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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ABSTRACT

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 0.5-3.8 $mol \cdot kg^{-1}$ and heats of dilution of $MgCl_2$(aq) at 523.15 and 573.15 K for ionic strengths 0.3-4.6 $mol \cdot kg^{-1}$ 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: calorimetry; heat of dilution; heat of mixing; high temperatures; magnesium chloride; sodium chloride; Pitzer equation; thermodynamic properties.

1. INTRODUCTION

Unsymmetrical mixtures of electrolytes have very interesting properties including theoretical terms arising from the interaction of ions with different charges of the same sign. Thermal properties, including heats of mixing at 25^0C, were reviewed and discussed by one of us [1] and others have measured additional systems since. Further complexities arise at higher temperatures where both hydrolysis and ion-interaction effects become stronger.

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 heat of dilution of $MgCl_2$(aq) at 523 and 573 K are presented for ionic strengths to 4.6 $mol{\cdot}kg^{-1}$ and at a pressure of 20.5 MPa. These values are combined with published data on the heat of mixing at 298.15 K 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 will be given in detail in a separate paper [10]. Heats of mixing for solutions of NaCl(aq) with $MgCl_2$(aq) were measured at 373.15, 423.15, 473.15, 523.15, and 573.15K, 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 NaCl(aq) and $MgCl_2$(aq) solutions were at constant ionic strengths in the heat of mixing measurements. Equal volumes of each solution were mixed in all cases. The measurements covered ionic strength ranges of 0.5-3.8 for the heat of mixing runs and 0.3-4.6 for the heat of dilution runs.

3. EQUATIONS

For the mixing 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

$$\frac{\Delta H_{mix}}{RT^2 I^2} = y(1-y)\left[\frac{2}{3}B^L_{MX} - \frac{2}{9}B^L_{NX} + \frac{2}{9}(6-y)IC^L_{MX} - \frac{2}{27}(5-y)IC^L_{NX} - \frac{2}{3}\Phi^L_{MN} - \frac{1}{9}(3-y)I\psi^L_{MNX}\right] \quad (1)$$

with y being the ionic strength fraction of salt 2,

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

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

$\beta^{(0)}_{ca}$, $\beta^{(1)}_{ca}$, and $\beta^{(2)}_{ca}$ the parameters from the binary cation-anion interactions, C_{ca} and ψ_{ijk} the third order interaction parameters, and ${}^S\theta_{ij}$ the short-range interaction parameter between two ions of the same sign while ${}^E\theta_{ij}$ 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 [1,11]; and

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

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, a_1 was chosen to be a constant value of 2.0 while there is no $b^{(2)}$ term hence no a_2 value being assigned for NaCl(aq). In the Holmes and Mesmer model, a linear function of temperature was used for a_1 while a_2 was chosen to be a constant value of 12.0.

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

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

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

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

with A_H the Debye-Huckel parameter for enthalpy and b the constant taken to be 1.2.

4. EVALUATION AND ANALYSIS OF EXPERIMENTAL DATA

4.1. Treatment for the Temperature Range 298.15 - 523.15 K

Heat of mixing data for NaCl(aq) solution with $MgCl_2$(aq) solution 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 effects of pressure on the heat of mixing of NaCl(aq) with $MgCl_2$(aq) solutions are unknown but are expected to be negligible for moderate pressures at temperatures of 373 K and below. The heat of mixing data from these authors were included in our data analysis. 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 result [12,13], the amount of $MgOH^+$ formed in reaction (7)

$$Mg^{2+} + H_2O = MgOH^+ + H^+ \quad (7)$$

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 the total magnesium concentration and with decreases in temperature. The hydrolysis of Mg^{2+} was neglected in the present study at all temperatures.

