The Semi-Ideal Solution Theory for Mixed Ionic Solutions at Solid−Liquid−Vapor Equilibrium

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The semi-ideal solution theory has been presented to describe the changes in thermodynamic properties accompanying the process of mixing the nonideal electrolyte solutions $M_iX_i-(NY)_{sat}-H_2O$ ($i = 1$ and 2) at constant activities of NY and H_2O, including concentration, chemical potential, activities of all M_iX_i, Gibbs free energy, enthalpy, entropy, thermal properties, and volumetric properties. The theory states that, under the conditions of equal activities of NY and H_2O, the average hydration numbers characterizing the ion−solvent interactions have the same values in the mixture as in the subsystems and the process of mixing these nonideal electrolyte solutions is as simple as that of mixing the ideal solutions if the contributions from the ion−ion interactions to the solvent activity are assumed to be the same in the mixture as in its subsystems, which has been justified by the calculations of the Pitzer equation. Therefore, a series of novel linear equations are established for the thermodynamic properties accompanying the process of mixing these nonideal solutions as well as mixing the ideal solutions $M_iX_i-(NY)_{sat}-H_2O$ ($i = 1$ and 2) of equal mole fractions of NY and H_2O. From these equations, the widely applied empirical Zdanovskii's rule is derived theoretically, and the important constant in the McKay−Perring equation under isopiestic equilibrium is determined theoretically, which has been substantiated by comparisons with the experimental results for 18 mixtures reported in the literature. Isopiestic measurements have been made for the systems $BaCl_2-LaCl_3-H_2O$, $NaCl-BaCl_2-LaCl_3-H_2O$, and $NaCl-LaCl_3-BaCl_2\cdot 2H_2O_{(sat)}-H_2O$ at 298.15 K. The results are used to test the novel linear concentration relations, and the agreement is excellent. The novel predictive equation for the activity coefficient of M_iX_i in $M_1X_1-M_2X_2-(NY)_{sat}-H_2O$ has been compared with the calculations of the Pitzer equation, and the agreement is good.

1. Introduction

The Zdanovskii's rule was first discovered empirically by Zdanovskii for ternary unsaturated electrolyte solutions[1] and was derived for unsaturated nonelectrolyte solutions by Stokes and Robinson.[2−5] Since then, it has been experimentally extended to unsaturated aqueous solutions of electrolytes and nonelectrolytes.[6,7] The Zdanovskii's rule coupled with the McKay−Perring equation[8] yields the simple equation for the activity coefficient of either solute in multicomponent unsaturated solutions.[9] However, while the model parameter in the McKay−Perring equation was announced to be an arbitrary proportionality constant, in practice it was empirically set equal to the salt stoichiometric coefficient.[9−12] Recently, this rule has received wide and growing attention[9−15] and has been used to establish the novel predictive equations for the thermodynamic properties[10,11] and viscosity[12] of multicomponent solutions.

Up to now, the Zdanovskii's rule has not been theoretically justified. Mikhailov derived the rule for very dilute electrolyte solutions where the Debye−Hückel theory applies.[16] However, extensive isopiestic results indicate that the rule is much more widely applicable than can be theoretically justified by Mikhailov.[17,18] Rard also derived the rule by assuming that the osmotic coefficients of the binary and multicomponent solutions are equal under isopiestic equilibrium,[19] which is evidently quite reasonable for the solutions of 1:1 electrolytes. Therefore, in this study, a semi-ideal solution theory is proposed on the basis of the Debye−Hückel theory and the concept of the stepwise hydration equilibrium, from which the novel concentration relations for multicomponent saturated electrolyte solutions are established and the Zdanovskii's rule (for unsaturated solutions) is theoretically derived. The simple equation for the activity coefficient of each unsaturated solute in saturated solutions is also derived, from which the simplified McKay−Perring equation for unsaturated solutions is reproduced and its proportionality constant is theoretically determined. A new set of simple predictive equations are proposed for thermodynamic properties of saturated electrolyte solutions from those of their subsystems. The isopiestic measurements at 298.15 K have been made for the systems $NaCl-BaCl_2-LaCl_3-H_2O$ and $NaCl-BaCl_2\cdot 2H_2O_{(sat)}-LaCl_3-H_2O$. The results together with the calculations based on the Pitzer equation[20,21] are used to test the proposed equations.

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2. The Semi-Ideal Solution Theory

Let electrolytes M_iX_i and NY represent the solute components present below their solubility limits and that present as saturated solutions, respectively. Let the superscript (io) denote the quantity in the ternary saturated subsystem $M_iX_i-(NY)_{sat}-H_2O$ or in the binary unsaturated subsystem $M_iX_i-H_2O$. The other notations used in this paper are summarized in the Glossary. In this study, it is assumed that all electrolyte solutes are completely dissociated and produce υ_{M_i} and υ_N cations of charges (z_{M_i} and z_N) and (υ_{X_i} and υ_Y) anions of charges (z_{X_i} and z_Y), respectively. Note that in this paper the cations and anions are denoted by (M_i and N) and (X_i and Y) instead of ($M_i^{z_{M_i}+}$ and N^{z_N+}) and ($X_i^{z_{X_i}-}$ and Y^{z_Y-}).[21]

2.1. Treatment of Ion−Ion and Ion−Solvent Interactions. In this study, the ion−ion interactions in the mixture $M_1X_1-M_2X_2-NY_{(sat)}-H_2O$ are treated with the Debye−Hückel theory, and the ion−solvent interactions are described by the stepwise hydration equilibrium.[2−5] That is, the Gibbs energy of the above system is composed of two terms, namely, $G = G^{DH} + G^{Hy}$, where G^{DH} is the Debye−Hückel contribution, and G^{Hy} describes the semi-ideal mixture of the resulting species based on the mole fraction x. Therefore, $\ln a = \ln a^{DH} + \ln a^{Hy}$, where $a^{Hy} = x$. The stepwise hydration equilibrium can be symbolized by

$$NY(s) + H_2O \leftrightarrows \upsilon_N N\cdot H_2O_{(1)} + \upsilon_Y Y(aq) \tag{1}$$

and

$$U\cdot H_2O_{(l-1)} + H_2O \leftrightarrows U\cdot H_2O_{(l)} \tag{2}$$

where U = N, Y, M_i, and X_i with $i = 1$ and 2, and $l = 2, ..., n$. If we assume that $a^{DH}_{U\cdot H_2O(l)}/a^{DH}_{U\cdot H_2O(l-1)} = 1$, then the equilibrium constants K_l^U for the hydration equilibrium denoted by eq 2 are given by

$$K_l^U = \frac{x_{U\cdot H_2O(l)}}{x_{U\cdot H_2O(l-1)}a_{H_2O}} \tag{3}$$

It is clear that K_l^U and thereby the average hydration numbers, $\bar{h}_{U-H_2O} = \sigma/\Sigma$ with $\sigma = \partial\Sigma/\partial \ln a_{H_2O} = \sum_{l=1}^{n} lK_1^U \ldots K_l^U a_{H_2O}^l$ and $\Sigma = 1 + \sum_{l=1}^{n} K_1^U \ldots K_l^U a_{H_2O}^l$, depend only on water activity a_{H_2O}. However, the equilibrium constant $K_1^N = x_{N\cdot H_2O_{(1)}}x_{Y_{(aq)}}/a_{H_2O}$ for the saturated solutes (equals $K'_0 = a_{NY_{(aq)}}/a_{NY_{(s)}} = a_{NY_{(aq)}}$ for NY(s) $\leftrightarrows$ NY(aq) times $K'_0 = x_{N\cdot H_2O_{(1)}}x_{Y_{(aq)}}/(a_{NY_{(aq)}}a_{H_2O})$ for $NY(aq) + H_2O \leftrightarrows \upsilon_N N\cdot H_2O_{(1)} + \upsilon_Y Y(aq)$) is different from $K_1^{M_1} = x_{M_1\cdot H_2O_{(1)}}/(x_{M_1\cdot H_2O_{(0)}}a_{H_2O})$ for unsaturated solutes, and thus, $\bar{h}_{N-H_2O}$ differs from $\bar{h}_{M_1-H_2O}$ for a given water activity a_{H_2O}.

2.2. Novel Linear Concentration Relations at Constant Activities of NY and H₂O. The water activity for the semi-ideal mixture $M_iX_i-(NY)_{sat}-H_2O$ ($i = 1$ and 2), $a^{(io)}_{H_2O}$, is given by[2−5]

$$\ln a^{(io)}_{H_2O} = \ln a^{(io),DH}_{H_2O} + \ln x^{(io),free}_{H_2O} \tag{4}$$

where the superscript free denotes the free quantity. $a^{(io),DH}_{H_2O}$ and $x^{(io),free}_{H_2O}$ are the Debye−Hückel contribution to water activity and the mole fraction of the free solvent H_2O in the mixture. $x^{(io),free}_{H_2O} = n^{(io),free}_{H_2O}/n^{(io)}_{total}$ with $n^{(io),free}_{H_2O} = n^{(io)}_{H_2O} - \nu_{M_iX_i}\bar{h}_{M_iX_i-H_2O}n^{(io)}_{M_iX_i} - \nu_{NY}\bar{h}_{NY-H_2O}n^{(io)}_{NY}$ and $n^{(io)}_{total} = n^{(io),free}_{H_2O} + \nu_{M_iX_i}n^{(io)}_{M_iX_i} + \nu_{NY}n^{(io)}_{NY}$, where n and ν are the mole number and the salt stoichiometric coefficient, $\nu_{M_iX_i} = \nu_{M_i} + \nu_{X_i}$, and $\nu_{M_iX_i}\bar{h}_{M_iX_i-H_2O} = \nu_{M_i}\bar{h}_{M_i-H_2O} + \nu_{X_i}\bar{h}_{X_i-H_2O}$. ν_{NY} and $\nu_{NY}\bar{h}_{NY-H_2O}$ are similarly defined.

