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Thermodynamics of the System $MgCl_2$–NaCl–H_2O to 573 K: New Measurements of Heat of Mixing and Heat of Dilution[1]

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Heats of mixing of NaCl(aq) with $MgCl_2$(aq) at 373.15, 423.15, 473.15, 523.15, and 573.15 K for ionic strengths of 0.5 to 3.8 $mol \cdot kg^{-1}$, and heats of dilution of $MgCl_2$(aq) at 523.15 and 573.15 K for ionic strengths of 0.3 to 4.6 $mol \cdot kg^{-1}$, have been measured at 20.5 MPa. These experimental data are combined with published heat of mixing data at 298 and 373 K to provide a comprehensive Pitzer ion-interaction treatment for the thermodynamic properties of the NaCl–$MgCl_2$–H_2O system to 573 K. The treatment includes a general equation valid to 523 K, incorporating the published equations for NaCl(aq) and $MgCl_2$(aq), and equations for $MgCl_2$(aq) and the mixed system valid at 573 K.

KEY WORDS: aqueous electrolyte; calorimetry, heat of dilution; heat of mixing; high temperatures; magnesium chloride; Pitzer equation; sodium chloride; thermodynamic properties.

1. INTRODUCTION

Unsymmetrical mixtures of electrolytes have very interesting properties, including those described by theoretical terms arising from the interaction of ions with different charges of the same sign. Thermal properties, including

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heats of mixing at 298 K, were reviewed and discussed by one of us [1], and others have since measured additional systems. Further complexities arise at higher temperatures where both hydrolysis and ion-interaction effects become more pronounced.

In this paper the results for the heat of mixing of $MgCl_2(aq)$ with NaCl(aq) at temperatures from 373 to 573 K and for the heat of dilution of $MgCl_2(aq)$ at 523 and 573 K are presented for ionic strengths to $4.6\ \mathrm{mol \cdot kg^{-1}}$ at a pressure of 20.5 MPa. These values are combined with published data on the heat of mixing at 298.15 and 373.15 K [2–5], and with the thermodynamic properties of the binary systems $NaCl–H_2O$ and $MgCl_2–H_2O$, to provide a comprehensive Pitzer ion-interaction treatment [6] for the thermodynamic properties of the $NaCl–MgCl_2–H_2O$ system to 573 K. Our treatment comprises one general equation valid to 523 K, incorporating the published equations for NaCl(aq) [7] and $MgCl_2(aq)$ [8, 9], and the treatment for 573 K comprising new equations for $MgCl_2(aq)$ and for the mixed system.

2. EXPERIMENTAL

The high-temperature, high-pressure flow calorimeter used in our experiments and the procedures for the measurements have been given in detail elsewhere [10, 11]. Heats of mixing for solutions of NaCl(aq) with $MgCl_2(aq)$ were measured at 373.15, 423.15, 473.15, 523.15, and 573.15 K, and heats of dilution of $MgCl_2(aq)$ were measured at 523.15 and 573.15 K. All of the measurements in this study were made at a pressure of 20.5 MPa. The heat of mixing measurements were conducted at constant ionic strengths, and the ionic strength fractions, $y = 3m_{MgCl_2}/(3m_{MgCl_2} + m_{NaCl})$, of the final mixtures are close to 0.5. The experiments covered ionic strength ranges of 0.5 to $3.8\ \mathrm{mol \cdot kg^{-1}}$ for the heat of mixing measurements and 0.3 to $4.6\ \mathrm{mol \cdot kg^{-1}}$ for the heat of dilution measurements.

3. EQUATIONS

For the mixing of solutions of a 1–1 salt MX (salt 1) with a 2–1 salt NX_2 (salt 2), each at ionic strength I, the Pitzer ion-interaction model [6] gives the heat of mixing ΔH_{mix} per unit mass of solvent as

$$\frac{\Delta H_{\mathrm{mix}}}{RT^2I^2} = y(1-y)\left[\frac{2}{3}B^{\mathrm{L}}_{\mathrm{MX}} - \frac{2}{9}B^{\mathrm{L}}_{\mathrm{NX}} + \frac{2}{9}(6-y)\,IC^{\mathrm{L}}_{\mathrm{MX}} - \frac{2}{27}(5-y)\,IC^{\mathrm{L}}_{\mathrm{NX}} - \frac{2}{3}\Phi^{\mathrm{L}}_{\mathrm{MN}} - \frac{1}{9}(3-y)\,I\Psi^{\mathrm{L}}_{\mathrm{MNX}}\right] \qquad (1)$$