The temperature dependencies of mixing parameters, ${}^{s}q^{L}_{NaMg}$ and y^{L}_{NaMgCl}, are to be evaluated in this study from the experimental heat of mixing data. Several forms of the equation for ${}^{s}q^{L}_{MN}$ and y^{L}_{MNX} were tested. The following equation was used in our final calculations:

$$f_L = p_1 + p_2 T + p_3 T^3 \quad (8)$$

where T is the temperature in Kelvin, and $p_1 - p_3$ are the parameters determined from a least-squares fitting of eq. (1) to the heat of mixing data. Temperature functions for osmotic/activity coefficient parameters, ${}^{s}q_{NaMg}$ and y_{NaMgCl}, can be derived from integration of eq.(8).

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

where values of p_0 were derived from values of ${}^{s}q_{NaMg}$ and y_{NaMgCl} at 298.15, which were obtained from the fitting of the osmotic coefficients reported by Rard and Miller [14] at 298.15 K. Table 1 gives parameters for equations (8) and (9) for the NaCl-$MgCl_2$-H_2O system from 298.15 to 523.15 K. Figure 1 compares our predicted heat 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 Figure 2. Detailed tables of our measurements

will be given in an extended paper [10]. The agreement between the predicted and the experimental heat of mixing data is good in general. 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 showed 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 is more challenging at 573 K than it is at lower temperatures due to the complexities arising from hydrolysis and ion association. Electrical conductance measurements by Frantz and Marshall [15] 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 further measurements of various properties of $MgCl_2$(aq) at 573 K or higher temperatures. Treatment has been made in this study based on two simplified formulations. Only a summary of the result is given here.

Formulation I. This treatment assumes the regular pattern first used by Pitzer and Mayorga [16] who introduced a term with an interaction parameter, $b^{(2)}$, and a large a_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 $b^{(2)}$ parameter is related to the ion association constant, K, by $b^{(2)}=-K/2$. In the comprehensive treatment for thermodynamic properties of $CaCl_2$, Holmes *et al*. [17] used the $b^{(2)}$ 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 was used. The same expression for $b^{(2)}$ 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 $b^{(2)}$ has been included in our treatment at 573 K.

The heat of dilution data at 573.15 K were first fitted to Eqs. (5) and (6) to obtain the ion-interaction parameters, $b^{(0)L}_{Mg,Cl}$, $b^{(1)L}_{Mg,Cl}$, $b^{(2)L}_{Mg,Cl}$, and $C^{L}_{Mg,Cl}$. However, use of these interaction parameters did not give a good fit of the heat of mixing data to equation (1) at 573 K. The limited number of data points for the heat of dilution at this temperature is not sufficient in determining unambiguously a full set of pure electrolyte parameters. Instead, a simultaneous fit of both the heat of dilution data to equations (5) and (6) and heat of mixing data to equation (1) gave good fits for both dilution and mixing data at 573 K. In this treatment, parameters for NaCl(aq), $b^{(0)L}_{NaCl}$, $b^{(1)L}_{NaCl}$, and C^{L}_{NaCl}, were calculated from Archer's equation, and the value of a_2 was set to be 12.0. A number of values for a_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, $b^{(0)L}_{Mg,Cl}$, $b^{(1)L}_{Mg,Cl}$, $b^{(2)L}_{Mg,Cl}$, $C^{L}_{Mg,Cl}$, ${}^{s}q^{L}_{Na,Mg}$, and $y^{L}_{Na,Mg,Cl}$, at 573.15 K are given in Table 2. In the Holmes *et al*. model [8,9,17], $b^{(2)L}$ was calculated to be -0.22 at 523 K while the $b^{(2)L}$ obtained in our study is -0.43 at 573 K. This result is reasonable. While the ion association constant, *K*, increases with temperature, $b^{(2)}$ becomes more negative, resulting in a

negative $\P b^{(2)} / \P T$ value. The larger $-b^{(2)L}$ value at 573 K than that is 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 [15].

