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Thermodynamics of Aqueous Mixtures of Magnesium Chloride with Sodium Chloride from 298.15 to 573.15 K. New Measurements of the Enthalpies of Mixing and of Dilution

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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 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 a constant pressure of 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 new equations for $MgCl_2$(aq) and the mixed system at 573 K.

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 (enthalpies) of mixing at 298 K, were reviewed and discussed by one of us (Pitzer, 1983) and others have measured additional systems since. Further complexities arise at higher temperatures where both hydrolysis and ion-interaction effects become stronger. Here we present new measurements for the system $MgCl_2$ + NaCl + H_2O extending to 573 K and its representation by equations of state. This system is also a very important component of many natural and industrial waters. Thermodynamic properties of this system at high temperatures are of practical importance to an understanding of hydrothermal mineral formation, geothermal brines, and corrosion at high temperatures. A similar study of the system $CaCl_2$ + NaCl + H_2O is being reported in a different journal (Oakes *et al.*, submitted).

Comprehensive treatments based on the Pitzer ion-interaction model (Pitzer, 1991) for each of the two pure electrolyte systems have been made up to 523.15 K for $MgCl_2$(aq) (Holmes and Mesmer, 1996; Holmes *et al.*, in press) and to 600 K for NaCl(aq) (Archer, 1992). Thermodynamic properties of aqueous mixtures of NaCl and $MgCl_2$ have been investigated by a number of researchers. Studies of NaCl + $MgCl_2$ activities prior to 1987 have been summarized by Rard and Miller (1987). More recently, osmotic and activity coefficients, apparent molar heat capacities, and volumes have been reported as a function of temperature (Rao and Ananthaswamy, 1989; Tishchenko, 1991; Saluja *et al.*, 1995). However, most of these studies were conducted at or near ambient temperatures and pressures. Studies relevant to hydrothermal regimes require data at high temperatures and pressures. Measurements of heats of mixing of electrolyte solutions are particularly useful since these can be integrated to yield activity and osmotic coefficients using integration constants evaluated from published 298 K data and can be differentiated to yield the heat capacities.

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 (Wood *et al.*, 1969; Srna and Wood, 1975; Wood and Mayrath, 1982; Zdanovskii and Deryabina, 1965) and with the thermodynamic properties of the binary systems NaCl+H_2O and $MgCl_2$ + H_2O, to provide a comprehensive treatment 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) and $MgCl_2$(aq), and the treatment for 573 K comprising new equations for $MgCl_2$(aq) and for the mixed system.

Experimental Section

Apparatus. The high-temperature, high-pressure flow calorimeter used in our experiments was based on the design of Christensen *et al.* (1986). Additional discussion of this calorimeter can be found elsewhere (Oakes *et al.*, submitted). The principal components of the calorimeter are a preheater cylinder coaxially wound with two inlet tubes and a heater, a heat sink plate containing a second, independently controlled heater, a passively heated ceramic dowel wound in a countercurrent arrangement with the two inlet tubes and the effluent tube, and an isothermal cylinder that is coaxially wound with a heater and the tube in which mixing/dilution occurs. The ceramic dowel assures thermal equilibration of the inlet and outlet streams before the inlet streams merge and mixing/dilution occurs. The cylinders and plate are nickel- and gold-plated copper and brass. The four principal pieces are contained within a suspended brass can that is insulated from the external environment using a several-inch-thick blanket of Carborundum ceramic fiber. The heat sink plate is completely insulated from the preheater and isothermal cylinder except for a single bolt that passes through a ceramic disk and connects the isothermal cylinder and heat sink plate. The plate is in thermal contact with the outer container only through a graphite ring. Heat transfer between the outer can and the internal parts is minimized by filling all open spaces with the ceramic fiber except that within the isothermal cylinder. All tubing directly contacting the high-temperature solutions is $^{1}/_{16}$ in. Pt−Rh alloy (80:20). Solutions are delivered to the calorimeter using four independent ISCO syringe pumps that push the solutions of interest from Teflon bags contained within separate