Similarly, a_{H_2O} for the mixture $M_1X_1-M_2X_2-(NY)_{sat}-H_2O$ is given by

$$\ln a_{H_2O} = \ln a^{DH}_{H_2O} + \ln\frac{n^{free}_{H_2O}}{n_{total}} \tag{5}$$

with $n^{free}_{H_2O} = n_{H_2O} - \sum_{i=1}^{2} \nu_{M_iX_i}\bar{h}_{M_iX_i-H_2O}n_{M_iX_i} - \nu_{NY}\bar{h}_{NY-H_2O}n_{NY}$ and $n_{total} = n^{free}_{H_2O} + \sum_{i=1}^{2} \nu_{M_iX_i}n_{M_iX_i} + \nu_{NY}n_{NY}$. Since $a_{H_2O} = a^{(io)}_{H_2O}$, if we assume that $a^{DH}_{H_2O} = a^{(io),DH}_{H_2O}$, then combination of eqs 4 and 5 yields (see Supporting Information for the detailed derivation)

$$\frac{n_{M_1X_1}}{n^{(1o)}_{M_1X_1}}n^{(1o)}_{H_2O} + \frac{n_{M_2X_2}}{n^{(2o)}_{M_2X_2}}n^{(2o)}_{H_2O} = n_{H_2O} \tag{6}$$

and

$$\frac{n_{M_1X_1}}{n^{(1o)}_{M_1X_1}}n^{(1o)}_{NY} + \frac{n_{M_2X_2}}{n^{(2o)}_{M_2X_2}}n^{(2o)}_{NY} = n_{NY} \tag{7}$$

at constant activities of H_2O and NY and within the range $0 \le [n_{M_iX_i}/n^{(io)}_{M_iX_i}] \le 1$. Equations 6 and 7 can be generalized to the mixtures $M_1X_1-\cdots-M_nX_n-(N_1Y_1)_{sat}-\cdots-(N_{n'}Y_{n'})_{sat}-H_2O$ in terms of the concentrations of its subsystems $M_iX_i-(N_1Y_1)_{sat}-\cdots-(N_{n'}Y_{n'})_{sat}-H_2O$ ($i = 1, 2, ..., n$) of equal activities of all $N_1Y_1, ..., N_{n'}Y_{n'}$ and H_2O

$$\sum_{i=1}^{n}\frac{n_{M_iX_i}}{n^{(io)}_{M_iX_i}}n^{(io)}_{H_2O} = n_{H_2O} \tag{8}$$

and

$$\sum_{i=1}^{n}\frac{n_{M_iX_i}}{n^{(no)}_{M_iX_i}}n^{(io)}_{N_jY_j} = n_{N_jY_j} \quad (j = 1, 2, ..., n') \tag{9}$$

where $0 \le [n_{M_iX_i}/n^{(io)}_{M_iX_i}] \le 1$, $a_{H_2O} = const$, and $a_{N_jY_j} = const$. That is

$$\sum_{i=1}^{n}\frac{m_{M_iX_i}}{m^{(io)}_{M_iX_i}} = 1 \tag{10}$$

$$\sum_{i=1}^{n}\frac{m_{M_iX_i}}{m^{(no)}_{M_iX_i}}m^{(io)}_{N_jY_j} = m_{N_jY_j} \quad (j = 1, 2, ..., n') \tag{11}$$

It is clear that for the mixtures $M_1X_1-M_2X_2-H_2O$ eq 10 reduces to the well-known Zdanovskii's rule[1]

$$\frac{m'_{M_1X_1}}{m'^{(1o)}_{M_1X_1}} + \frac{m'_{M_2X_2}}{m'^{(2o)}_{M_2X_2}} = 1 \tag{12}$$

where $m'^{(io)}_{M_iX_i}$ ($i = 1$ and 2) are the molalities of M_iX_i in $M_iX_i-H_2O$ ($i = 1$ and 2) at the water activity of the mixed solution $M_1X_1-M_2X_2-H_2O$ of given molalities $m'_{M_iX_i}$.

2.3. New Simple Equations for the Thermodynamic Properties. The thermodynamic relations for the system M_iX_i-

$(\mathrm{NY})_{\mathrm{sat}}-\mathrm{H_2O}$ ($i = 1$ and 2) at constant temperature and pressure can be expressed as

$$\nu_{\mathrm{M}_i} n^{(io)}_{\mathrm{M}_i\mathrm{X}_i} d\mu^{(io)}_{\mathrm{M}_i} + \nu_{\mathrm{X}_i} n^{(io)}_{\mathrm{M}_i\mathrm{X}_i} d\mu^{(io)}_{\mathrm{X}_i} + n^{(io)}_{\mathrm{H_2O}} d\mu^{(io)}_{\mathrm{H_2O}} = 0$$

$$(\mu^{(io)}_{\mathrm{H_2O}} = \mathit{const} \text{ and } \mu^{(io)}_{\mathrm{NY}} = \mathit{const}) \tag{13}$$

If we define the chemical potential $\mu^{(io)}_{\mathrm{M}_i\mathrm{X}_i} = (1/\nu_{\mathrm{M}_i\mathrm{X}_i})(\nu_{\mathrm{M}i}\mu^{(io)}_{\mathrm{M}_i} + \nu_{\mathrm{X}_i}\mu^{(io)}_{\mathrm{X}_i})$, then eq 13 can be rewritten as

$$\nu_{\mathrm{M}_i\mathrm{X}_i} n^{(io)}_{\mathrm{M}_i\mathrm{X}_i} d\ \ln\mu^{(io)}_{\mathrm{M}_i\mathrm{X}_i} + n^{(io)}_{\mathrm{H_2O}} d\ \ln\mu^{(io)}_{\mathrm{H_2O}} = 0$$

$$(\mu^{(io)}_{\mathrm{H_2O}} = \mathit{const} \text{ and } \mu^{(io)}_{\mathrm{NY}} = \mathit{const}) \tag{14}$$

That is

$$\left(\frac{\partial\mu^{(io)}_{\mathrm{M}_i\mathrm{X}_i}}{\partial\mu^{(io)}_{\mathrm{H_2O}}}\right)_{n^{(io)}_{\mathrm{MiXi}}} = -\left(\frac{n^{(io)}_{\mathrm{H_2O}}}{\nu_{\mathrm{M}_i\mathrm{X}_i} n^{(io)}_{\mathrm{M}_i\mathrm{X}_i}}\right)_{\mu^{(io)}_{\mathrm{H_2O}}}$$

$$(\mu^{(io)}_{\mathrm{H_2O}} = \mathit{const} \text{ and } \mu^{(io)}_{\mathrm{NY}} = \mathit{const}) \tag{15}$$

In literature, a similar equation has been given for the system $\mathrm{J-H_2O}$.[22] For the system $\mathrm{M_1X_1-M_2X_2-(NY)_{sat}-H_2O}$, we reach

$$\left(\frac{\partial\mu_{\mathrm{M}_i\mathrm{X}_i}}{\partial\mu_{\mathrm{H_2O}}}\right)_{n_{\mathrm{M1X1}}, n_{\mathrm{M2X2}}} = \left(\frac{\partial n_{\mathrm{H_2O}}}{\nu_{\mathrm{M}_i\mathrm{X}_i}\partial n_{\mathrm{M}_i\mathrm{X}_i}}\right)_{\mu_{\mathrm{H2O,nMi'Xi'}\neq\mathrm{M}_i\mathrm{X}_i}}$$

$$(\mu_{\mathrm{H_2O}} = \mathit{const} \text{ and } \mu_{\mathrm{NY}} = \mathit{const}) \tag{16}$$

with $i' \in (1, 2)$. Combination of eqs 8, 15, and 16 gives (see Supporting Information for the detailed derivation)

$$\mu_{\mathrm{M}_i\mathrm{X}_i} = \mu^{(io)}_{\mathrm{M}_i\mathrm{X}_i} + RT \ln\frac{\nu_{\mathrm{M}_i\mathrm{X}_i} x_{\mathrm{M}_i\mathrm{X}_i}}{\nu_{\mathrm{M_1X_1}} x_{\mathrm{M_1X_1}} + \nu_{\mathrm{M_2X_2}} x_{\mathrm{M_2X_2}}} \tag{17}$$

$$a_{\mathrm{M}_i\mathrm{X}_i} = \frac{\nu_{\mathrm{M}_i\mathrm{X}_i} x_{\mathrm{M}_i\mathrm{X}_i}}{\nu_{\mathrm{M_1X_1}} x_{\mathrm{M_1X_1}} + \nu_{\mathrm{M_2X_2}} x_{\mathrm{M_2X_2}}} a^{(io)}_{\mathrm{M}_i\mathrm{X}_i} \tag{18}$$

and

$$f_{\mathrm{M}_i\mathrm{X}_i} = \frac{\nu_{\mathrm{M}_i\mathrm{X}_i} x^{(io)}_{\mathrm{M}_i\mathrm{X}_i}}{\nu_{\mathrm{M_1X_1}} x_{\mathrm{M_1X_1}} + \nu_{\mathrm{M_2X_2}} x_{\mathrm{M_2X_2}}} f^{(io)}_{\mathrm{M}_i\mathrm{X}_i} \tag{19}$$

where $i = 1$ and 2, $a_{\mathrm{H_2O}} = \mathit{const}$, and $a_{\mathrm{NY}} = \mathit{const}$. a and $f_{\mathrm{M}_i\mathrm{X}_i}$ are the activity and the activity coefficient on the mole fraction scale. Equation 18 is equivalent to

$$a_{\mathrm{M}_i\mathrm{X}_i} = \frac{\nu_{\mathrm{M}_i\mathrm{X}_i} m_{\mathrm{M}_i\mathrm{X}_i}}{\nu_{\mathrm{M_1X_1}} m_{\mathrm{M_1X_1}} + \nu_{\mathrm{M_2X_2}} m_{\mathrm{M_2X_2}}} a^{(io)}_{\mathrm{M}_i\mathrm{X}_i} \quad (i = 1 \text{ and } 2)$$

$$(a_{\mathrm{H_2O}} = \mathit{const} \text{ and } a_{\mathrm{NY}} = \mathit{const}) \tag{20}$$