with y being the ionic strength fraction of salt 2, and B_{ca} and Φ_{ij} are given by

$$B_{ca} = \beta_{ca}^{(0)} + 2\beta_{ca}^{(1)}[1 - (1 + \alpha_1 \sqrt{I}) \exp(-\alpha_1 \sqrt{I})]/(\alpha_1{}^2 I) \\ + 2\beta_{ca}^{(2)}[1 - (1 + \alpha_2 \sqrt{I}) \exp(-\alpha_2 \sqrt{I})]/(\alpha_2{}^2 I) \quad (2)$$

$$\Phi_{ij} = {}^{S}\theta_{ij} + {}^{E}\theta_{ij}(I) \quad (3)$$

where $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, and $\beta_{ca}^{(2)}$ are the parameters from the binary cation–anion interactions, C_{ca} and ψ_{ijk} are the third-order interaction parameters, ${}^{S}\theta_{ij}$ is the short-range interaction parameter between two ions of the same sign, and ${}^{E}\theta_{ij}$ is the theoretical electrostatic function for the unsymmetrical mixing and depends only on the charges of the ions, the total ionic strength, and the solvent properties [1, 12]. B^L, C^L, Φ^L, and Ψ^L are the temperature derivatives of the above quantities:

$$B^{L} = \partial B/\partial T; \qquad C^{L} = \partial C/\partial T; \qquad \Phi^{L} = \partial \Phi/\partial T; \qquad \psi^{L} = \partial \psi/\partial T \quad (4)$$

For the NaCl–$MgCl_2$–H_2O system, the B_{ca} and C_{ca} terms include those for NaCl(aq) (B_{NaCl} and C_{NaCl}) and for $MgCl_2$(aq) (B_{MgCl} and C_{MgCl}). These terms can be calculated using the model for NaCl(aq) by Archer [7] and the model for $MgCl_2$(aq) by Holmes and Mesmer [8] and Holmes et al. [9]. In the Archer model, α_1, was chosen to have a constant value of 2.0, and there is no $\beta^{(2)}$ term; hence, no α_2 value is assigned for NaCl(aq). In the Holmes and Mesmer model, a linear function of temperature was used for α_1, and α_2 was chosen to have a constant value of 12.0.

The molar enthalpy of dilution ΔH_{dil} of the electrolyte solution is defined as

$$\Delta H_{dil} = L_{\Phi}(m_f) - L_{\Phi}(m_i) \quad (5)$$

where L_{Φ} is the apparent molar enthalpy at initial and final molalities m_i and m_f, respectively. For a 2–1 electrolyte NX_2, L_{Φ} is given by

$$L_{\Phi} = \frac{3A_H}{b} \ln(1 + b\sqrt{I}) - 4RT^2(mB_{NX}^{L} + 2m^2 C_{NX}^{L}) \quad (6)$$

with A_H the Debye–Hückel parameter for enthalpy, which is based on the Archer and Wang dielectric constant equation [13] and the Hill equation of state for water [14], and b a constant taken to be 1.2.

4. EVALUATION AND ANALYSIS OF EXPERIMENTAL DATA

4.1. Treatment for the Temperature Range 298.15 to 523.15 K

Heat of mixing data for NaCl(aq) with $MgCl_2$(aq) have been reported by Wood et al. [3], Srna and Wood [2], and Zdanovskii and Deryabina [5] at 298.15 K and by Wood and Mayrath [4] at 373.15 K. All of their measurements were made at 0.1 MPa. The effect of pressure on the heat of mixing of NaCl(aq) with $MgCl_2$(aq) solutions is unknown, but the volumetric data for a similar system, $CaCl_2$–NaCl–H_2O, indicate that ψ^V_{CaNaCl} and θ^V_{CaNa}, the pressure derivatives of ψ_{CaNaCl} and θ_{CaNa}, are very small and can be taken as constants below 373 K [15]. The same effect is expected for the $MgCl_2$–NaCl–H_2O system. Therefore, the 0.1-MPa heat of mixing data [2, 3, 5] were included in our analysis without adjustment for the pressure difference. Corrections for the pressure effects at higher temperatures are pending until further volumetric data are available.