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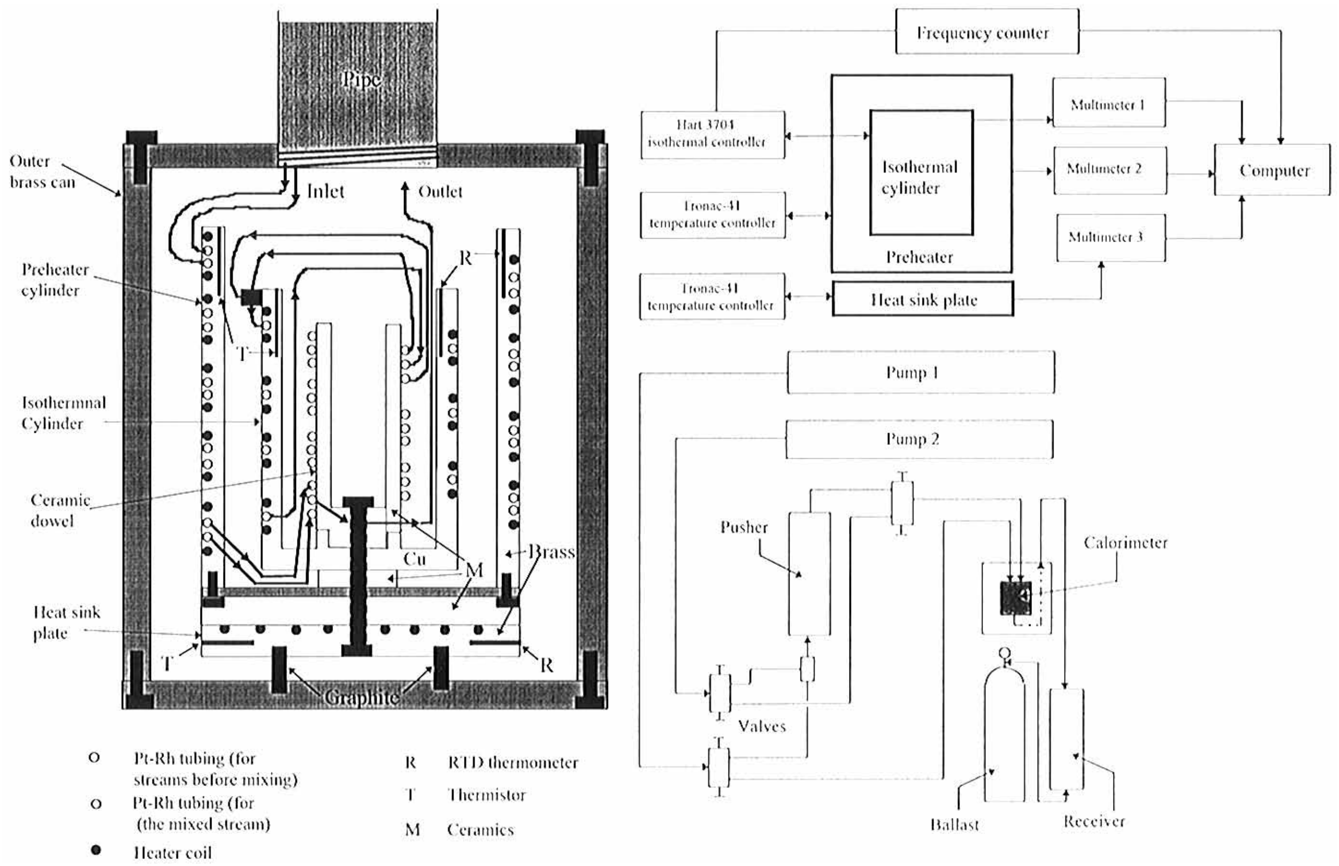

Figure 1. Schematic diagrams of (a) the calorimeter, (b) the temperature control system, and (c) the pressure regulation and fluid delivery system.

pressure vessels. The valving, fluid reservoir, effluent containment, and pressure regulation are similar to that of Busey *et al.* (1984).

Temperatures on the preheater, heat sink plate, and the isothermal cylinder were controlled by two Tronac PTC-41 temperature controllers and a Hart Scientific model 3704 precision isothermal controller, respectively, and were measured using platinum resistance temperature detectors (RTD). The RTD used to measure the temperature on the isothermal cylinder was calibrated against an Instrulab secondary standard temperature sensor (Model 841) from 373.15 to 623.15 K.