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 [18] and $InCl_3$ [19]. 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 $MgCl^+$ ($K = \propto$) 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 will be given in a separate paper [10]. Parameters obtained based on Formulation II are given in Table 4, together with those obtained based on Formulation I.

Comparisons of the experimental and calculated heat of dilution and heat of mixing at 573.15 K are shown in Figures 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 in two cases. A slightly better result is obtained for heat of mixing with Formulation I. But note that Formulation I has more adjustable parameters. As expected, less negative ΔH_{dil} values with smaller Debye-Huckel slopes are observed for Formulation II at low molalities compared to those from Formulation I. The latter is valid in the limit of zero ionic strength. The actual ionic speciation in the dilute solutions of $MgCl_2$(aq) is

expected to lie between the two extreme cases considered here. Enthalpies of dilution of $MgCl_2$(aq) in the dilute region are therefore expected to have values between those of the two extreme cases. The lower values of ΔH_{mix} in the dilute region for the Formulation II treatment than those for the Formulation I appear to arise from the Debye-Huckel term in the equation for Formulation II which yields negative values in the whole concentration range of our study, but is absent in the Eq. (1) for Formulation I. Since our heat of mixing data do not extend below an ionic strength of 0.9 mol-kg^{-1} at 573 K, our data can not give a clear conformation of the ΔH_{mix} values in the dilute region.

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

Parameter	${}^{S}q_{Na,Mg}$ (kg-mol^{-1}) ${}^{S}q^{L}_{Na,Mg}$ (kg-mol^{-1}-K^{-1})	$y_{Na,Mg,Cl}$ (kg^{2}-mol^{-2}) $y^{L}_{Na,Mg,Cl}$ (kg^{2}-mol^{-2}-K^{-1})
p_0	7.66109x10^{-2}	-6.67238x10^{-2}
p_1	-1.11639x10^{-4}	4.12766x10^{-4}
p_2	3.55254x10^{-8}	-1.48260x10^{-6}
p_3	-2.64307x10^{-13}	3.73211x10^{-12}

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

Formulation I (Mg^{2+}, Na^+, Cl^-)		Formulation II ($MgCl^+$, Na^+, Cl^-)	
$b^{(0)L}_{Mg,Cl}$ (kg-mol^{-1}-K^{-1})	7.59218x10^{-4}	$b^{(0)L}_{MgCl,Cl}$ (kg-mol^{-1}-K^{-1})	-1.93826x10^{-3}
$b^{(1)L}_{Mg,Cl}$ (kg-mol^{-1}-K^{-1})	2.45190x10^{-2}	$b^{(1)L}_{MgCl,Cl}$ (kg-mol^{-1}-K^{-1})	-4.17288x10^{-2}
$b^{(2)L}_{Mg,Cl}$ (kg-mol^{-1}-K^{-1})	-0.425749		
$C^{L}_{Mg,Cl}$ (kg^2-mol^{-2}-K^{-1})	-3.45882x10^{-5}	$C^{L}_{MgCl,Cl}$ (kg^2-mol^{-2}-K^{-1})	0.0
${}^{S}q^{L}_{Na,Mg}$ (kg-mol^{-1}-K^{-1})	2.58857x10^{-4}	${}^{S}q^{L}_{MgCl,Na}$ (kg-mol^{-1}-K^{-1})	3.84243x10^{-4}
$y^{L}_{Na,Mg,Cl}$ (kg^2-mol^{-2}-K^{-1})	4.16692x10^{-5}	$y^{L}_{MgCl,Na,Cl}$ (kg^2-mol^{-2}-K^{-1})	4.98770x10^{-4}
a_1 (kg$^{1/2}$-mol$^{-1/2}$)	2.0	a_1 (kg$^{1/2}$-mol$^{-1/2}$)	3.5
a_2 (kg$^{1/2}$-mol$^{-1/2}$)	12.0		