$f_{\mathrm{M}_i\mathrm{X}_i}$ is related to its molal value $\gamma_{\mathrm{M}_i\mathrm{X}_i}$ by $f_{\mathrm{M}_i\mathrm{X}_i} = \gamma_{\mathrm{M}_i\mathrm{X}_i}[1 + M_{\mathrm{H_2O}}/1000(\sum_{i=1}^{2} m_{\mathrm{M}_i\mathrm{X}_i} + m_{\mathrm{NY}})]$, where M is the molar mass. Therefore, eq 19 can be rewritten as

$$\gamma_{\mathrm{M}_i\mathrm{X}_i} = \frac{\nu_{\mathrm{M}_i\mathrm{X}_i} m^{(io)}_{\mathrm{M}_i\mathrm{X}_i}}{\nu_{\mathrm{M_1X_1}} m_{\mathrm{M_1X_1}} + \nu_{\mathrm{M_2X_2}} m_{\mathrm{M_2X_2}}} \gamma^{(io)}_{\mathrm{M}_i\mathrm{X}_i} \quad (i = 1 \text{ and } 2)$$

$$(a_{\mathrm{H_2O}} = \mathit{const} \text{ and } a_{\mathrm{NY}} = \mathit{const}) \tag{21}$$

For the unsaturated solution $\mathrm{M_1X_1-M_2X_2-H_2O}$, eq 21 reduces to the following well-known equation derived by Vdovenko and Ryazanov[14]

$$\gamma'_{\mathrm{M}_i\mathrm{X}_i} = \frac{\nu_{\mathrm{M}_i\mathrm{X}_i} m'^{(io)}_{\mathrm{M}_i\mathrm{X}_i}}{\nu_{\mathrm{M_1X_1}} m'_{\mathrm{M_1X_1}} + \nu_{\mathrm{M_2X_2}} m'_{\mathrm{M_2X_2}}} \gamma'^{(io)}_{\mathrm{M}_i\mathrm{X}_i} \quad (i = 1 \text{ and } 2)$$

$$(a_{\mathrm{H_2O}} = \mathit{const}) \tag{22}$$

where the superscript ′ denotes the quantity of $\mathrm{M}_i\mathrm{X}_i$ in unsaturated solutions $\mathrm{M}_i\mathrm{X}_i-\mathrm{H_2O}$ ($i = 1$ and 2) and $\mathrm{M_1X_1-M_2X_2-H_2O}$.

Now, let $\Delta_{\mathrm{mix}}G^{(io)}$, $\Delta_{\mathrm{mix}}H^{(io)}$, $\Delta_{\mathrm{mix}}S^{(io)}$, and $\Delta_{\mathrm{mix}}V^{(io)}$ denote the changes in Gibbs free energy, enthalpy, entropy, and volume accompanying the process of preparing the subsystems $\mathrm{M}_i\mathrm{X}_i-(\mathrm{NY})_{\mathrm{sat}}-\mathrm{H_2O}$ ($i = 1$ and 2). Let $\Delta_{\mathrm{mix}}G$, $\Delta_{\mathrm{mix}}H$, $\Delta_{\mathrm{mix}}S$, and $\Delta_{\mathrm{mix}}V$ represent the corresponding properties accompanying preparation of the system $\mathrm{M_1X_1-M_2X_2-(NY)_{sat}-H_2O}$ having the same activities of NY and $\mathrm{H_2O}$ as those of the subsystems $\mathrm{M}_i\mathrm{X}_i-(\mathrm{NY})_{\mathrm{sat}}-\mathrm{H_2O}$ ($i = 1$ and 2). Then, combination of eqs 8 and 9 with eq 18 and the thermodynamic relations (remembering the fact that $a_{\mathrm{H_2O}} = a^{(1o)}_{\mathrm{H_2O}} = a^{(2o)}_{\mathrm{H_2O}}$ and $a_{\mathrm{NY}} = a^{(1o)}_{\mathrm{NY}} = a^{(2o)}_{\mathrm{NY}}$) gives

$$\Delta_{\mathrm{mix}}G = \sum_{i=1}^{2}\frac{n_{\mathrm{M}_i\mathrm{X}_i}}{n^{(io)}_{\mathrm{M}_i\mathrm{X}_i}}\Delta_{\mathrm{mix}}G^{(io)} + RT\sum_{i=1}^{2}\nu_{\mathrm{M}_i\mathrm{X}_i} n_{\mathrm{M}_i\mathrm{X}_i} \ln\frac{\nu_{\mathrm{M}_i\mathrm{X}_i} x_{\mathrm{M}_i\mathrm{X}_i}}{\nu_{\mathrm{M_2X_2}} x_{\mathrm{M_2X_2}} + \nu_{\mathrm{M_1X_1}} x_{\mathrm{M_1X_1}}} \tag{23}$$

$$\Delta_{\mathrm{mix}}H = \frac{n_{\mathrm{M_1X_1}}}{n^{(1o)}_{\mathrm{M_1X_1}}}\Delta_{\mathrm{mix}}H^{(1o)} + \frac{n_{\mathrm{M_2X_2}}}{n^{(2o)}_{\mathrm{M_2X_2}}}\Delta_{\mathrm{mix}}H^{(2o)} \tag{24}$$

$$\Delta_{\mathrm{mix}}V = \frac{n_{\mathrm{M_1X_1}}}{n^{(1o)}_{\mathrm{M_1X_1}}}\Delta_{\mathrm{mix}}V^{(1o)} + \frac{n_{\mathrm{M_2X_2}}}{n^{(2o)}_{\mathrm{M_2X_2}}}\Delta_{\mathrm{mix}}V^{(2o)} \tag{25}$$

$$\Delta_{\mathrm{mix}}S = \sum_{i=1}^{2}\frac{n_{\mathrm{M}_i\mathrm{X}_i}}{n^{(io)}_{\mathrm{M}_i\mathrm{X}_i}}\Delta_{\mathrm{mix}}S^{(io)} + R\sum_{i=1}^{2}\nu_{\mathrm{M}_i\mathrm{X}_i} n_{\mathrm{M}_i\mathrm{X}_i} \ln\frac{\nu_{\mathrm{M}_i\mathrm{X}_i} x_{\mathrm{M}_i\mathrm{X}_i}}{\nu_{\mathrm{M_2X_2}} x_{\mathrm{M_2X_2}} + \nu_{\mathrm{M_1X_1}} x_{\mathrm{M_1X_1}}} \tag{26}$$

$$C_{\mathrm{P}} = \frac{n_{\mathrm{M_1X_1}}}{n^{(1o)}_{\mathrm{M_1X_1}}} C^{(1o)}_{\mathrm{P}} + \frac{n_{\mathrm{M_2X_2}}}{n^{(2o)}_{\mathrm{M_2X_2}}} C^{(2o)}_{\mathrm{P}} \tag{27}$$

$$d = \frac{y_{\mathrm{M_1X_1}} + y_{\mathrm{M_2X_2}}}{\sum_{i=1}^{2}(y_{\mathrm{M}_i\mathrm{X}_i}/d^{(io)})} \tag{28}$$

with $y_{\mathrm{M}_i\mathrm{X}_i} = (n_{\mathrm{M}_i\mathrm{X}_i}/n^{(io)}_{\mathrm{M}_i\mathrm{X}_i}) n^{(io)}_{\mathrm{H_2O}} M_{\mathrm{H_2O}} + n_{\mathrm{M}_i\mathrm{X}_i} M_{\mathrm{M}_i\mathrm{X}_i} + (n_{\mathrm{M}_i\mathrm{X}_i}/n^{(io)}_{\mathrm{M}_i\mathrm{X}_i}) n^{(io)}_{\mathrm{NY}} M_{\mathrm{NY}}$, where C_{P} and $C^{(io)}_{\mathrm{P}}$ are the specific heat capacities. d and $d^{(io)}$ denote the densities. Note that $n_{\mathrm{M}_i\mathrm{X}_i}/n^{(io)}_{\mathrm{M}_i\mathrm{X}_i}$ and n in eqs 23−28 can be replaced by $m_{\mathrm{M}_i\mathrm{X}_i}/m^{(io)}_{\mathrm{M}_i\mathrm{X}_i}$ and m, respectively, and that under this condition eqs 23−26 are the changes in the Gibbs free energies, enthalpy, entropy, and volume of mixing per kilogram of solvent, respectively.