The stock solution under study was loaded into a Teflon bag, which was then placed into one of three 10 000 psi HiP pressure vessels. Each of the pressure vessels has two outlet connectors on the top and an inlet connector in the bottom. One outlet from the pressure vessel was connected through a tubing and valve system to a Heise pressure gauge, while the other outlet was connected to the Teflon bag internally and a valve and tubing system externally, which ultimately led to the calorimeter. The inlet connector on the bottom was connected to a valve and tube system and to two syringe pumps charged with distilled, deionized, argon sparged water. Water from the syringe pumps was either delivered to the pressure vessels to expel solutions from the Teflon bags or directly to a three-way valve on the downstream side of the pressure vessel. Using different combinations of valves and pumps, either pure stock solution, pure water, or any dilution of a stock solution could be delivered to the calorimeter from either of the two inlet tubes within the calorimeter.

Schematic diagrams of the calorimeter and its temperature control, pressure regulation, and fluid delivery systems are given in Figure 1.

Procedure. Stock solutions of NaCl (4.109 mol·kg^{-1}) and $MgCl_2$ (1.545 mol·kg^{-1}) were made from NaCl and $MgCl_2 \cdot 6H_2O$ (Fisher Scientific Certified A.C.S. crystals) and deionized water. Both solutions were analyzed for Cl^-(aq) contents by Mohr titration using a standard $AgNO_3$ solution (Fisher Scientific Certified A.C.S.). The NaCl stock solution was also standardized by a gravimetric analysis. The agreement between the results of Mohr titration and gravimetric analysis is better than 0.4% and that between the results of the repeated titrations is better than 0.1%. Solutions were filtrated before analysis and sparged of any dissolved oxygen by argon, using the Kontes four-valve filtration/delivery cap systems.

The heat of mixing/dilution experiments were conducted by measuring the energy output (in terms of pulse·s^{-1}) provided by the isothermal controller (Hart 3704) to maintain the isothermal cylinder at a constant temperature when the two inlet streams are mixed in the calorimeter. While the calorimeter was designed with the intention of conducting electrical calibrations to determine the output of Hart 3704 in terms of J·pulse^{-1}, there are differences between the chemical and electrical power dissipation on the isothermal cylinder (Oakes *et al.*, submitted). Heats of dilution for a similar aqueous electrolyte, $CaCl_2$(aq), have been measured by Holmes *et al.* (1994) over the temperature range of 298−526 K and for pressures of 7−40 MPa. Using this calorimeter, heats of dilution for $CaCl_2$(aq) determined using electrical calibrations produced results that systematically differed from those of Holmes *et al.* while heats of dilution determined with “chemical” calibration via heat of dilution measurements of NaCl(aq) produced results in agreement with those of Holmes *et al.* Heats of dilution for NaCl(aq) are well known (Mayrath and Wood, 1982; Busey *et al.*, 1984; Archer, 1986) over the temperatures and pressures to 600 K and 41 MPa, respectively, and have been represented by an extended Pitzer ion-interaction model equation by Archer (1992) on which

Table 1. Experimental Heat of Mixing of NaCl(aq) with $MgCl_2$(aq) at $P = 20.5$ MPa and at Ionic Strength Fraction $y = 0.5$