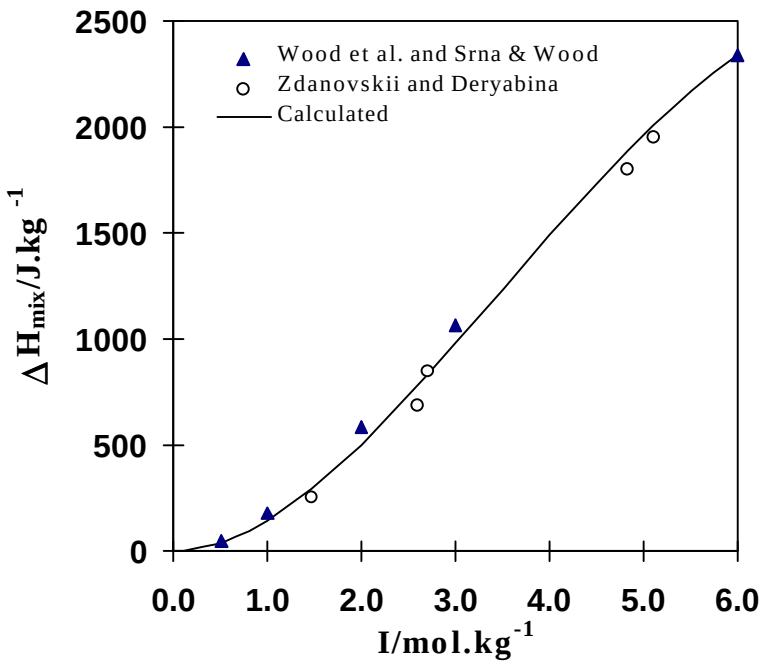
FIGURE CAPTIONS

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 heat of mixing at 373.15, 423.15, 473.15, and 523.15 K with experimental values of this study and those of Wood and Mayrath [4] at 373.15 K.

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 Formulation I and II, respectively.

Fig. 4. The experimental (symbols) and calculated (curves) heat of mixing of $MgCl_2$(aq) with NaCl(aq) at 573.15 K. Solid and dashed curves are based on Formulation I and II, respectively.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500
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1.0
2.0
3.0
4.0
5.0
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Wood et al. and Srna & Wood
Zdanovskii and Deryabina
Calculated
ΔHmix/J.kg-1
I/mol.kg-1

Figure 1.