For the unsaturated solutions, eqs 23−28 reduce to the simple predictive equations for the Gibbs free energy, thermal properties, and volumetric properties of unsaturated solution $M_1X_1-M_2X_2-H_2O$ from the properties of its subsystems $M_iX_i-H_2O$ (i = 1 and 2) of equal water activities, and the equations reproduced from eqs 27 and 28 have been shown to be in good agreement with the experimental results reported in the literature.[10,11]

3. Comparisons with the Experimental Measurements and the Pitzer Equations

3.1. Justification of the Basic Assumption. According to the Pitzer equation,[20,21] the Debye−Hückel contribution to the osmotic coefficient $\phi_{H_2O}^{DH}$ can be determined from

$$\phi_{H_2O}^{DH} = \frac{2}{\sum_i \nu_{M_iX_i} m_{M_iX_i} + \nu_{NY} m_{NY}} \frac{-A^{\phi} I^{3/2}}{1 + bI^{1/2}} \tag{29}$$

where I is the molal ionic strength (mol kg^{-1}), and A^{ϕ} is the molal Debye−Hückel coefficient (0.3915 at 298.15 K). b is a universal parameter with the value 1.2 kg$^{1/2}$ mol$^{-1/2}$. Therefore, $a_{H_2O}^{DH}$ can be calculated from eq 29 and

$$\ln a_{H_2O}^{DH} = -M_{H_2O}\phi^{DH}\left(\sum_i \nu_{M_iX_i} m_{M_iX_i} + \nu_{NY} m_{NY}\right) \tag{30a}$$

The average deviation $\Delta_{H_2O}^{(io),DH}$ for the saturated solution $M_1X_1-M_2X_2-(NY)_{sat}-H_2O$ from the relation $a_{H_2O}^{(io),DH}/a_{H_2O}^{DH} = 1$ is then defined as

$$\Delta_{H_2O}^{(io),DH} = 100 \times \frac{\sum_N \left| \frac{a_{H_2O}^{(io),DH}}{a_{H_2O}^{DH}} - 1 \right|}{N} \tag{30b}$$

where N is the number of experimental data points. The function $\Delta'^{(io),DH}_{H_2O}$ for the unsaturated solutions is similarly defined.

The calculated values of $a'^{DH}_{H_2O}$ $(= -M_{H_2O}\phi'^{DH}\sum_i \nu_{M_iX_i} m'_{M_iX_i})$ for 24 ternary unsaturated systems $M_1X_1-M_2X_2-H_2O$ at 298.15 K and those of $a'^{(io),DH}_{H_2O}$ for their binary systems $M_iX_i-H_2O$ (i = 1 and 2) of equal water activity are shown in Table S1 (Supporting Information). The values of $\Delta'^{(io),DH}_{H_2O}$ are as follows: (1) $0.01\% \le \Delta'^{(1o),DH}_{H_2O} \le 0.12\%$ and $0.02\% \le \Delta'^{(2o),DH}_{H_2O} \le 0.12\%$ within the range $0.1 \le I \le 4.2$ mol kg^{-1} for the (1:1 + 1:1) electrolyte mixtures, including NaCl−KCl−H_2O, NaCl−LiCl−H_2O, NaCl−$NaClO_4$−H_2O, and NaCl−$NaNO_3$−H_2O. (2) $0.09\% \le \Delta'^{(1o),DH}_{H_2O} \le 0.84\%$ and $0.36\% \le \Delta'^{(2o),DH}_{H_2O} \le 1.36\%$ within the range $0.22 \le I \le 4.92$ mol kg^{-1} for the first 13 (1:1 + 1:2) electrolyte mixtures, including NaCl−$CaCl_2$−H_2O, NaCl−$BaCl_2$−H_2O, NaCl−$MgCl_2$−H_2O, NaCl−$SrCl_2$−H_2O, HCl−$BaCl_2$−H_2O, HCl−$CaCl_2$−H_2O, HCl−$CoCl_2$−H_2O, HCl−$NiCl_2$−H_2O, HCl−$SrCl_2$−H_2O, HCl−$MnCl_2$−H_2O, HBr−$BaBr_2$−H_2O, HBr−$CaBr_2$−H_2O, and HBr−$MgBr_2$−H_2O. Note that the $\Delta'^{(io),DH}_{H_2O}$ values for these solutions are in general less than 0.60%. (3) ($2.96\% \le \Delta'^{(1o),DH}_{H_2O} \le 4.08\%$, and $0.55\% \le \Delta'^{(2o),DH}_{H_2O} \le 1.0\%$ within the range $0.70 \le I \le 7.6$ mol kg^{-1}) and ($6.43\% \le \Delta'^{(1o),DH}_{H_2O} \le 13.78\%$ and $2.0\% \le \Delta'^{(2o),DH}_{H_2O} \le 3.25$ within the range $9.0 \le I \le 16.8$ mol kg^{-1}) for the ternary systems KCl−$CdCl_2$−H_2O and KI−CdI_2−H_2O. (4) $0.13\% \le \Delta'^{(1o),DH}_{H_2O} \le 1.85\%$ and $0.58\% \le \Delta'^{(2o),DH}_{H_2O} \le 1.76\%$ within the range $0.22 \le I \le 7.8$ mol kg^{-1} for the (1:1 + 1:3), (1:1 + 1:4), and (1:2 + 1:3) electrolyte mixtures, including HCl−$LaCl_3$−H_2O, HCl−$SmCl_3$−H_2O, NaCl−$LaCl_3$−H_2O, HCl−$ThCl_4$−H_2O, and $BaCl_2$−$LaCl_3$−H_2O. The results for the examined (1:1 + 1:1) mixtures within the whole examined experimental range are in good agreement with the assumption (in derivation of eqs 6−12) that $a'^{(io),DH}_{H_2O}/a'^{DH}_{H_2} = 1$, suggesting that these mixtures conform to eq 12 exactly, which is in accordance with the isopiestic measurements. For the first 13 (1:1 + 1:2) electrolyte mixtures, the values of $\Delta'^{(io),DH}_{H_2O}$ are in general less than 0.60%, implying that these systems also conform to eq 12 very well when recalling the fact that eq 12 is expressed in terms of molality but eq 30 in ionic strength. In fact, isopiestic measurements show that NaCl−MCl_2−H_2O and HCl−MCl_2−H_2O with M = Ba, Ca, Mg, and Sr obey eq 12 exactly or at least quite well within the whole examined molality ranges. The values of $\Delta'^{(io),DH}_{H_2O}$ for the examined (1:1 + 1:3), (1:1 + 1:4), and (1:2 + 1:3) mixtures are larger than those of the (1:1 + 1:1) and (1:1 + 1:2) electrolyte mixtures; however, these systems may still conform to eq 12 well, as supported by the isopiestic results for NaCl−$LaCl_3$−H_2O[23] and $BaCl_2$−$LaCl_3$−H_2O (see Table 1), which is attributed to, as mentioned above, the fact that eq 12 is expressed in terms of molality but eq 30 in ionic strength.

The results for the complex-forming systems KCl−$CdCl_2$−H_2O and KI−CdI_2−H_2O are noticeable. Their $\Delta'^{(1o),DH}_{H_2O}$ is considerably larger than $\Delta'^{(2o),DH}_{H_2O}$, and $\Delta'^{(1o),DH}_{H_2O}$ and $\Delta'^{(2o),DH}_{H_2O}$ increase rapidly with increasing molality, indicating that the deviations of these systems from eq 12 increase progressively as the concentration increases and the deviations from the Zdanovskii's linear plot are not symmetrical (the largest deviation does not appear at the point where $m'_{M_1X_1} = m'_{M_2X_2}$). All these are substantiated by the isopiestic results reported in the literature such as those for the system KI−CdI_2−H_2O at 298.15 K[24] illustrated in Figure 1. It is seen from Table S1 and Figure 1 that, while $|\Delta'^{(1o),DH}_{H_2O}/\Delta'^{(2o),DH}_{H_2O}| > 1$, the deviations from the Zdanovskii plot correspondingly increase toward the regions where $m'_{M_1X_1}/m'_{M_2X_2} > 1$.

3.2. Test Whether $k_{M_iX_i}$ Must Be Set Equal to $\nu_{M_iX_i}$. McKay and Perring[8] derived an equation for the activity coefficient of either solute in ternary aqueous solution $M_1X_1-M_2X_2-H_2O$

$$\ln \gamma'_{M_1X_1} = \ln \gamma'^{(1o)}_{M_1X_1} + \ln \frac{k_{M_1X_1} m'^{(1o)}_{M_1X_1}}{m^*} + \frac{1}{M_{H_2O}} \frac{k_{M_1X_1}}{\nu_{M_1X_1}} \int_0^{\ln a'_{H_2O}} \left\{ -\frac{1}{m^{*2}} \left(\frac{\partial m^*}{\partial \ln r_{M_2X_2}} \right)_{a_{H2O}} - \frac{1}{m^*} + k_{M_1X_1} m'^{(1o)}_{M_1X_1} \right\} d \ln a'_{H_2O} \tag{31}$$

where $\gamma'_{M_1X_1}$ is the activity coefficient of solute M_1X_1 in the mixture, and $\gamma'^{(1o)}_{M_1X_1}$ is its value in $M_1X_1-H_2O$ at the water activity of the mixture. $k_{M_1X_1}$ is an arbitrary proportionality constant for solute M_1X_1. m^* is equal to $(k_{M_1X_1} m'_{M_1X_1} + k_{M_2X_2} m'_{M_2X_2})$, and it may be, for example, the ionic strength if $k_{M_1X_1}$ and $k_{M_2X_2}$ are suitably chosen (here, we denote $k_{M_1X_1}$ and $k_{M_2X_2}$ under this condition by $k^I_{M_1X_1}$ and $k^I_{M_2X_2}$ for convenience).[8] The ratio $r_{M_2X_2}$ is equal to $k_{M_2X_2} m'_{M_2X_2}/m^*$. For the unsaturated solution $M_1X_1-M_2X_2-H_2O$ obeying eq 12, eq 31 reduces to

$$\gamma'_{M_1X_1} = \frac{k_{M_1X_1} m'^{(1o)}_{M_1X_1}}{k_{M_1X_1} m'_{M_1X_1} + k_{M_2X_2} m'_{M_2X_2}} \gamma'^{(1o)}_{M_1X_1} \tag{32}$$

TABLE 1: Isopiestic Results for the Systems $BaCl_2(M_2X_2)-LaCl_3(M_3X_3)-H_2O$ and $NaCl(M_1X_1)-BaCl_2(M_2X_2)-LaCl_3(M_3X_3)-H_2O$ at 298.15 K, Taking Aqueous NaCl as the Reference Solution[a]