I/mol·kg H_2O^{-1}	ΔH_{mix}/J·kg H_2O^{-1}	unc[a]/J·kg H_2O^{-1}	I/mol·kg H_2O^{-1}	ΔH_{mix}/J·kg H_2O^{-1}	unc[a]/J·kg H_2O^{-1}
$T = 373.15$ K					
0.5102	17	12	1.8324	208	14
0.7681	47	16	2.1061	290	14
0.7681	51	7	2.3833	342	22
1.0309	70	14	2.3833	360	22
1.2941	163	10	2.6627	423	10
1.2941	116	20	2.9442	482	18
1.2941	73	10	2.9442	436	12
1.5622	140	30	2.9442	534	12
1.5622	170	14	3.2310	544	20
1.8324	198	16	3.7308	679	14
1.8324	285	20	3.7830	696	14
$T = 423.15$ K					
0.5100	59	12	1.8320	313	14
0.5100	66	8	2.1056	349	12
0.7679	88	14	2.3829	373	16
0.7679	103	12	2.6623	453	12
1.0306	118	14	2.9439	464	18
1.2937	173	12	3.2307	564	10
1.5618	225	10	3.7307	642	12
1.5618	216	8	3.7828	645	14
1.8320	296	14			
$T = 473.15$ K					
0.5100	46	36	1.5618	307	42
0.7679	146	52	1.8320	337	33
1.0306	259	49	2.1056	374	62
1.0306	202	38	2.3829	434	50
1.0306	150	31	2.6623	550	34
1.2937	342	46	2.6623	521	55
1.2937	305	37	2.9439	506	55
1.2937	352	56	3.2307	540	39
1.5618	224	49	3.7307	673	70
1.5618	271	58	3.7828	723	72
$T = 523.15$ K					
0.5092	295	118	2.1056	813	91
0.7682	404	101	2.1223	909	121
0.9012	474	89	2.3829	819	78
1.0306	471	118	2.6613	786	151
1.2042	538	109	2.6623	861	109
1.2937	565	94	2.9439	949	109
1.5618	640	84	3.2307	937	88
1.8320	646	98	3.7297	1099	93
$T = 573.15$ K					
0.9012	412	64	2.4323	926	32
0.9012	505	64	2.7407	991	37
1.2042	697	66	3.0529	1137	37
1.5085	705	37	3.3662	1289	29
1.8154	883	53	3.7450	1366	47
2.1222	882	40			

[a] Uncertainties were estimated to be $C(2\sigma)/W$, where σ is the standard deviation of the Hart output and C and W are the same as those in eq 1; see text.

Table 2. Experimental Heat of Dilution of $MgCl_2$(aq) at $P = 20.5$ MPa

m_i/mol·kg H_2O^{-1}	m_f/mol·kg H_2O^{-1}	ΔH_{dil}/J·mol^{-1}	unc[a]/J·mol^{-1}	m_i/mol·kg H_2O^{-1}	m_f/mol·kg H_2O^{-1}	ΔH_{dil}/J·mol^{-1}	unc[a]/J·mol^{-1}
$T = 523.15$ K							
0.5151	0.1998	−12887	546	1.5451	0.1998	−34491	569
0.5151	0.3004	−7435	373	1.5451	0.3004	−29417	370
1.0391	0.1998	−24805	468	1.5451	0.5030	−17797	200
1.0391	0.4521	−13216	287	1.5451	0.7589	−14616	111
1.0391	0.6050	−9595	165				
$T = 573.15$ K							
0.2471	0.0997	−17177	378	1.5451	0.1497	−59364	355
0.2470	0.1597	−7698	204	1.5451	0.3004	−44552	189
0.5197	0.2249	−18078	244	1.5451	0.5030	−32492	76
0.5199	0.3004	−12064	149	1.5451	0.7589	−21774	153
0.5199	0.3534	−9819	546				

[a] See footnote in Table 1.

our chemical calibrations were based. Chemical calibrations were conducted at each temperature for the heat of dilution and heat of mixing experiments at the same pressure (20.5 MPa).

The heat of mixing/dilution, $\Delta H_{mix/dil}$, is calculated from the equation

$$\Delta H_{mix/dil}/\mathrm{J{\cdot}kg\ H_2O^{-1}} = C(R_{m/d} - R_b)/W \qquad (1)$$

where C is the chemically determined calibration factor in J·pulse^{-1}, $R_{m/d}$ and R_b are the output of Hart 3704 in pulse·s^{-1} for mixing or dilution and for base line runs, respectively, and W is the amount of water flowing through the calorimeter in units of kg $H_2O{\cdot}s^{-1}$. The value of W was determined from eq 2

$$W = \left[\rho_w F_{w,1} + \rho_1 F_1\left(1 - \frac{M_{w,1} m_1}{1000 + M_{w,1} m_1}\right)\right] + \left[\rho_w F_{w,2} + \rho_2 F_2\left(1 - \frac{M_{w,2} m_2}{1000 + M_{w,2} m_2}\right)\right] \qquad (2)$$