Hydrolysis of the Mg^{2+} ion in high-temperature aqueous solutions has been reported. Using the published results [16, 17], the amount of $MgOH^+$ formed in the reaction,

$$Mg^{2+} + H_2O = MgOH^+ + H^+ \tag{7}$$

was estimated to be only 1 % at 573 K at the lowest concentrations in our study. The degree of hydrolysis decreases with increasing ionic strength and total magnesium concentration and with decreasing temperature. The hydrolysis of Mg^{2+} was neglected in the present study at all temperatures.

The temperature dependence of the mixing parameters, ${}^s\theta^L_{\mathrm{NaMg}}$ and ψ^L_{NaMgCl}, were evaluated from the experimental heat of mixing data. Several forms of the equation for ${}^s\theta^L_{\mathrm{MN}}$ and ψ^L_{MNX} were tested. The following equation was used in our final calculations:

$$f_L = p_1 + p_2 T + p_3 T^3 \tag{8}$$

where T is the temperature in K, and the p_i are parameters determined from a least-squares fit of Eq. (1) to the heat of mixing data. Integration of Eq. (8) yields the temperature function for osmotic/activity coefficient parameters ${}^s\theta_{\mathrm{NaMg}}$ and ψ_{NaMgCl}.

$$f_G = p_0 + p_1 T + \tfrac{1}{2} p_2 T^2 + \tfrac{1}{4} p_3 T^4 \tag{9}$$

where values of p_0 were derived from values of ${}^s\theta_{\mathrm{NaMg}}$ and ψ_{NaMgCl} at 298.15, which were obtained from fitting the osmotic coefficients reported

Table I. Parameters for Eqs. (8) and (9) for the NaCl–$MgCl_2$–H_2O System from 298.15 to 523.15 K

Parameter	${}^{S}\theta_{Na,Mg}$ ($kg \cdot mol^{-1}$) ${}^{S}\theta^{L}_{Na,Mg}$ ($kg \cdot mol^{-1} \cdot K^{-1}$)	$\psi_{Na,Mg,Cl}$ ($kg^2 \cdot mol^{-2}$) $\psi^{L}_{Na,Mg,Cl}$ ($kg^2 \cdot mol^{-2} \cdot K^{-1}$)
p_0	7.66109×10^{-2}	-6.67238×10^{-2}
p_1	-1.11639×10^{-4}	4.12766×10^{-4}
p_2	3.55254×10^{-8}	-1.48260×10^{-6}
p_3	-2.64307×10^{-13}	3.73211×10^{-12}

by Rard and Miller [18] at 298.15 K. Table I gives parameters for Eqs. (8) and (9) for the NaCl–$MgCl_2$–H_2O system from 298.15 to 523.15 K. Figure 1 compares our predicted heats of mixing at 298.15 K with the published experimental data [2, 3, 5]. The calculated and experimental heat of mixing data from our measurements at 373.15 to 523.15 K and from Wood and Mayrath [4] at 373.15 K are compared in Fig. 2. Detailed tables of our measurements are given in an extended paper [11]. The agreement between the predicted and the experimental heat of mixing data is good.

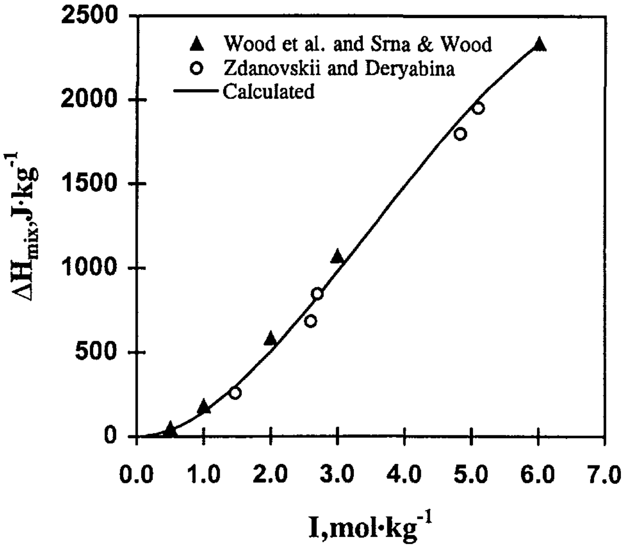

Fig. 1. Comparison of the predicted heat of mixing at 298.15 K with experimental data of Srna and Wood [2], Wood et al. [3], and Zdanovskii and Deryabina [5].