$m'_{M_1X_1}$	$m'_{M_2X_2}$	$m'_{M_3X_3}$	$\gamma'^{L}_{M_1X_1}$ [b]	$\gamma'^{P}_{M_1X_1}$ [c]	$\gamma'^{L}_{M_2X_2}$	$\gamma'^{P}_{M_2X_2}$	$\gamma'^{L}_{M_3X_3}$	$\gamma'^{P}_{M_3X_3}$
$BaCl_2(M_2X_2)-LaCl_3(M_3X_3)-H_2O$, $\Delta'_{average}$ [d] $= 0.08\%$								
$m^{(1o)\prime}_{M_1X_1} = 0.5058$, $m^{(2o)\prime}_{M_2X_2} = 0.3650$, $m'^{(3o)}_{M_3X_3} = 0.2815$								
	0.1020	0.2027			0.4080	0.4053	0.2665	0.2856
	0.1582	0.1594			0.4096	0.4071	0.2676	0.2872
	0.1987	0.1281			0.4110	0.4084	0.2685	0.2889
	0.2086	0.1207			0.4109	0.4088	0.2684	0.2894
$m'^{(1o)}_{M_1X_1} = 0.8142$, $m'^{(2o)}_{M_2X_2} = 0.5769$, $m'^{(3o)}_{M_3X_3} = 0.4286$								
	0.1264	0.3349			0.4008	0.3963	0.2611	0.2771
	0.3016	0.2043			0.4000	0.3970	0.2606	0.2780
	0.3682	0.1550			0.3995	0.3976	0.2608	0.2785
	0.4252	0.1126			0.3991	0.3980	0.2600	0.2788
$m'^{(1o)}_{M_1X_1} = 1.1726$, $m'^{(2o)}_{M_2X_2} = 0.8134$, $m'^{(3o)}_{M_3X_3} = 0.5825$								
	0.1215	0.4956	1.0004		0.4126	0.4035	0.2707	0.2846
	0.2268	0.4198	0.9994		0.4104	0.4021	0.2693	0.2830
	0.4060	0.2912	0.9992		0.4062	0.4004	0.2665	0.2809
	0.5126	0.2158	1.0005		0.4035	0.3998	0.2648	0.2801
$m'^{(1o)}_{M_1X_1} = 1.5068$, $m'^{(2o)}_{M_2X_2} = 1.0243$, $m'^{(3o)}_{M_3X_3} = 0.7160$								
	0.1508	0.6109			0.4271	0.4180	0.2842	0.2995
	0.3467	0.4731			0.4218	0.4142	0.2807	0.2946
	0.5520	0.3292			0.4161	0.4105	0.2769	0.2904
	0.7022	0.2260			0.4109	0.4087	0.2734	0.2881
$m'^{(1o)}_{M_1X_1} = 1.7950$, $m'^{(2o)}_{M_2X_2} = 1.2015$, $m'^{(3o)}_{M_3X_3} = 0.8201$								
	0.2562	0.6465			0.4417	0.4315	0.2990	0.3135
	0.5185	0.4655			0.4337	0.4251	0.2936	0.3056
	0.8002	0.2754			0.4231	0.4202	0.2864	0.2990
	0.9860	0.1462			0.4185	0.4171	0.2836	0.2952
$m'^{(1o)}_{M_1X_1} = 2.1425$, $m'^{(2o)}_{M_2X_2} = 1.4124$, $m'^{(3o)}_{M_3X_3} = 0.9467$								
	0.3167	0.7332			0.4637	0.4521	0.3220	0.3363
	0.5860	0.5552			0.4524	0.4450	0.3142	0.3270
	0.8255	0.3926			0.4458	0.4387	0.3096	0.3188
	1.0962	0.2134			0.4347	0.4334	0.3018	0.3116
$m'^{(1o)}_{M_1X_1} = 2.4569$, $m'^{(2o)}_{M_2X_2} = 1.6001$, $m'^{(3o)}_{M_3X_3} = 1.0505$								
	0.1991	0.9186			0.4931	0.4786	0.3487	0.3672
	0.6012	0.6548			0.4760	0.4652	0.3367	0.3496
	1.0025	0.3910			0.4609	0.4536	0.3262	0.3350
	1.3996	0.1307			0.4461	0.4451	0.3155	0.3228
$NaCl(M_1X_1)$-$BaCl_2(M_2X_2)$-$LaCl_3(M_3X_3)$-H_2O, $\Delta'_{average}$ [d] $= 0.09\%$								
$m'^{(1o)}_{M_1X_1} = 0.7351$, $m'^{(2o)}_{M_2X_2} = 0.5237$, $m'^{(3o)}_{M_3X_3} = 0.3926$								
0.1659	0.2864	0.0896	0.6316	0.6421	0.4064	0.4033	0.2644	0.2885
0.2864	0.1726	0.1100	0.6385	0.6489	0.4109	0.4056	0.2671	0.2948
0.2015	0.3015	0.0588	0.6336	0.6403	0.4077	0.4051	0.2656	0.2918
0.0988	0.3419	0.0837	0.6280	0.6391	0.4041	0.4020	0.2629	0.2858
$m'^{(1o)}_{M_1X_1} = 1.8868$, $m'^{(2o)}_{M_2X_2} = 1.2544$, $m'^{(3o)}_{M_3X_3} = 0.8569$								
0.2743	0.5936	0.3285	0.6882	0.7020	0.4276	0.4230	0.2942	0.3085
0.4164	0.3778	0.4112	0.6942	0.7106	0.4315	0.4228	0.2967	0.3122
0.3155	0.2498	0.5436	0.7056	0.7296	0.4385	0.4271	0.3016	0.3157
0.6349	0.3550	0.3271	0.6885	0.6980	0.4276	0.4187	0.2942	0.3128
$m'^{(1o)}_{M_1X_1} = 2.6308$, $m'^{(2o)}_{M_2X_2} = 1.7088$, $m'^{(3o)}_{M_3X_3} = 1.1082$								
0.6456	0.8976	0.2526	0.7306	0.7421	0.4594	0.4571	0.3287	0.3471
0.4981	1.1120	0.1776	0.7350	0.7365	0.4551	0.4566	0.3256	0.3428
1.2603	0.5782	0.2010	0.7324	0.7295	0.4536	0.4515	0.3248	0.3526
0.6195	0.6131	0.4486	0.7608	0.7630	0.4706	0.4608	0.3370	0.3542

[a] Results in mol/kg. [b] Calculated from eq 22. [c] Calculated from the Pitzer equation. [d] The average experimental deviation from eq 12, $\Delta'_{average} = 100 \times \sum_N |m'_{M_1X_1}/m'^{(1o)}_{M_1X_1} + m'_{M_2X_2}/m'^{(2o)}_{M_2X_2} + m'_{M_3X_3}/m'^{(3o)}_{M_3X_3} - 1|/N$, where N is the number of experimental data points.

However, according to eq 21, the value of $\gamma'_{M_iX_i}$ for the unsaturated solution $M_1X_1-M_2X_2-H_2O$ obeying eq 12 is related to the $\gamma'^{(io)}_{M_iX_i}$ values of its subsystems $M_iX_i-H_2O$ ($i = 1$ and 2) by eq 22, that is, $k_{M_iX_i}$ is not an arbitrary constant, and for eq 32 to hold, it is necessary that $k_{M_iX_i} = \upsilon_{M_iX_i}$ under isopiestic equilibrium. The 18 electrolyte solutions shown in Table 2 conform to eq 12 well, and thus, the activity coefficients of each solute in these systems are calculated from eq 22 and eq 32 with $k_{M_iX_i} = k^{I}_{M_iX_i}$ and then compared with the experimental results.[23,25−42] An inspection of the second and third columns of Table 2 reveals that eq 22 is in good agreement with the experimental results for all the systems being examined. Note that the present comparisons are limited to the cases where the Zdanovskii's rule works. However, eq 32 with $k_{M_iX_i} = k^{I}_{M_iX_i}$ shows significant deviations from the experimental results for all the examined systems except for the mixed solutions of 1:1

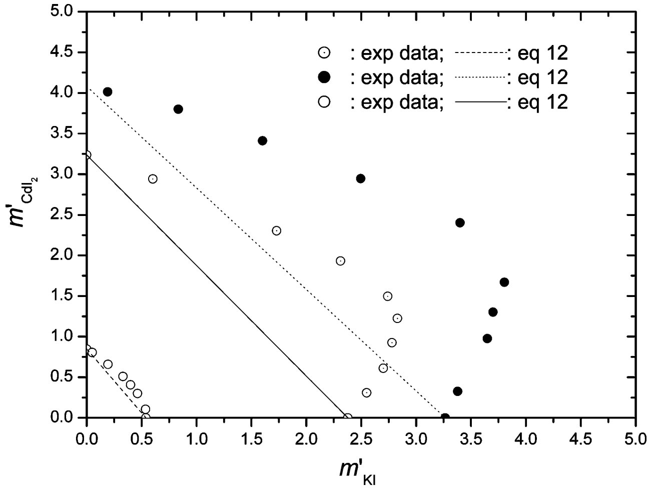

Figure 1. Deviations from the Zdanovskii's linear isopiestic plot for the system KI−CdI$_2$−H$_2$O at 298.15 K.[24]

TABLE 2: Values of the Δ'_γ Functions for the 18 Ternary Electrolyte Solutions at 298.15 K[a]