where ρ_w, ρ_1, ρ_2 are densities of pure water and stock solutions 1 [NaCl(aq)] and 2 [$MgCl_2$(aq)], respectively, at the reservoir temperature and pressure; $F_{w,1}$ and $F_{w,2}$ are volumetric flow rates of pure water used to dilute streams from the stock solutions and to adjust the ionic strengths of NaCl(aq) and $MgCl_2$(aq) before mixing/dilution; F_1 and F_2 are flow rates of NaCl(aq) and $MgCl_2$(aq) stock solutions; m_1 and m_2 are molalities of the two stock solutions; $M_{w,1}$ and $M_{w,2}$ are molar weights of NaCl and $MgCl_2$, respectively.

All of the measurements in this study were made at a total flow rate of 30.00 cm^3·h^{-1}. Flow rates were adjusted so that the NaCl(aq) and $MgCl_2$(aq) solutions were at equal ionic strengths in the heat of mixing runs. The measurements covered ionic strength ranges of 0.5−3.8 mol.kg^{-1} for the heat of mixing runs and 0.3−4.6 mol.kg^{-1} for the heat of dilution runs. The influence of the total flow and the flow ratio of the inlet streams on the base line signals has been discussed (Oakes *et al.*, submitted). In order to obtain the most accurate results, consecutive base line and mixing or dilution runs were conducted as matched pairs for each ionic strength at all temperatures. The temperature on the isothermal cylinder was controlled to ±0.008 K, and the pressure fluctuation during measurements was less than ±0.1 MPa as indicated by the Heise pressure gauge.

Experimental Results

The observed heat of mixing for solutions of NaCl(aq) with $MgCl_2$(aq) at 373.15, 423.15, 473.15, 523.15, and 573.15 K are presented in Table 1. Equal volumes of the two solutions were mixed in all cases. Thus, the ionic strength fractions for each of the two pure electrolytes in the final mixtures are close to 0.5 in all of the heat of mixing experiments. Heats of dilution of $MgCl_2$(aq) at 523.15 and 573.15 K are given in Table 2; the initial and final molalities are given. All data were determined at a constant pressure of 20.5 MPa. The properties of water used in the calculations were derived from the equation of state of Hill (1990). Densities of NaCl(aq) and $MgCl_2$(aq) solutions at the experimental reservoir temperature and 20.5 MPa were calculated from the models of Archer (1992) and of Holmes and Mesmer (1996) and Holmes *et al.* (in press), respectively. The uncertainties in the heat of mixing and the heat of dilution given in Tables 1 and 2 were estimated using standard deviations of the Hart output recorded over a time period (typically, 45 min).

Equations

In the Pitzer ion-interaction model, the excess Gibbs free energy, G^E, of a mixed electrolyte solution can be expressed as

$$G^{E}/(w_{w}RT) = -A_{\phi}\frac{4I}{b}\ln(1 + b\sqrt{I}) + 2\sum_{c}\sum_{a}m_{c}m_{a}[B_{ca} + (\sum mz)C_{ca}] + \sum_{c}\sum_{c'}m_{c}m_{c'}[\Phi_{cc'} + \sum_{a}m_{a}\psi_{cc'a}/2] + \sum_{a}\sum_{a'}m_{a}m_{a'}[\Phi_{aa'} + \sum_{c}m_{c}\psi_{caa'}/2] \quad (3)$$

with

$$B_{ca} = \beta_{ca}^{(0)} + 2\beta_{ca}^{(1)}[1 - (1 + \alpha_{1}\sqrt{I})\exp(-\alpha_{1}\sqrt{I})]/(\alpha_{1}{}^{2}I) + 2\beta_{ca}^{(2)}[1 - (1 + \alpha_{2}\sqrt{I})\exp(-\alpha_{2}\sqrt{I})]/(\alpha_{2}{}^{2}I) \quad (4a)$$

$$C_{ca} = C_{ca}^{(0)} + 4C_{ca}^{(1)}[6 - (6 + 6\alpha_{c}\sqrt{I} + 3\alpha_{c}^{2}I + \alpha_{c}^{3}I^{2/3})\exp(-\alpha_{c}\sqrt{I})]/(\alpha_{c}^{4}I^{2}) \quad (4b)$$

