | 0.6746 | 0.546 | 0.553 | 0.117 |
| 22.0 | 0.6269 | 0.589 | 0.628 | 0.121 |
| 24.0 | 0.5634 | 0.664 | 0.720 | 0.129 |
| 26.6 | 0.5024 | 0.718 | 0.866 | 0.146 |

## Theoretical Background and Approach

The solubility of a hydrated salt in concentrated electrolyte solutions can be calculated from thermodynamic considerations if the equilibrium constant of the hydrated salt is known and the activity coefficients of all the electrolytes are known. For a hydrated salt, $M\nu_M X\nu_X \cdot \nu_0 H_2O$, where the dissolution reaction is

$$M\nu_M X\nu_X \cdot \nu_0 H_2O = \nu_M M^{+z_m} + \nu_X X^{-z_X} + \nu_0 H_2O \qquad (1)$$

where $\nu_i$ is the number of ions $i$ and $z_i$ is the number of charge on ion $i$.

The equilibrium constant $K_{sp}$ at a temperature is

$$\ln K_{sp} = \mu_s^0/RT - \left(\nu_M \mu_M^0 + \nu_X \mu_X^0 + \nu_0 \mu_{H_2O}^0\right)/RT \qquad (2)$$

In terms of molalities, the equilibrium constant for the solubility is given by

$$\ln K_{sp} = \nu_M \ln(m_M \cdot \gamma_M) + \nu_X \ln(m_X \cdot \gamma_X) + \nu_0 \ln a_w \qquad (3)$$

where $\mu_i^0 s$, $m_i$, and $\gamma_i$ represent the chemical potential of the solid or the aqueous species at their defined reference state, the molality and activity coefficient of the aqueous ion $i$, respectively, and $a_w$ is the activity of water. The absolute values of $\gamma_i$ for ions could not be determined, but the mean activity coefficient is $\gamma_\pm$ defined as

$$\ln \gamma_\pm = (\nu_M \ln \gamma_M + \nu_X \ln \gamma_X)/\nu \quad \text{with} \quad \nu = \nu_M + \nu_X \qquad (4)$$

The activity of water is related to the osmotic coefficient $\phi$ by

$$\ln a_w = -\phi(M_w/1000)\sum_i m_i \qquad (5)$$

where $M_w$ is the molar mass of water and the sum covers all solute species. $m_i$ is the molality of the species $i$ (mol·kg$^{-1}$). The activity and osmotic coefficients were calculated from the Pitzer model.[24−26]

## Experimental

The water activity was determined using the hygrometric method described previously.[12,15] 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 functional relation between the diameter of the droplet and relative humidity was determined by calibration experiments in which a suspended droplet of NaCl(aq) in the vapor phase was equilibration with a solution of

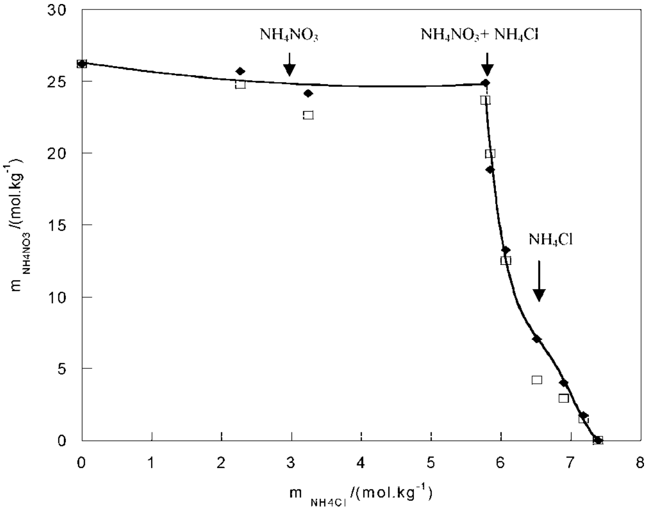

**Figure 1.** □, Calculated solubility in the system $\{NH_4Cl + NH_4NO_3\}$ (aq) compared with ◆, experimental data[27a] at $T$ = 298.15 K.