$M_1X_1-M_2X_2-H_2O$	$\Delta'_{\gamma,M1X1}$	$\Delta'_{\gamma,M2X2}$	I_{max} mol kg^{-1}	$k^I_{M_1X_1}$	$k^I_{M_2X_2}$
NaCl−KCl−H$_2$O[25 b]	0.0172	0.0172	4.2	1	1
NaCl−LiCl−H$_2$O[26]	0.0102	0.0102	3.0	1	1
NaCl−NaNO$_3$−H$_2$O[27]	0.0043	0.0043	3.0	1	1
NaCl−NaClO$_4$−H$_2$O[27]	0.0176	0.0176	3.2	1	1
NaCl−BaCl$_2$−H$_2$O[27]	0.0040	0.2296	5.0	1	3
NaCl−CaCl$_2$−H$_2$O[27]	0.0032	0.1260	1.2	1	3
NaCl−MgCl$_2$−H$_2$O[27]	0.0041	0.0868	5.2	1	3
NaCl−SrCl$_2$−H$_2$O[27]	0.0025	0.1969	3.0	1	3
HCl−BaCl$_2$−H$_2$O[28]	0.0134	0.2048	2.0	1	3
HCl−CaCl$_2$−H$_2$O[29]	0.0117	0.1866	4.8	1	3
HCl−CoCl$_2$−H$_2$O[30]	0.0022	0.1747	2.0	1	3
HCl−SrCl$_2$−H$_2$O[31]	0.0050	0.2436	4.0	1	3
HCl−MnCl$_2$−H$_2$O[32]	0.0058	0.1585	2.5	1	3
HBr−CaBr$_2$−H$_2$O[33]	0.0069	0.2052	2.0	1	3
HBr−MgBr$_2$−H$_2$O[34]	0.0051	0.2326	2.5	1	3
HCl−LaCl$_3$−H$_2$O[35]	0.0165	0.2820	3.0	1	6
HCl−SmCl$_3$−H$_2$O[36]	0.0028	0.1932	2.5	1	6
HCl−ThCl$_4$−H$_2$O[37]	0.0042	0.1455	1.0	1	10

[a] $\Delta'_{\gamma,M1X1}$ and $\Delta'_{\gamma,M2X2}$ are the mean standard deviations of the predictions of eqs 22 and 32 with $k_{M_iX_i} = k^I_{M_iX_i}$ from the experimental results ($\Delta'_{\gamma,MiXi} = \sum_N|\gamma'^{Pred}_{M_iX_i} - \gamma'^{Exp}_{M_iX_i}|/N$, where N is the experimental data points). [b] Reference.

electrolytes, of which $k_{M_iX_i} = \nu_{M_iX_i}$ (eq 32 is equal to eq 22). Therefore, the results from Table 2 substantiate that $k_{M_iX_i}$ is not an arbitrary constant and must be set equal to $\nu_{M_iX_i}$.

Table S2 (Supporting Information) shows the calculated values of $a'^{(io),DH}_{H_2O}$ and $a'^{DH}_{H_2O}$ for the system NaCl(M$_1$X$_1$)−BaCl$_2$-(M$_2$X$_2$)−LaCl$_3$(M$_3$X$_3$)−H$_2$O and its three binary subsystems at 298.15 K. The results are $\Delta'^{(1o),DH}_{H_2O} = 1.5\%$, $\Delta'^{(2o),DH}_{H_2O} = 0.24\%$, and $\Delta'^{(3o),DH}_{H_2O} = 1.22\%$. These results along with those shown in Table S1 for BaCl$_2$(M$_2$X$_2$)−LaCl$_3$(M$_3$X$_3$)−H$_2$O suggest that both these systems may obey eq 12 well, which is supported by their isopiestic behavior at 298.15 K shown in Table 1. Because the systems NaCl(M$_1$X$_1$)−BaCl$_2$(M$_2$X$_2$)−H$_2$O and NaCl(M$_1$X$_1$)−LaCl$_3$(M$_3$X$_3$)−H$_2$O also obey eq 12 very well,[18,23] the activity coefficients of the solutes in these systems are calculated from eq 22. The Pitzer's parameters, Table 3, are determined from the resulting $\gamma'_{M_2X_2}$ and $\gamma'_{M_3X_3}$ in three ternary systems and then are used to give predictions for the activity coefficients of each solute in NaCl(M$_1$X$_1$)−BaCl$_2$(M$_2$X$_2$)−LaCl$_3$(M$_3$X$_3$)−H$_2$O at 298.15 K. The results are compared in Table 1 with those from eq 22, and the agreement is good. Note that, while the tests of eq 12 reported in the literature are in general limited to (1:1 + 1:1),[39] (1:1 + 1:2),[18] (1:1 + 1:3),[23] (1:2 + 1:2),[40] and (2:2 + 1:2)[41] electrolyte mixtures, the present results show that the simple equation also holds for the mixtures of (1:2 + 1:3) and (1:1 + 1:2 + 1:3) electrolytes.

TABLE 3: Pitzer Parameters Determined from the $\gamma'_{M_2X_2}$ in the Ternary Systems NaCl(M$_1$X$_1$)−BaCl$_2$(M$_2$X$_2$)−H$_2$O,[18] LaCl$_3$ (M$_1$X$_1$)−BaCl$_2$(M$_2$X$_2$)−H$_2$O, and NaCl(M$_1$X$_1$)−LaCl$_3$(M$_2$X$_2$)−H$_2$O[23] at 298.15 K

solute	$\beta^{(o)}$	$\beta^{(1)}$	C^ϕ
NaCl	0.0519	0.3614	0.010
BaCl$_2$	0.2792	1.4387	0.0259
LaCl$_3$	0.5889	5.600	0.0238
$\theta_{Na,Ba}$ (kg mol^{-1})	$\theta_{Na,La}$ (kg mol^{-1})	$\theta_{Ba,La}$ (kg mol^{-1})	
0.0076	0.3479	0.02775	
$\psi_{Na,Ba,Cl}$ (kg^2 mol^{-2})	$\psi_{Na,La,Cl}$ (kg^2 mol^{-2})	$\psi_{Ba,La,Cl}$ (kg^2 mol^{-2})	
0.0187	−0.070	−0.0185	

3.3. Test of Novel Linear Isopiestic Relations and the Novel Simple Equation for Activity Coefficient. The isopiestic behavior of the saturated solution M$_1$X$_1$−M$_2$X$_2$−(NY)$_{sat}$−H$_2$O can be described by eqs 10 and 11. In this study, the experimental deviations from these equations are defined by $\Delta_0 = m_{M_1X_1}/m^{(1o)}_{M_1X_1} + m_{M_2X_2}/m^{(2o)}_{M_2X_2} - 1$ and $\Delta_1 = (m_{M_1X_1}/m^{(1o)}_{M_1X_1})m^{(1o)}_{NY} + (m_{M_2X_2}/m^{(2o)}_{M_2X_2})m^{(2o)}_{NY} - m_{NY}$ at constant activities of water and NY and within the range $0 \leq [m_{M_iX_i}/m^{(io)}_{M_iX_i}] \leq 1$.

Tables 4 and S3 show the isopiestic results and the calculated values of $a^{DH}_{H_2O}$ for the saturated system NaCl(M$_1$X$_1$)−LaCl$_3$-(M$_2$X$_2$)−BaCl$_2$·2H$_2$O$_{(sat)}$((NY)$_{sat}$)−H$_2$O at 298.15 K and those of $a^{(1o),DH}_{H_2O}$ and $a^{(2o),DH}_{H_2O}$ for its subsystems, NaCl(M$_1$X$_1$)−BaCl$_2$·2H$_2$O$_{(sat)}$((NY)$_{sat}$)−H$_2$O and LaCl$_3$ (M$_2$X$_2$)−BaCl$_2$·2H$_2$O$_{(sat)}$((NY)$_{sat}$)−H$_2$O. The values of $\Delta^{(1o),DH}_{H_2O}$ and $\Delta^{(2o),DH}_{H_2O}$ are 1.30% and 0.92%, and the maximum values of $|\Delta_0|$ and $|\Delta_1^{Exp}|$ ($\Delta_1^{Exp} = (m_{M_1X_1}/m^{(1o)}_{M_1X_1})m^{(1o)}_{NY} + (m_{M_2X_2}/m^{(2o)}_{M_2X_2})m^{(2o)}_{NY} - m_{NY}$) are 0.0012 and 0.0042, respectively, where the superscript Exp indicates that the solubilities in the quaternary system are calculated from the new linear relation along with the $m^{(io)}_{NY}$ determined experimentally. The solubilities of NY in ternary and quaternary saturated solutions are also calculated from the Pitzer equation along with the Pitzer's parameters determined above. The results ($m^{(1o),P}_{NY}$, $m^{(2o),P}_{NY}$, and m^{P}_{NY} shown in the fifth column of Table 4) agree well with the experimental data. The resulting solubilities ($m^{(1o),P}_{NY}$ and $m^{(2o),P}_{NY}$) are substituted into eq 11 to provide the solubilities $m^{L,P}_{NY}$ ($m^{L,P}_{NY} = (m_{M_1X_1}/m^{(1o)}_{M_1X_1})m^{(1o),P}_{NY} + (m_{M_2X_2}/m^{(2o)}_{M_2X_2})m^{(2o),P}_{NY}$) of NY in the quaternary saturated solutions, where the superscript L,P implies that the solubilities in the quaternary system are calculated from the new linear equation together with the $m^{(1o),P}_{NY}$ and $m^{(2o),P}_{NY}$ (in the subsystems) calculated from the Pitzer equation. The results ($m^{L,P}_{NY}$) are in good agreement with the predictions (m^{P}_{NY}) of the Pitzer equation, with $\Delta_1^{L,P}$ ($\Delta_1^{L,P} = (m_{M_1X_1}/m^{(1o)}_{M_1X_1})m^{(1o),P}_{NY} + (m_{M_2X_2}/m^{(2o)}_{M_2X_2})m^{(2o),P}_{NY} - m^{P}_{NY}$) being less than 0.0068.