$$\Phi_{ij} = {}^{S}\theta_{ij} + {}^{E}\theta_{ij}(I) \quad (5)$$

and w_w being the mass of water in kg, m the molality of the subscribed ion, I the ionic strength, A_ϕ the Debye–Huckel osmotic coefficient parameter, $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, and $\beta_{ca}^{(2)}$ the parameters from the binary cation–anion interactions, $C_{ca}^{(0)}$, $C_{ca}^{(1)}$, and ψ_{ijk} the third-order interaction parameters with $\sum mz = \sum_{c}m_{c}z_{z} = \sum_{a}m_{a}z_{a}$, 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, depends only on the charges of the ions, the total ionic strength, and the solvent properties (Pitzer, 1975, 1983). The quantity b is set to the standard value of 1.2. For the NaCl + $MgCl_2$ + H_2O system, the B_{ca} and C_{ca} terms include those for NaCl(aq) ($B_{Na,Cl}$ and $C_{Na,Cl}$) and for $MgCl_2$(aq) ($B_{Mg,Cl}$ and $C_{Mg,Cl}$). These terms can be calculated using the model for NaCl(aq) by Archer (1992) and the model for $MgCl_2$(aq) by Holmes and Mesmer (1996) and Holmes *et al.* (in press). In the Archer model, α_1 was chosen to be a constant value of 2.0 while there is no $\beta^{(2)}$ term and hence no α_2 value being assigned for NaCl(aq). The $C_{ca}^{(1)}$ term is pertinent only to the Archer model with an α_c value of 2.5. In the Holmes and Mesmer model, a linear function of temperature was used for α_1

$$\alpha_{1} = 2 - 0.001\,81(T/\mathrm{K} - 298.15) \quad (6)$$

while α_2 was chosen to be a constant value of 12.0. No $C_{ca}^{(1)}$ term and hence no α_c value were assigned for $MgCl_2$(aq).

The equation for excess enthalpy $L = H^E$ follows directly from differentiation of eq 3.

$$\frac{L}{w_{w}RT^{2}} = \frac{A_{H}I}{RT^{2}b}\ln(1 + b\sqrt{I}) - 2\sum_{c}\sum_{a}m_{c}m_{a}[B_{ca}^{L} + (\sum mz)C_{ca}^{L}] - \sum_{c}\sum_{c'}m_{c}m_{c'}[\Phi_{cc'}^{L} + \sum_{a}m_{a}\psi_{cc'a}^{L}/2] - \sum_{a}\sum_{a'}m_{a}m_{a'}[\Phi_{aa'}^{L} + \sum_{c}m_{c}\psi_{caa'}^{L}/2] \quad (7)$$

where A_H is the Debye–Huckel enthalpy parameter and

$$B^{L} = \partial B/\partial T \quad (8)$$

$$C^{L} = \partial C/\partial T \quad (9)$$

$$\Phi^{L} = \partial \Phi/\partial T \quad (10)$$

$$\psi^{L} = \partial \psi/\partial T \quad (11)$$

Heat of mixing ΔH_{mix} per unit mass of solvent of solutions of the two salts can be written as

$$\Delta H_{mix} = [L_{mix} - (1 - y)L_{1} - yL_{2}]/w_{w} \quad (12)$$

where L_{mix}, L_1, and L_2 are the excess enthalpies of the mixture and the two pure electrolyte solutions, respectively, and y is the ionic strength fraction of salt 2. 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 heat of mixing can be obtained by substituting eq 7 into eq 12:

$$\frac{\Delta H_{mix}}{RT^{2}I^{2}} = y(1 - y)\Big[\frac{2}{3}B_{MX}^{L} - \frac{2}{9}B_{NX}^{L} + \frac{2}{9}(6 - y)IC_{MX}^{L} - \frac{2}{27}(5 - y)IC_{NX}^{L} - \frac{2}{3}{}^{E}\theta_{MN}^{L} - \frac{2}{3}{}^{S}\theta_{MN}^{L} - \frac{1}{9}(3 - y)I\psi_{MNX}^{L}\Big] \quad (13)$$