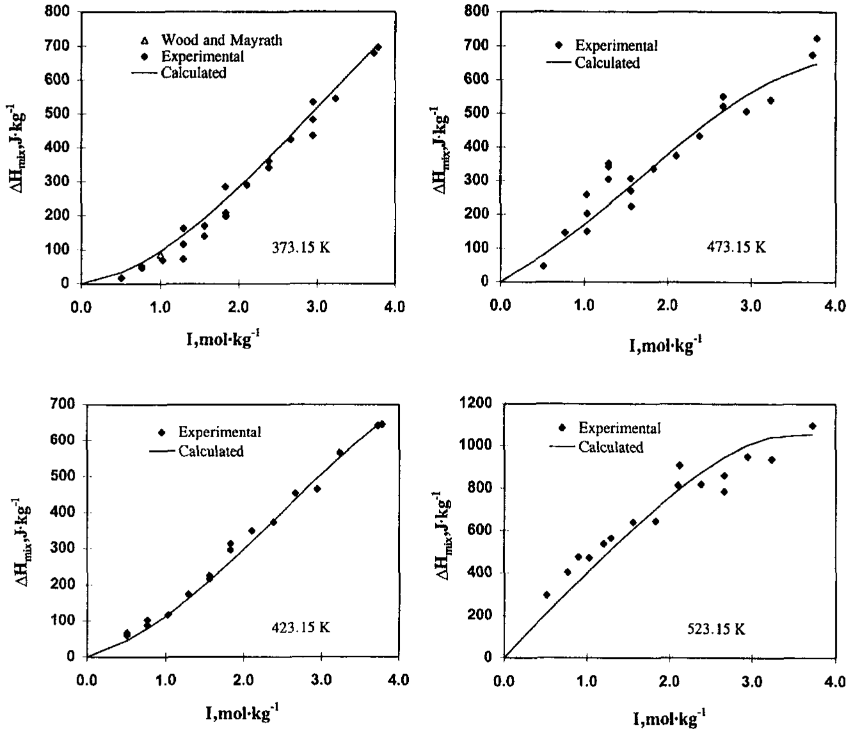

Fig. 2. Comparison of the calculated heats of mixing at 373.15, 423.15, 473.15, and 523.15 K and $y = 0.5$ with experimental values of this study and those of Wood and Mayrath [4] at 373.15 K.

The standard deviation for the overall fit with the heat of mixing is 54.0 J · kg H_2O^{-1}, which is about the same as the experimental uncertainties. The standard deviation of the fit for Rard and Miller's osmotic coefficient data is 0.0036. These results show that the present model satisfactorily represents thermodynamic properties of the $NaCl-MgCl_2-H_2O$ system in the temperature range up to 523 K.

4.2. Treatment for the Single Temperature 573.15 K

The thermodynamics of the $NaCl-MgCl_2-H_2O$ system at 573 K is more challenging due to the complexities arising from hydrolysis and ion association. Electrical conductance measurements [19] clearly indicate ion association at and above 573 K in dilute solutions of $MgCl_2$ and $CaCl_2$. Thus, a new comprehensive model for $MgCl_2$(aq) covering the full temperature range up to 573 K or higher, while highly desirable, must await additional thermodynamic measurements. Treatment has been made in this study based on two simplified formulations. Only a summary of the result is given here.

Formulation I assumes the regular pattern first used by Pitzer and Mayorga [20], who introduced a term with an interaction parameter, $\beta^{(2)}$, and a large α_2, for an electrolyte system where ions are associated to a moderate extent. They found that in the ion-interaction treatment without explicit association equilibria, this $\beta^{(2)}$ parameter is related to the ion association constant, K, by $\beta^{(2)} = -K/2$. In the comprehensive treatment for thermodynamic properties of $CaCl_2$, Holmes et al. [21] used the $\beta^{(2)}$ parameter as defined and expressed based on the above relationship and on the ionization constant of $CaCl^+(aq)$ from Frantz and Marshall, and obtained a much better fit of the high-temperature, low-molality enthalpy of dilution results than if the standard ion-interaction model were used. The same expression for $\beta^{(2)}$ has been adopted for other alkaline-earth metal chlorides including $MgCl_2(aq)$ in a similar treatment [8] with satisfactory fits of thermodynamic properties at high temperatures. These are the anticipated results with the behavior attributed to ion association in high-temperature, low-molality aqueous solutions. Thus, the parameter $\beta^{(2)}$ has been included in our treatment at 573 K.