The above comparisons show that eqs 10 and 11 are in good agreement with the experimental results. Therefore, $\gamma^{(1o),P}_{M_1X_1}$ and $\gamma^{(2o),P}_{M_2X_2}$ are calculated from the Pitzer equation and then substituted into eq 21 to yield $\gamma^{L,P}_{M_1X_1}$ and $\gamma^{L,P}_{M_2X_2}$ in NaCl(M$_1$X$_1$)−LaCl$_3$(M$_2$X$_2$)−BaCl$_2$·2H$_2$O$_{(sat)}$((NY)$_{sat}$)−H$_2$O, where the superscript L,P indicates that the activity coefficient is calculated from the new simple equation along with the $\gamma^{(1o),P}_{M_1X_1}$ and $\gamma^{(2o),P}_{M_2X_2}$

TABLE 4: Isopiestic Results (mol/kg) for the Saturated Systems $NaCl(M_1X_1)-LaCl_3(M_2X_2)-BaCl_2\cdot 2H_2O_{(sat)}$-$((NY)_{sat})-H_2O$ at 298.15 K, Taking Aqueous NaCl as the Reference Solution

$m_{M_1X_1}$	$m_{M_2X_2}$	m_{NY}^{Exp}	$m_{NY}^{L,Exp\ a}$	$m_{NY}^{P\ b}$	$m_{NY}^{L,P\ c}$	a_{H_2O}
3.0736^d	0	0.7442^d		0.7464^d		0.8420
0	1.3920^e	0.3816^e		0.3850^e		
0.3146	1.2502	0.4162	0.4189	0.4203	0.4202	
0.7128	1.0682	0.4620	0.4656	0.4685	0.4671	
1.3660	0.7726	0.5406	0.5430	0.5458	0.5449	
2.0678	0.4560	0.6276	0.6255	0.6297	0.6288	
1.5065^d	0	1.2002^d		1.2025^d		0.8746
0	0.7186^e	0.9970^e		0.9925^e		
0.3182	0.5885	1.0691	1.0725	1.0744	1.0695	
0.6019	0.4485	1.1012	1.1031	1.1058	1.0990	
0.9107	0.2942	1.1336	1.1362	1.1380	1.1316	
1.2528	0.1210	1.1660	1.1621	1.1643	1.1602	
0.9476^d	0	1.4542^d		1.4631^d		0.8869
0	0.4980^e	1.2429^e		1.2499^e		
0.1509	0.4183	1.2788	1.2751	1.2824	1.2829	
0.2332	0.3752	1.2969	1.2942	1.3000	1.3017	
0.4481	0.2622	1.3426	1.3420	1.3461	1.3498	
0.6250	0.1693	1.3837	1.3811	1.3856	1.3896	
0.4480^d	0	1.6481^d		1.6485^d		0.8950
0	0.2623^e	1.5102^e		1.5146^e		
0.07282	0.2196	1.5362	1.5320	1.5378	1.5360	
0.1240	0.1896	1.5496	1.5478	1.5528	1.5512	
0.2196	0.1340	1.5825	1.5796	1.5805	1.5820	
0.3145	0.07806	1.6089	1.6065	1.6095	1.6078	

[a] Calculated from eq 11 along with $m_{NY}^{(io),Exp}$ determined experimentally. [b] Calculated from the Pitzer equation. [c] Calculated from eq 11 together with $m_{NY}^{(1o),P}$ (the solubility of NY in $M_1X_1-(NY)_{sat}-H_2O$) and $m_{NY}^{(2o),P}$ (the solubility of NY in $M_2X_2-(NY)_{sat}-H_2O$) calculated from the Pitzer equation. [d] The values for $m_{M_1X_1}^{(1o)}$, $m_{NY}^{(1o),Exp}$, and $m_{NY}^{(1o),P}$, respectively. [e] The values for $m_{M_1X_1}^{(2o)}$, $m_{NY}^{(2o),Exp}$, and $m_{NY}^{(2o),P}$, respectively.

TABLE 5: Activity Coefficients in the Saturated Systems $NaCl(M_1X_1)-LaCl_3(M_2X_2)-BaCl_2\cdot 2H_2O_{(sat)}((NY)_{sat})-H_2O$ at 298.15 K

$m_{M_1X_1}$ mol kg^{-1}	$m_{M_2X_2}$ mol kg−1	m_{NY} mol kg−1	$\gamma_{M_1X_1}^{P\ a}$	$\gamma_{M_1X_1}^{L\ b}$	$\gamma_{M_2X_2}^{P}$	$\gamma_{M_2X_2}^{L}$
3.0736^c	0	0.7442^c	0.9031			
0	1.3920^d	0.3816^d			0.5796	
0.3146	1.2502	0.4162	0.9912	0.9742	0.5456	0.5665
0.7128	1.0682	0.4630	0.9936	0.9860	0.5582	0.5732
1.3660	0.7726	0.5406	0.9465	0.9536	0.5306	0.5542
2.0678	0.4560	0.6276	0.9196	0.9315	0.5377	0.5416
1.5065^c	0	1.2002^c	0.8192			
0	0.7186^d	0.9970^d			0.4171	
0.3182	0.5885	1.0700	0.8490	0.8255	0.4195	0.4012
0.6019	0.4485	1.1012	0.8434	0.8235	0.4118	0.4000
0.9107	0.2942	1.1336	0.8232	0.8234	0.4054	0.3996
1.2528	0.1210	1.1658	0.8028	0.8258	0.4008	0.4011
0.9476^c	0	1.4542^c	0.7786			
0	0.4980^d	1.2429^d			0.3860	
0.1509	0.4183	1.2788	0.7660	0.7476	0.3834	0.3892
0.2332	0.3752	1.2965	0.7665	0.7508	0.3821	0.3907
0.4481	0.2622	1.3426	0.7689	0.7590	0.3801	0.3950
0.6250	0.1693	1.3837	0.7721	0.7662	0.3796	0.3986
0.4480^c	0	1.6481^c	0.7572			
0	0.2623^d	1.5102^d			0.3585	
0.07282	0.2196	1.5362	0.6646	0.6626	0.3580	0.3632
0.1240	0.1896	1.5496	0.6768	0.6742	0.3574	0.3667
0.2196	0.1340	1.5825	0.7006	0.6958	0.3571	0.3696
0.3145	0.07806	1.6089	0.7242	0.7209	0.3565	0.3716

[a] Calculated from the Pitzer equation. [b] Calculated from eq 21 with $\gamma_{NY}^{(1o)}$ and $\gamma_{NY}^{(2o)}$ calculated from the Pitzer equation. [c] The values for $m_{M_1X_1}^{(1o)}$, and $m_{NY}^{(1o)}$, respectively. [d] The values for $m_{M_1X_1}^{(2o)}$ and $m_{NY}^{(2o)}$, respectively.

calculated from the Pitzer equation. The results are compared in Table 5 with the predictions of the Pitzer equation ($\gamma_{M_1X_1}^{P}$ and $\gamma_{M_2X_2}^{P}$), and the agreement is good. The above treatments do not include the cases where the examined rules are not accurate.

4. Conclusions

The semi-ideal solution theory has been presented to describe the thermodynamic behavior of the multicomponent electrolyte solutions $M_1X_1-\cdots-M_nX_n-(N_1Y_1)_{sat}-\cdots-(N_{n'}Y_{n'})_{sat}-H_2O$ at constant activities of all N_1Y_1, $\cdots$, $N_{n'}Y_{n'}$, and H_2O. The theory proves that, under the condition of constant activities of all N_1Y_1, $\cdots$, $N_{n'}Y_{n'}$, and H_2O, the average hydration numbers characterizing the ion−solvent interactions have the same values in the mixture as in the subsystems, and it assumes that the contributions from the ion−ion interactions to the solvent activity are also the same in the mixture as in the subsystems if there exists no complex formation. Therefore, the process of mixing the nonideal electrolyte mixtures $M_iX_i-(N_1Y_1)_{sat}-\cdots-(N_{n'}Y_{n'})_{sat}-H_2O$ ($i = 1, 2, ..., n$) at constant activities of all N_1Y_1, $\cdots$, $N_{n'}Y_{n'}$, and H_2O is as simple as that of mixing the ideal mixtures $M_iX_i-(N_1Y_1)_{sat}-\cdots-(N_{n'}Y_{n'})_{sat}-H_2O$ ($i = 1, 2, ..., n$) of equal mole fractions of all N_1Y_1, $\cdots$, $N_{n'}Y_{n'}$, and H_2O, so that the changes in thermodynamic properties accompanying the process of mixing the nonideal solutions obey the same linear *iso−a* relations as mixing the classical ideal solutions, including the linear concentration relations, the linear equations for changes in Gibbs free energy, enthalpy, entropy, thermal properties, and volumetric properties. From these linear *iso−a* relations, the well-known Zdanovskii's rule has been reproduced, and the value of the important parameter $k_{M_iX_i}$ in the McKay−Perring equation under isopiestic equilibrium has been theoretically determined.

The basic assumption made in the derivation of the novel linear isopiestic relations has proven to be exact or at least quite reasonable. As theoretically justified, the comparisons with the experimental results substantiate that $k_{M_iX_i}$ in the McKay−Perring equation under isopiestic equilibrium must be set equal to $\nu_{M_iX_i}$. The novel linear relations have been shown to be in good agreement with the isopiestic measurements for the unsaturated systems $BaCl_2-LaCl_3-H_2O$ and $NaCl-BaCl_2-LaCl_3-H_2O$ and the saturated system $NaCl-LaCl_3-BaCl_2\cdot 2H_2O_{(sat)}-H_2O$ at 298.15 K. The new simple linear equation for $\gamma_{M_1X_1}$ and $\gamma_{M_2X_2}$ in $M_1X_1-M_2X_2-(NY)_{sat}-H_2O$ has been compared with the predictions of the Pitzer equation, and the agreement is good. Its reduced form for $\gamma'_{M_1X_1}$ and $\gamma'_{M_2X_2}$ in $M_1X_1-M_2X_2-H_2O$ and for $\gamma'_{M_1X_1}$, $\gamma'_{M_2X_2}$, and $\gamma'_{M_3X_3}$ in $NaCl-BaCl_2-LaCl_3-H_2O$ has been shown to be in good agreement with the experimental results reported in the literature.