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

$$\Delta H_{dil} = L_{\phi}(m_{f}) - L_{\phi}(m_{i}) \quad (14)$$

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 was derived from eq 7 as

$$L_{\phi} = \frac{3A_{H}}{b}\ln(1 + b\sqrt{I}) - 4RT^{2}(mB_{NX}^{L} + 2m^{2}C_{NX}^{L}) \quad (15)$$

Evaluation and Analysis of Experimental Data

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.* (1969), Srna and Wood (1975), and Zdanovskii and Deryabina (1965) at 298.15 K and by Wood and Mayrath (1982) 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 (Walther, 1986; Brown *et al.*, 1996; Palmer and Wesolowski, 1997). Using the results presented by Palmer and Wesolowski and Walther, the amount of $MgOH^+$ formed in reaction 16

$$Mg^{2+} + H_{2}O = MgOH^{+} + H^{+} \quad (16)$$

was estimated to be only 0.2% at 523 K and 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.

In order to express the heat of mixing as a function of temperature, equations for the temperature dependence of $B_{Na,Cl}^{L}$, $C_{Na,Cl}^{L}$, $B_{Mg,Cl}^{L}$, $C_{Mg,Cl}^{L}$, ${}^{E}\theta_{Na,Mg}^{L}$, ${}^{S}\theta_{Na,Mg}^{L}$, and $\psi_{Na,Mg,Cl}^{L}$ are needed for insertion in eq 13. Parameters for NaCl(aq), $B_{Na,Cl}^{L}$ and $C_{Na,Cl}^{L}$, were calculated using Archer's formulation and those for $MgCl_2$(aq), $B_{Mg,Cl}^{L}$ and $C_{Mg,Cl}^{L}$, were from the model of Holmes and Mesmer. The unsymmetrical mixing parameter, ${}^{E}\theta_{ij}^{L}$, was calculated from formulas given by Pitzer (1975, 1983). The temperature dependencies of mixing parameters, ${}^{S}\theta_{Na,Mg}^{L}$ and $\psi_{Na,Mg,Cl}^{L}$, are to be evaluated from the experimental heat of mixing data.

Table 3. Parameters for Equations 18 and 19 for the NaCl + MgCl$_2$ + H$_2$O System from 298.15 to 523.15 K

parameter	${}^{S}\theta_{Na,Mg}$/kg·mol^{-1}, ${}^{S}\theta^{L}_{Na,Mg}$/kg·mol^{-1}·K^{-1}	$\psi_{Na,Mg,Cl}$/kg^2·mol^{-2}, $\psi^{L}_{Na,Mg,Cl}$/kg^2·mol^{-2}·K^{-1}
p_0	$7.661\ 09 \times 10^{-2}$	$-6.672\ 38 \times 10^{-2}$
p_1	$-1.116\ 39 \times 10^{-4}$	$4.127\ 66 \times 10^{-4}$
p_2	$3.552\ 54 \times 10^{-8}$	$-1.482\ 60 \times 10^{-6}$
p_3	$-2.643\ 07 \times 10^{-13}$	$3.732\ 11 \times 10^{-12}$

Several temperature dependent forms for ${}^{S}\theta^{L}_{Na,Mg}$ and $\psi^{L}_{Na,Mg,Cl}$ were tested to fit the heat of mixing data in the temperature range of 298.15−523.15 K. The following equation was used in our final calculations

$$f_L = p_1 + p_2T + p_3T^3 \tag{17}$$

where T is the temperature in kelvin and p_1-p_3 are the parameters determined from a least-squares fitting of eq 13 to the heat of mixing data. Temperature functions for osmotic/activity coefficient parameters, ${}^{s}\theta_{Na,Mg}$ and $\psi_{Na,Mg,Cl}$, can be derived from integration of eq 17

$$f_G = p_0 + p_1T + {}^1\!/_2p_2T^2 + {}^1\!/_4p_3T^4 \tag{18}$$

where values of p_0 were derived from values of ${}^{s}\theta_{Na,Mg}$ and $\psi_{Na,Mg,Cl}$ at 298.15 K, which were obtained from fitting eq 19