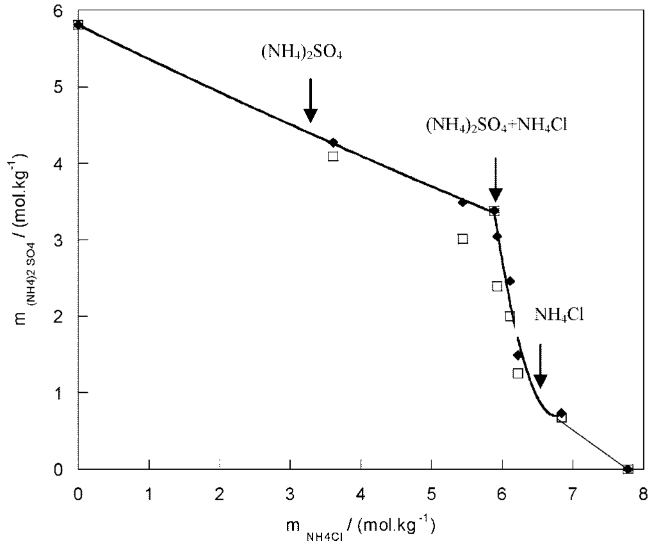

**Figure 2.** □, Calculated solubility in the system $\{NH_4Cl + (NH_4)_2SO_4\}$(aq) compared with ◆, experimental data[27b] at $T = 298.15$ K.

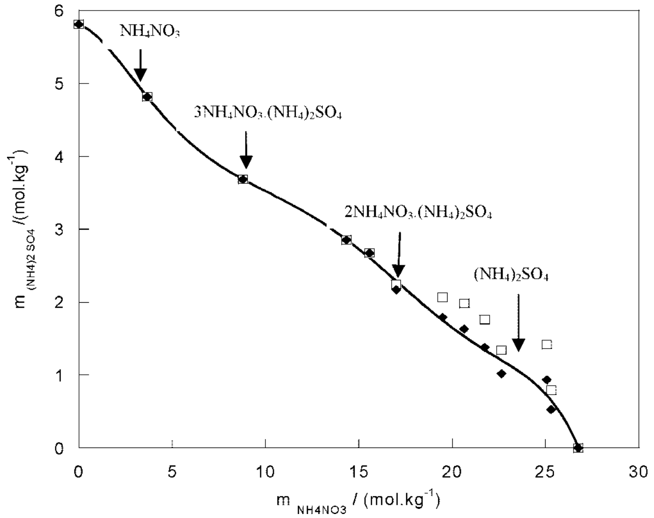

**Figure 3.** □, Calculated solubility in the system $\{NH_4NO_3 + (NH_4)_2SO_4\}$(aq) compared with ◆, experimental data[27c] at $T = 298.15$ K.

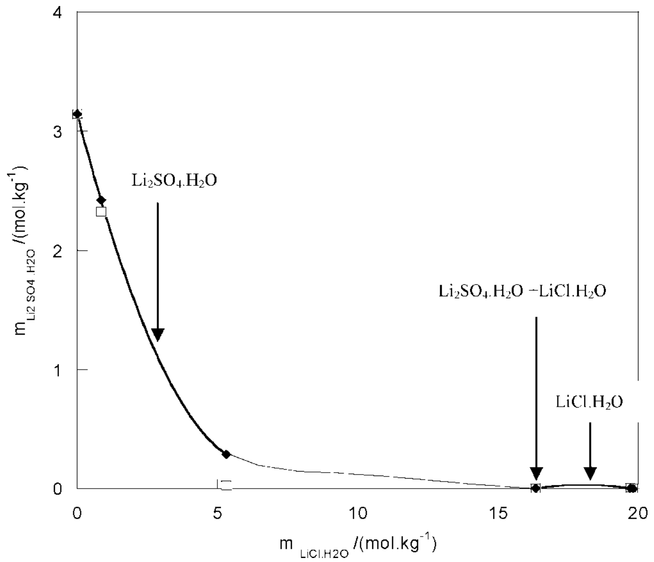

**Figure 4.** □, Calculated solubility in the system $\{LiCl + Li_2SO_4\}$(aq) compared with ◆, experimental data[27d] at $T = 298.15$ K.