The heat of dilution data at 573.15 K were first fit to Eqs. (5) and (6) to obtain the ion-interaction parameters, $\beta^{(0)\,L}_{Mg,\,Cl}$, $\beta^{(1)\,L}_{Mg,\,Cl}$, $\beta^{(2)\,L}_{Mg,\,Cl}$, and $C^{L}_{Mg,\,Cl}$. However, use of these interaction parameters did not give a good fit of the heat of mixing data to Eq. (1) at 573 K. The number of data points and the range of morality covered at this temperature are not sufficient to determine unambiguously a full set of pure electrolyte parameters. Instead, a simultaneous fit of both the heat of dilution data to Eqs. (5) and (6) and the heat of mixing data to Eq. (1) gave good fits for both dilution and mixing data at 573 K. In this treatment, parameters for NaCl(aq), $\beta^{(0)\,L}_{NaCl}$, $\beta^{(1)\,L}_{NaCl}$, and C^{L}_{NaCl} were calculated from Archer's equation, and the value of α_2 was taken to be 12.0. A number of values for α_1, were tested, and the usual value of 2.0 seems to give the best fit for both heat of dilution and heat of mixing data, and has been adopted in our treatment. Ion-interaction parameters, $\beta^{(0)\,L}_{Mg,\,Cl}$, $\beta^{(1)\,L}_{Mg,\,Cl}$, $\beta^{(2)\,L}_{Mg,\,Cl}$, $C^{L}_{Mg,\,Cl}$, ${}^{s}\theta^{L}_{Na,\,Mg}$, and $\psi^{L}_{Na,\,Mg,\,Cl}$, at 573.15 K are given in Table II. In the Holmes et al. model [8, 9, 21], $\beta^{(2)\,L}$ was calculated to be -0.22 at 523 K while the $\beta^{(2)\,L}$ obtained in our study is -0.43 at 573 K. This result is explained as follows. While the ion association constant, K, increases with temperature, $\beta^{(2)}$ becomes more negative, resulting in a negative $\partial\beta^{(2)}/\partial T$ value. The larger $-\beta^{(2)\,L}$ value at 573 K than that at 523 K is consistent with the fact that the increase in the ion-association constant with temperature is accelerated as the temperature becomes higher [19]. It is noteworthy that, as our value of $\beta^{(2)\,L}$ was deter-

Table II. Parameters for the $NaCl–MgCl_2–H_2O$ System at 573.15 K

Formulation I (Mg^{2+}, Na^{+}, Cl^{-})		Formulation II ($MgCl^{+}$, Na^{+}, Cl^{-})	
$\beta^{(0)L}_{Mg,Cl}$ ($kg \cdot mol^{-1} \cdot K^{-1}$)	7.59218×10^{-4}	$\beta^{(0)L}_{MgCl,Cl}$ ($kg \cdot mol^{-1} \cdot K^{-1}$)	-1.93826×10^{-3}
$\beta^{(1)L}_{Mg,Cl}$ ($kg \cdot mol^{-1} \cdot K^{-1}$)	2.45190×10^{-2}	$\beta^{(1)L}_{MgCl,Cl}$ ($kg \cdot mol^{-1} \cdot K^{-1}$)	-4.17288×10^{-2}
$\beta^{(2)L}_{Mg,Cl}$ ($kg \cdot mol^{-1} \cdot K^{-1}$)	-0.425749		
$C^{L}_{Mg,Cl}$ ($kg^2 \cdot mol^{-2} \cdot K^{-1}$)	-3.45882×10^{-5}	$C^{L}_{MgCl,Cl}$ ($kg^2 \cdot mol^{-2} \cdot K^{-1}$)	0.0
${}^{S}\theta^{L}_{Na,Mg}$ ($kg \cdot mol^{-1} \cdot K^{-1}$)	2.58857×10^{-4}	${}^{S}\theta^{L}_{MgCl,Na}$ ($kg \cdot mol^{-1} \cdot K^{-1}$)	3.84243×10^{-4}
$\psi^{L}_{Na,Mg,Cl}$ ($kg^2 \cdot mol^{-2} \cdot K^{-1}$)	4.16692×10^{-5}	$\psi^{L}_{MgCl,Na,Cl}$ ($kg^2 \cdot mol^{-2} \cdot K^{-1}$)	4.98770×10^{-4}
α_1 ($kg^{1/2} \cdot mol^{-1/2}$)	2.0	α_1 ($kg^{1/2} \cdot mol^{-1/2}$)	3.5
α_2 ($kg^{1/2} \cdot mol^{-1/2}$)	12.0		

mined solely from enthalpies of dilution and of mixing data, which do not extend to sufficiently low molalities, the extent of ion association may have been underestimated in the very dilute region where ion association could be rather extensive. A similar study on enthalpies of dilution of HCl(aq) [22] indicated that the $\beta^{(2)L}$ treatment resulted in a smaller ion-association constant. In the dilute region, values for enthalpy of dilution from the $\beta^{(2)L}$ treatment differ significantly from those obtained using a speciation treatment [22]. Thus, our Formulation I treatment with $\beta^{(2)L}$ representation cannot clearly confirm the ΔH_{dil} in the very dilute region.