5. Experimental Section

All the examined chemicals are reagent grade and recrystallized twice from doubly distilled water. NaCl was dried under vacuum over $CaCl_2$ for 7 days at 423 K. $BaCl_2$ was dehydrated in an anhydrous HCl atmosphere rising from 298.15 to 573 K and treated by introducing purified argon gas at 573 K. The molalities of $LaCl_3$ stock solutions ware analyzed by EDTA and titration (of Cl^- with $AgNO_3$) methods.

The isopiestic apparatus and the sample cups used here are the same as those used in our previous studies.[15] Preliminary experiments showed that equilibration could be achieved within 5 to 6 days. The real equilibration period for each run was then chosen as 9 days. At isopiestic equilibrium, the molality of each solute was determined by using the following procedure: (1)

After weighing the equilibrium saturated samples, the liquid sample phase was withdrawn by a pipet fitted with a sintered-glass filter tip preheated slightly above 298.15 K[42] and then was weighed and diluted. (2) All solutions were analyzed by 4−8 titrations of Cl^- with $AgNO_3$, with results agreeing to within ±0.05%. (3) Calculation of the solute molalities was carried out by the following procedure.

Let w, w^{Eq}, and w_{total} denote the mass of initial unsaturated solution before equilibration, the mass of saturated equilibrium solution, and that of the saturated equilibrium solution withdrawn by the sintered-glass filter tip. Let n_{BaCl_2} and $n_{M_iX_i}$ (M_iX_i = NaCl and $LaCl_3$) represent the amount of $BaCl_2$ and unsaturated solute M_iX_i in a mass w of initial unsaturated solution, and $n^{S}_{BaCl_2}$ and $n^{Sd}_{BaCl_2}$ the amount of anhydrous solid $BaCl_2$ added to the sample cup before equilibration and that dissolved during equilibration. Then, the amount of Cl^-, $n^{Cl^-}_{total}$, in a mass w_{total} of saturated solution can be expressed as

$$n^{Cl^-}_{total} = 2(n_{BaCl_2} + n^{Sd}_{BaCl_2})w_{total}/w^{Eq} \tag{33}$$

with

$$w^{Eq} = w + w^{Tr}_{H_2O} + M_{BaCl_2}n^{Sd}_{BaCl_2} - w^{Hy}_{H_2O} \tag{34a}$$

$$w^{Hy}_{H_2O} = 2M_{H_2O}(n^{S}_{BaCl_2} - n^{Sd}_{BaCl_2}) \tag{34b}$$

where $w^{Tr}_{H_2O}$ and $w^{Hy}_{H_2O}$ are the mass of water transported through the vapor phase during the equilibration and that needed to form the thermodynamically stable solid phase of $BaCl_2\cdot 2H_2O$[18] at isopiestic equilibrium. M_{BaCl_2} is the molar mass of anhydrous barium chloride. Combining eqs 33 and 34, we obtain

$$n^{Sd}_{BaCl_2} = \frac{n^{Cl^-}_{total}(w + w^{Tr}_{H_2O} - 2M_{H_2O}n^{S}_{BaCl_2}) - 2w_{total}n_{BaCl_2}}{2w_{total} - n^{Cl^-}_{total}M_{BaCl_2} - 2M_{H_2O}n^{Cl^-}_{total}} \tag{35a}$$

The mass of water ($w^{Eq}_{H_2O}$) in a mass w^{Eq} of equilibrium solution is given by

$$w^{Eq}_{H_2O} = w_{H_2O} + w^{Tr}_{H_2O} - 2M_{H_2O}(n^{S}_{BaCl_2} - n^{S}_{BaCl_2}) \tag{35b}$$

where w_{H_2O} is the mass of water in a mass w of initial unsaturated solution. Because the molalities of M_iX_i and $BaCl_2$ of the initial unsaturated solutions are known, and the values of $w^{Tr}_{H_2O}$ and $n^{Cl^-}_{total}$ can be determined simply by weighing the samples at isopiestic equilibrium ($w^{Tr}_{H_2O} = w^{Eq} - w$) and by the titration measurements noted previously, the molality of each solute in $NaCl-LaCl_3-BaCl_2\cdot 2H_2O_{(sat)}-H_2O$ can be determined by

$$m_{M_iX_i} = \frac{n_{M_iX_i}}{w^{Eq}_{H_2O}} \quad (M_iX_i = \mathrm{NaCl\ or\ LaCl_3}) \tag{36a}$$

$$m_{NY} = \frac{n_{BaCl_2} + n^{Sd}_{BaCl_2}}{w^{Eq}_{H_2O}} \quad (NY = BaCl_2\cdot 2H_2O) \tag{36b}$$

The results, the average between the duplicate cups for unsaturated solute and the mean of 4−8 replicate titration measurements for saturated solute in the duplicate cups, are reproducible to ±0.05% for the former and to ±0.10% for the latter.

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Supporting Information Available: S1: Derivation of linear concentration relation. S2: Derivation of the simple equations. Also three tables of supporting data. This material is available free of charge via the Internet at http://pubs.acs.org.

Glossary

a	activity
A^{ϕ}	the molal Debye−Hückel coefficient
b	the universal parameter in eq 29 with the value 1.2 $kg^{1/2}\ mol^{-1/2}$
C_P	specific heat capacity
d	density
f	the activity coefficient on the mole fraction scale
G^{DH}	the Gibbs energy resulted from the Debye−Hückel contribution
G^{Hy}	the Gibbs energy of the semi-ideal mixture of the resulting species based on the mole fraction (x)
$\bar{h}$	average hydration number
I	molal ionic strength (mol kg^{-1})
$k_{M_iX_i}$	the proportionality constant for solute M_iX_i in McKay−Perring equation
K	hydration equilibrium constant
m	molality (mol kg^{-1})
M	molar mass
M_iX_i	the electrolyte solute components present below their solubility limits
n	mole number
$n^{Sd}_{BaCl_2}$	the amount of anhydrous solid $BaCl_2$ dissolved during equilibration
N	the number of experimental data points
NY	the electrolyte solute component present as saturated solutions
R	gas constant
w	the mass of initial unsaturated solution before equilibration
w_{H_2O}	the mass of water in a mass w of initial unsaturated solution
w_{total}	the mass of the saturated equilibrium solution withdrawn by the sintered-glass-filter tip
w^{Eq}	the mass of saturated equilibrium solution
$w^{Hy}_{H_2O}$	the mass of water needed to form the thermodynamically stable solid phase of $BaCl_2\cdot 2H_2O$ at isopiestic equilibrium
$w^{Tr}_{H_2O}$	the mass of water transported through the vapor phase during equilibration
x	mole fraction
$(\Delta_{mix}G$, $\Delta_{mix}G^{(io)})$, $(\Delta_{mix}H$, $\Delta_{mix}H^{(io)})$, $(\Delta_{mix}S$, $\Delta_{mix}S^{(io)})$, $(\Delta_{mix}V$, $\Delta_{mix}V^{(io)})$	the changes in Gibbs free energy, enthalpy, entropy, and volume accompanying the process of preparing the system $M_1X_1-M_2X_2-(NY)_{sat}-H_2O$ and its subsystems $M_iX_i-(NY)_{sat}-H_2O$
Δ_0	the function defined by $\Delta_0 = m_{M_1X_1}/m^{(1o)}_{M_1X_1} + m_{M_2X_2}/m^{(2o)}_{M_2X_2} - 1$
Δ_1	the function defined by $\Delta_1 = (m_{M_1X_1}/m^{(1o)}_{M_1X_1})m_{NY}{}^{(1o)} + (m_{M_2X_2}/m_{M_2X_2}{}^{(2o)})m_{NY}{}^{(2o)} - m_{NY}$
$\Delta_1^{L,P}$	the function defined by $\Delta_1^{L,P} = (m_{M_1X_1}/m^{(1o)}_{M_1X_1})m^{(1o),P}_{NY} + (m_{M_2X_2}/m^{(2o)}_{M_2X_2})\ m^{(2o),P}_{NY} - m^{P}_{NY}$

$\Delta_{H_2O}^{(io),DH}$	the function defined by $\Delta_{H_2O}^{(io),DH} = 100 \times \sum_N (a_{H_2O}^{(io),DH}/a_{H_2O}^{DH} - 1)/N$
z	charge

Greek Symbols

γ	molal activity coefficient
ϕ	osmotic coefficient
ν	salt stoichiometric coefficient
μ	chemical potential

Subscripts

average	average property
i, j, n, n'	component indexes
ideal	ideal solution
mix	property of mixing at constant temperature and pressure
sat	saturated solute(s)
total	total property

Superscripts

$'$	the quantity of M_iX_i in unsaturated solutions $M_iX_i-H_2O$ (i = 1 and 2) and $M_1X_1-M_2X_2-\cdots-H_2O$
dilute	infinite dilute behavior
DH	the property resulted from the Debye−Hückel contribution
Exp.	experimental property
free	free quantity
Hy	the property of the semi-ideal mixture of the resulting species based on the mole fraction (x)
ideal	ideal solution
L,P	the property calculated using the linear relation $m_{NY}^{L,P} = (m_{M_1X_1}/m_{M_1X_1}^{(1o)})m_{NY}^{(1o),P} + (m_{M_2X_2}/m_{M_2X_2}^{(2o)})m_{NY}^{(2o),P}$
(io)	the properties of the components in the subsystems $M_iX_i-(NY)_{sat}-H_2O$ or $M_iX_i-H_2O$
P	the property calculated using the Pitzer equation
Pred	predicted property

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