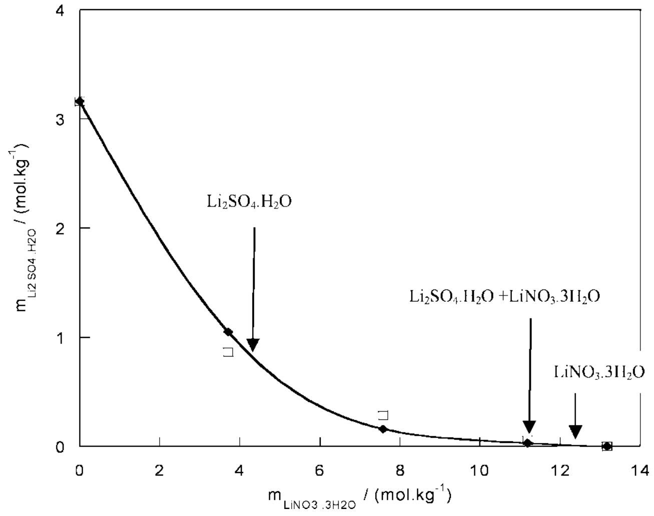

**Figure 5.** □, Calculated solubility in the system $\{LiNO_3 + Li_2SO_4\}$(aq) compared with ◆, experimental data[27e] at $T = 298.15$ K.

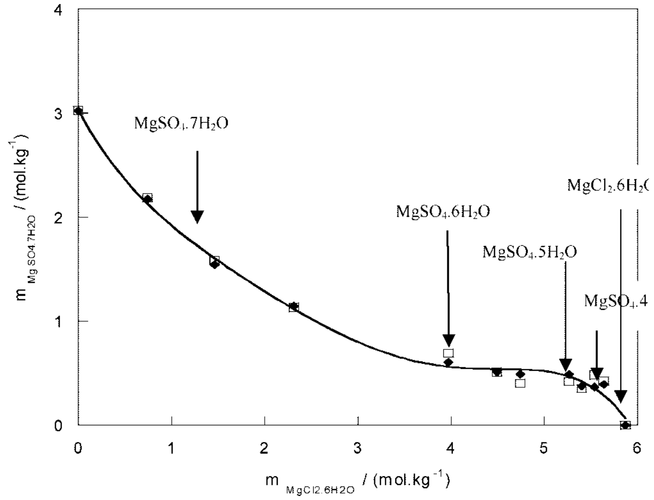

**Figure 6.** □, Calculated solubility in the system $\{MgCl_2 + MgSO_4\}$(aq) compared with ◆, experimental data[27f] at $T = 298.15$ K.

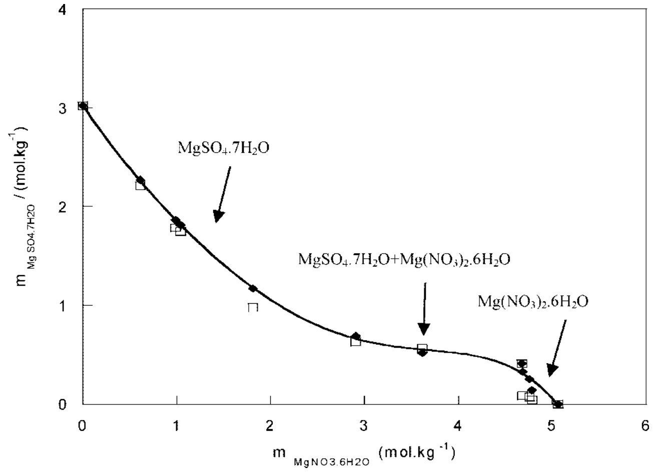

**Figure 7.** □, Calculated solubility in the system $\{Mg(NO_3)_2 + MgSO_4\}$(aq) compared with ◆, experimental data[27g] at $T = 298.15$ K.

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 then equilibrated with a suspended drop of NaCl(aq) or LiCl(aq) which served as a