In the case of strong ion association, it would be interesting to make an alternate calculation with an explicit presentation of the associated species and the equilibrium constant K for the formation of the associated species. Calculations of this type have been made for several aqueous systems including H_2SO_4 [23] and $InCl_3$ [24]. However, such calculations involve complex equations and more parameters. With our limited data at 573 K, the determination of these parameters is not possible. For the simplified case of complete ion association to $MgCl^+$ ($K = \infty$) and no further association to $MgCl_2^0$ (Formulation II), calculations were made under all conditions in our experiments. Details of the Formulation II treatment have been given in a separate paper [11]. Parameters obtained based on Formulation II are given in Table II, together with those obtained based on Formulation I.

Comparisons of the experimental and calculated heats of dilution and heats of mixing at 573.15 K are shown in Figs. 3 and 4, respectively, where I is the ionic strength assuming complete dissociation of $MgCl_2$ to Mg^{2+} and $2Cl^-$. The dashed curves are calculated based on Formulation II. The agreement is about equally good for the heat of dilution. A slightly better

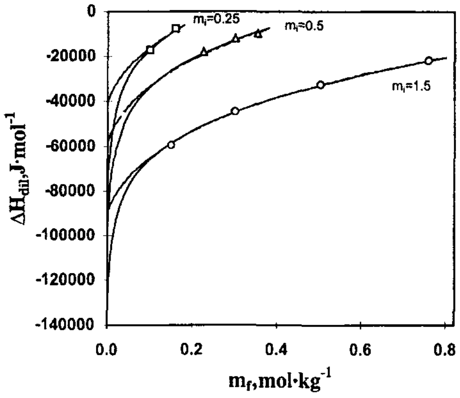

Fig. 3. The experimental (symbols) and calculated (curves) heat of dilution of $MgCl_2(aq)$ at 573.15 K. Solid and dashed curves are based on Formulations I and II, respectively.

result is obtained for heat of mixing with Formulation I, but note that Formulation I has more adjustable parameters. Contributions from the electrostatic unsymmetrical mixing parameter, pure electrolyte parameters, and the mixing parameters of ${}^{s}\theta^{L}_{Na,Mg}$ and $\psi^{L}_{Na,Mg,Cl}$ to the overall fit of ΔH_{mix} in Formulation I treatment were discussed in Ref. 11. As expected, less negative ΔH_{dil} values with smaller Debye–Hückel slopes are observed

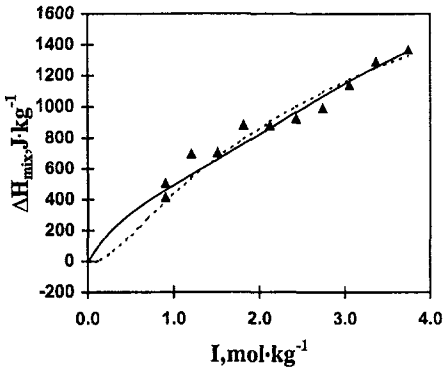

Fig. 4. The experimental (symbols) and calculated (curves) heat of mixing of $MgCl_2(aq)$ with NaCl(aq) at 573.15 K and $y = 0.5$. Solid and dashed curves are based on Formulations I and II, respectively.

for Formulation II at low moralities compared to those from Formulation I. The Formulation II treatment gives a lower limit for $|\Delta H_{\text{dil}}|$ values in the dilute region. The lower values of ΔH_{mix} in the dilute region for the Formulation II treatment than those for Formulation I appear to arise from the Debye–Hückel term in the Formulation II equation, which yields negative values in the whole concentration range of our study, but is absent in Eq. (1) for Formulation I. Since our heat of mixing data do not extend below an ionic strength of 0.9 $\text{mol} \cdot \text{kg}^{-1}$ at 573 K, a clear confirmation of the ΔH_{mix} values in the dilute region must await further measurements.

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