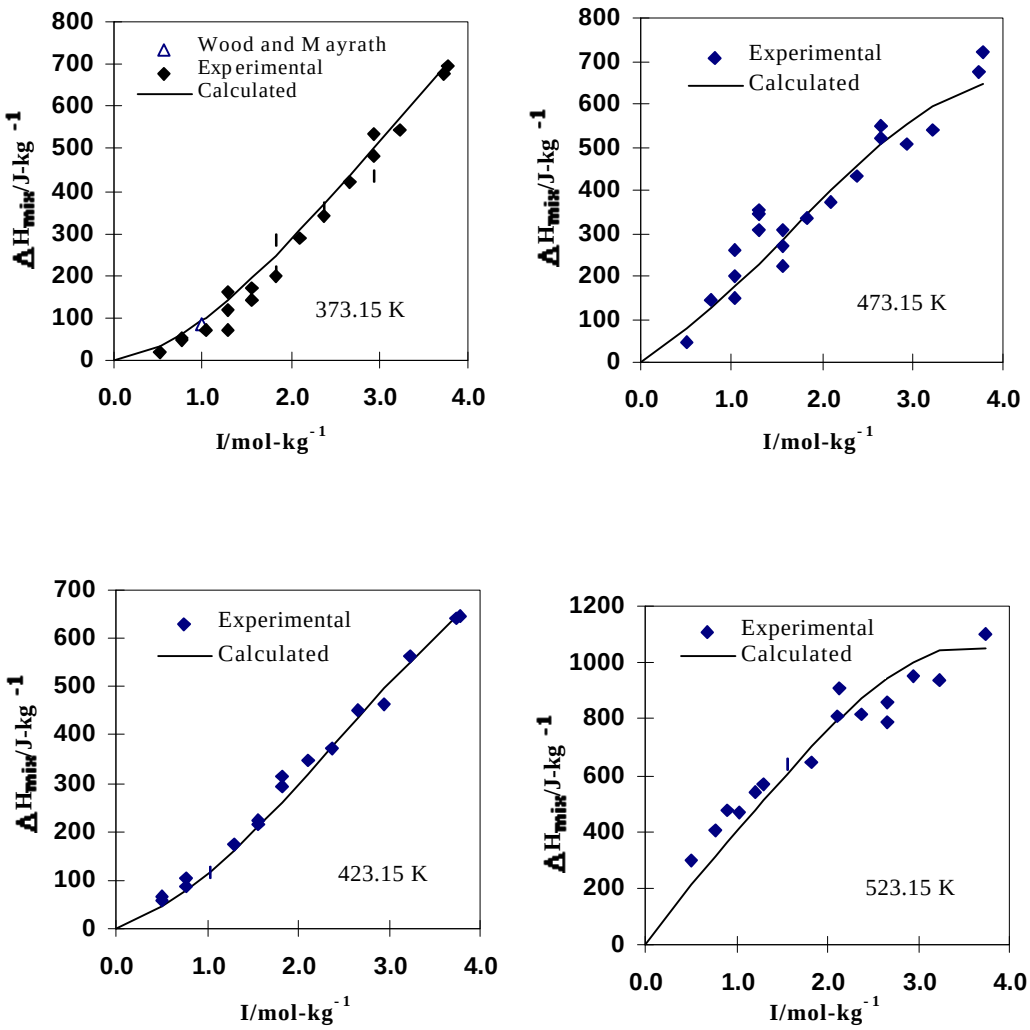
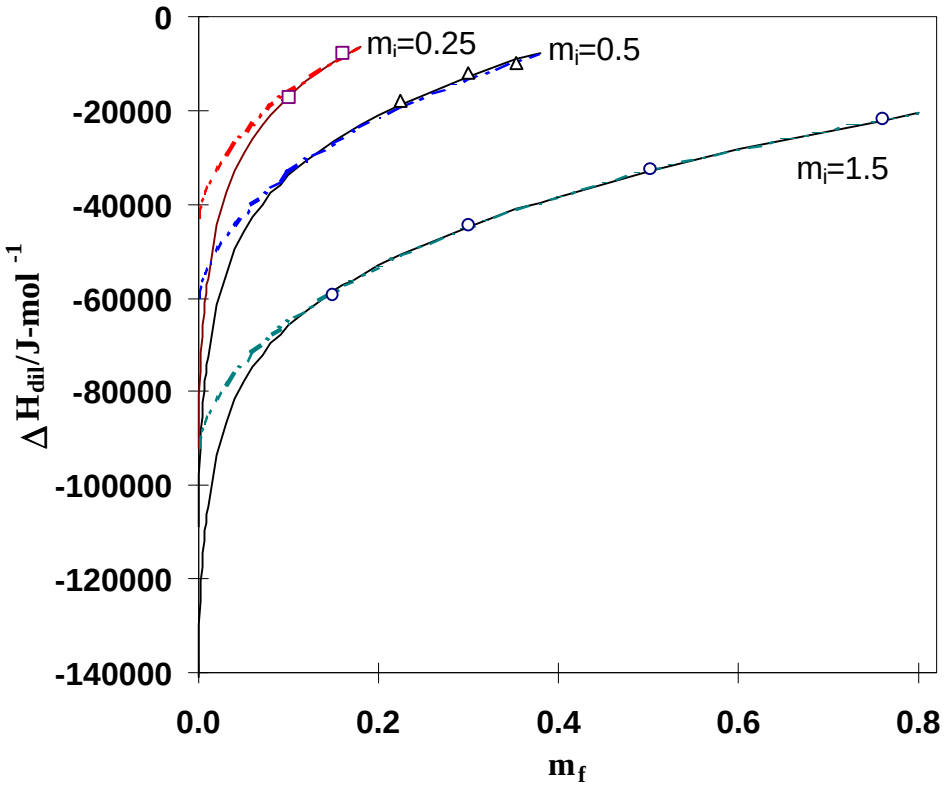