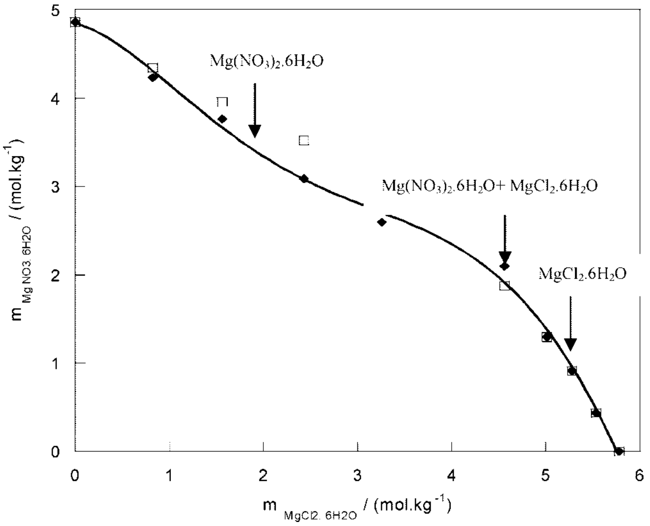

**Figure 8.** □, Calculated solubility in the system $\{MgCl_2 + Mg(NO_3)_2\}(aq)$ compared with ◆, experimental data[27h] at $T = 298.15$ K.

standard. The unknown relative humidity can therefore be determined from measurement of the equilibrium diameter $D$ ($a_w$) at this humidity. Knowing the diameter $D$ ($a_w = 0.84$) of this droplet at the reference relative humidity of 0.84, we can then calculate $K$ and determine graphically the value of $a_w$. The values of the ratio of growth $K$ are calculated from the equation ($K = D(a_w)/D(a_{w(ref)})$) for reference NaCl(aq) and LiCl(aq). Generally, the reference relative humidity is 0.84. For a middle dilute solution, the reference is 0.98.

The solutions of $LiCl \cdot H_2O$, $LiNO_3 \cdot 3H_2O$, and $NH_4NO_3$ were prepared from crystalline material (extrapur-grade chemicals, mass fraction > 0.99) and deionized distilled water. The reference solutions are NaCl(aq) and LiCl(aq).

The uncertainty in the water activity depends on the accuracy of the diameter measurements and is therefore less than ± 0.02 % for $a_w > 0.97$, ± 0.05 % for $0.97 > a_w > 0.95$, ± 0.09 % for $0.95 > a_w > 0.90$, and ± 0.2 % for $a_w < 0.90$. Also the overall uncertainty of the osmotic coefficient is estimated to be, at most, ± 0.006.

## Results

***Water Activity and Osmotic Coefficient.*** In this paper, we have completed measurements of water activities from 6 $mol \cdot kg^{-1}$ to saturation of the pure electrolyte solutions for LiCl(aq), $LiNO_3$(aq), and $NH_4NO_3$(aq) using the hygrometric method at 298.15 K. The experimental values of water activity are listed in Tables 1 to 3. Using the obtained experimental results of the water activity, we have evaluated the osmotic coefficients of the solvent for these binary systems using eq 5.

The corresponding values of ionic parameters $\beta^{(0)}$, $\beta^{(1)}$, and $C^{\phi}$ of the pure electrolytes LiCl(aq), $LiNO_3$(aq), and $NH_4NO_3$(aq) were obtained from Pitzer's expressions by the fits of the experimental osmotic coefficients (Table 4). These parameters are used to predict the solute activity coefficients (Tables 1 to 3).

**Table 5. Calculated Values of the Logarithm of Solubility Product $K^0_{sp}$, the Molality of the Saturated Binary Solutions $m_s$, and the Standard Molar Gibbs Energy of Formation $\Delta G^0_{fm}$ of Simple Salts**

| | $m_s$/($mol \cdot kg^{-1}$) | | | $\Delta G^0_{fm}$ |
|---|---|---|---|---|
| salt | calc | exp[27] | ln $K^0_{sp}$ | $kJ \cdot mol^{-1}$ |
| $NH_4Cl$ | 7.402 | 7.416 | 2.86 | −82.11 |
| $NH_4NO_3$ | 26.532 | 26.421 | 2.70 | −74.23 |
| $(NH_4)_2SO_4$ | 5.806 | 5.808 | −0.82 | −365.25 |
| $LiCl.H_2O$ | 19.959 | 19.833 | 11.85 | −255.11 |
| $LiNO_3 \cdot 3H_2O$ | 12.76 | 12.753 | 4.69 | −445.59 |
| $Li_2SO_4 \cdot H_2O$ | 3.07 | 2.846 | 1.01 | −631.71 |
| $MgCl_2 \cdot 6H_2O$ | 5.86 | 5.862 | 9.06 | −854.41 |
| $Mg(NO_3)_2 \cdot 6H_2O$ | 4.862 | 4.858 | 8.33 | −839.07 |
| $MgSO_4 \cdot 7H_2O$ | 3.026 | 3.027 | −4.36 | −1158.00 |