Wood and Mayrath
Experimental
Calculated
373.15 K
473.15 K
423.15 K
523.15 K
ΔHmix/J-kg -1
I/mol-kg-1
0
100
200
300
400
500
600
700
800
1000
1200
0.0
1.0
2.0
3.0
4.0

Figure 2.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-40000
-60000
-80000
-100000
-120000
-140000
0.0
0.2
0.4
0.6
0.8
m_f
ΔH_{dil}/J-mol^{-1}
m_i=0.25
m_i=0.5
m_i=1.5

Figure 3.

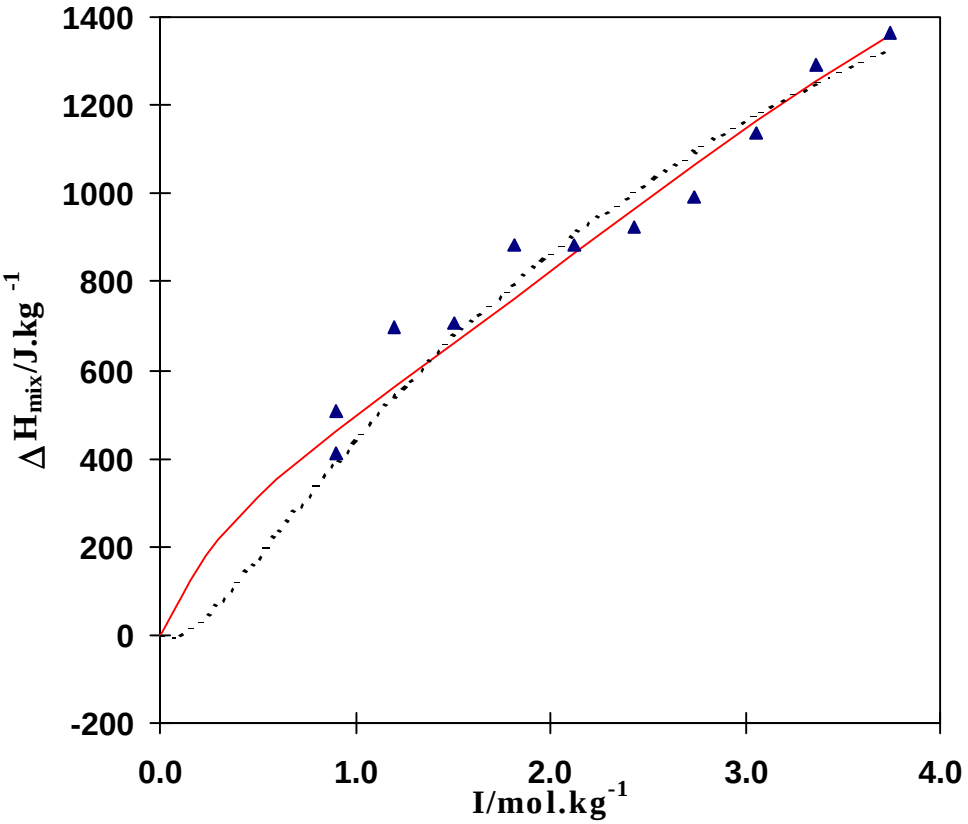
1400
1200
1000
800
600
400
200
0
-200
0.0
1.0
2.0
3.0
4.0
Δ H_mix/J.kg^-1
I/mol.kg^-1

Figure 4.