***Solubility Calculations. Parameterization.*** The Pitzer ion interaction model has been used for thermodynamic analysis of the experimental solubility data, presented in the literature.[27] The values of the pure and mixing parameters are available in previous papers in the range of molality from dilution to saturation.[11−19] We have completed measurements of water activities from 6 $mol \cdot kg^{-1}$ to saturation of the pure electrolyte solutions for LiCl(aq), $LiNO_3$(aq), and $NH_4NO_3$(aq) using the hygrometric method described in a previous work.[12,15] The results are presented in Tables 1 to 3. The parameters for these binary systems are also determined. These parameters were fitted from osmotic coefficients by a least-squares method, and the values are listed in Table 4.

***Binary Systems.*** From the results of measurements of water activities for the total molality range from dilution to saturation for binary electrolyte solutions $\{NH_4Cl(aq), LiCl \cdot H_2O(aq), MgCl_2 \cdot 6H_2O(aq), NH_4NO_3(aq), LiNO_3 \cdot 3H_2O(aq), (NH_4)_2SO_4(aq), Li_2SO_4(aq), Mg(NO_3)_2 \cdot 6H_2O, \text{and } MgSO_4 \cdot 7H_2O(aq)\}$, the osmotic coefficients of the solvent are evaluated for the solutions. These values agree well with the results given by Stokes and Robinson.[28,29]

The experimental data are used to calculate solute activity coefficients using the ion interaction model with our ionic parameters. The results are then used to predict solubility of these electrolyte aqueous solutions. Then, the binary parameters for the entire range of molality up to the saturation are used for the prediction of solubility.

On the basis of the values obtained for $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and $C^{\phi}$ and the molality $m_s$ of the saturated binary solutions, the logarithm of the thermodynamic solubility product (ln $K^0_{sp}$) for the crystalline hydrates was calculated (Table 5). The small deviation between obtained values of ln $K^0_{sp}$ and those determined in the literature is mainly due to the different $m_s$ values used for calculation. The standard molar Gibbs energy

**Table 4. Binary Parameters for a Single Electrolyte at $T = 298.15$ K**

| | | | | | $m_{max}$ | | |
|---|---|---|---|---|---|---|---|
| system | $\beta^{(0)}$ | $\beta^{(1)}$ | $\beta^{(2)}$ | $C^{\phi}$ | $mol \cdot kg^{-1}$ | $\sigma_{\phi}$ | ref |
| $NH_4Cl + H_2O$ | 0.0527 | 0.2011 | - | −0.00306 | 6.00 | 0.0081 | 11 |
| $NH_4NO_3 + H_2O$ | −0.0514 | 0.2228 | - | 0.00214 | 26.60 | 0.006 | this study |
| $(NH_4)_2SO_4 + H_2O$ | 0.04022 | 0.5911 | - | −0.00106 | 5.00 | 0.0009 | 13 |
| $LiCl + H_2O$ | 0.20972 | −0.3438 | - | −0.00433 | 19.22 | 0.053 | this study |
| $LiNO_3 + H_2O$ | 0.1922 | 0.2082 | - | −0.0060 | 13.00 | 0.005 | this study |
| $Li_2SO_4 - H_2O$ | 0.13608 | 1.2513 | - | −0.00399 | 3.00 | 0.001 | 13 |
| $MgCl_2 + H_2O$ | 0.3492 | 1.6653 | - | 0.00598 | 5.00 | 0.0049 | 11 |
| $Mg(NO_3)_2 + H_2O$ | 0.3216 | 1.7578 | - | −0.0051 | 5.00 | 0.0009 | 12 |
| $MgSO_4 + H_2O$ | 0.2305 | 3.267 | −47.93 | 0.0232 | 3.00 | 0.003 | 13 |

**Table 6. Pitzer Mixing Parameters $\theta_{aa'}$ and $\psi_{aa'c}$ for Ternary Aqueous Systems at $T$ = 298.15 K**

| common cation M, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$ with M = $NH_4^+$, $Li^+$, or $Mg^{2+}$ | system | $\theta_{aa'}$ | $\psi_{aa'c}$ | ref |
|---|---|---|---|---|
| $H_4^+$ | $NH_4Cl + NH_4NO_3 + H_2O$ | 0.0180 | −0.0023 | 14 |
| | $NH_4Cl + (NH_4)_2SO_4 + H_2O$ | −0.021 | 0.002 | 15 |
| | $NH_4NO_3 + (NH_4)_2SO_4 + H_2O$ | −0.0099 | −0.0004 | 16 |
| $Li^+$ | $LiCl + LiNO_3 + H_2O$ | 0.0175 | −0.0014 | 17 |
| | $LiCl + Li_2SO_4 + H_2O$ | −0.0072 | −0.0004 | 17 |
| | $LiNO_3 + Li_2SO_4 + H_2O$ | 0.0656 | −0.0204 | 17 |
| $Mg^{2+}$ | $MgCl_2 + Mg\ (NO_3)_2 + H_2O$ | 0.0528 | −0.0082 | 18 |
| | $MgCl_2 + MgSO_4 + H_2O$ | 0.0383 | −0.0094 | 19 |
| | $Mg\ (NO_3)_2 + MgSO_4 + H_2O$ | 0.0447 | −0.0046 | 19 |

**Table 7. Standard Deviation of the Calculated and Experimental[27] Solubility of the Ternary Aqueous Systems Containing M, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$ with M = $NH_4^+$, $Li^+$, or $Mg^{2+}$[a]**

| ternary systems | SD/mol·kg$^{-1}$ |
|---|---|
| $NH_4Cl + NH_4NO_3 + H_2O$ | 0.1318 |
| $NH_4Cl + (NH_4)_2SO_4 + H_2O$ | 0.3451 |
| $NH_4NO_3 + (NH_4)_2SO_4 + H_2O$ | 0.2526 |
| $LiCl + Li_2SO_4 + H_2O$ | 0.1230 |
| $LiNO_3 + Li_2SO_4 + H_2O$ | 0.1006 |
| $MgCl_2 + Mg(NO_3)_2 + H_2O$ | 0.2184 |
| $MgCl_2 + MgSO_4 + H_2O$ | 0.0797 |
| $Mg(NO_3)_2 + MgSO_4 + H_2O$ | 0.1207 |

[a] Standard deviation SD calculated by: $\mathrm{SD} = \sqrt{(s_{cal} - s_{exp})^2/(N - 1)}$, with $s_{cal}$ and $s_{exp}$ being calculated and experimental solubility, respectively.

of formation $\Delta G_{f\,m}^{\,0}$ of simple salts crystallizing from saturated binary solutions was calculated on the basis of $\ln K^0_{sp}$ values and using thermodynamic data of aqueous species.[30]

***Ternary Systems.*** The results of measurements of water activities allow the deduction of osmotic coefficients of the solvent. From these measurements, ionic mixing parameters are determined and used to predict the solute activity coefficients in the mixture, using Pitzer's model. The parameters $\theta_{aa'}$ and $\psi_{aa'c}$ are evaluated for these systems[14−19] (Table 6) and used to predict solubility data for the ternary aqueous solutions $MCl + M_2SO_4 + H_2O$, $MCl + MNO_3 + H_2O$, and $M_2SO_4 + MNO_3 + H_2O$ with M = $NH_4^+$, $Li^+$, and $MgCl_2 + MgSO_4 + H_2O$, $MgCl_2 + Mg(NO_3)_2 + H_2O$, and $MgSO_4 + Mg(NO_3)_2 + H_2O$ at $T$ = 298.15 K.

The phase diagrams according to the calculated and experimental data are shown in Figures 1 to 8. The results of the calculation agree with the experimental data given in the literature[27] with a standard deviation (SD/mol·kg$^{-1}$) ranging from 0.0717 to 0.3451 (Table 7).

## Conclusion

The solubility isotherms of the ternary aqueous solutions containing M, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$ with M = $NH_4^+$, $Li^+$, or $Mg^{2+}$ at $T$ = 298.15 K were calculated by the ion interaction model using our binary parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and $C^{\phi}$ and ternary mixing parameters $\theta_{aa'}$ and $\psi_{aa'c}$ in the range of molality from dilution to saturation. From the measurements of water activities for aqueous electrolyte solutions at total molality up to saturation, the parameters of ionic interaction were obtained and used to predict solubility. The results of solubility prediction agree with the literature experimental data.

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