$$\phi - 1 = \frac{2}{\sum_i m_i}\{-A_\phi I^{3/2}/(1 + b\sqrt{I}) + m_{NaCl}(m_{NaCl} + 2m_{MgCl_2})[B^{\phi}_{Na,Cl} + (m_{NaCl} + 2m_{MgCl_2})C^{\phi}_{Na,Cl}] + m_{MgCl_2}(m_{NaCl} + 2m_{MgCl_2})[B^{\phi}_{Mg,Cl} + (m_{NaCl} + 2m_{MgCl_2})C^{\phi}_{Mg,Cl}/\sqrt{2}] + m_{NaCl}m_{MgCl_2}[{}^{E}\theta_{Na,Mg} + {}^{S}\theta_{Na,Mg} + I\,{}^{E}\theta'_{Na,Mg} + (m_{NaCl} + 2m_{MgCl_2})\psi_{Na,Mg,Cl}]\} \tag{19}$$

to the osmotic coefficient values of Rard and Miller (1987) at 298.15 K. Here $B^{\phi}_{Na,Cl}$, $C^{\phi}_{Na,Cl}$, $B^{\phi}_{Mg,Cl}$, and $C^{\phi}_{Mg,Cl}$ are the interaction parameters as defined and calculated from Archer (1992), Holmes and Mesmer (1996), and Holmes *et al.* (in press) and ${}^{E}\theta'_{Na,Mg}$ is the derivative of ${}^{E}\theta_{Na,Mg}$ with respect to the ionic strength of the solution. Equation 19 was derived from differentiation of the excess Gibbs free energy G^E (eq 3) with respect to w_w with $\sum_i m_i$ being the sum of molalities of all ions in the mixture. Table 3 gives parameters for eqs 18 and 19 for the heat of mixing and osmotic/activity coefficient of the NaCl + MgCl$_2$ + H$_2$O system from 298.15 to 523.15 K. Figure 2 compares our predicted heat of mixing at 298.15 K with experimental data from Wood *et al.* (1969), Srna and Wood (1975), and Zdanovskii and Deryabina (1965). Figure 3 shows a comparison of the heat of mixing calculated from our fitting equations with our experimental values from 373.15 to 523.15 K given in Table 1 and the experimental data from Wood and Mayrath (1982) at 373.15 K. The agreement is good in general. The standard deviation for the overall fit with the heat of mixing is 54.0 J·kg H$_2$O^{-1}, which is about the same as the experimental uncertainties. In Figure 4, the osmotic coefficient values calculated using our fitting equations are compared with those from Rard and Miller at 298.15 K. 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$_2$O system in the temperature range up to 523 K.

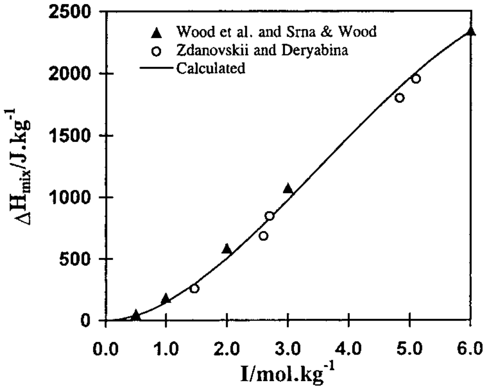

Figure 2. Comparison of the predicted heat of mixing at 298.15 K with experimental data of Wood *et al.* (1969), Srna and Wood (1975), and Zdanovskii and Deryabina (1965).

Treatment for the Single Temperature 573.15 K. The thermodynamics of the NaCl + MgCl$_2$ + H$_2$O 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 (1982) clearly indicate ion association at and above 573 K in dilute solutions of MgCl$_2$ and CaCl$_2$. At this time we present treatments in two simplified formulations. These treatments can be superseded by a new comprehensive model for MgCl$_2$(aq) covering the full temperature range up to 573 K or higher based on the published experimental data in the temperature range 523−623 K such as those of Urusova and Valyashko (1983, 1984, 1987), Emons *et al.* (1986), Valyashko *et al.* (1987, 1988), White *et al.* (1988), Pepinov *et al.* (1993), and Gillespie *et al.* (1992) and our own heat of dilution data obtained in this study.

(a) Formulation I. This treatment assumes the regular pattern first used by Pitzer and Mayorga (1974), 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.* (1994) used the $\beta^{(2)}$ parameter as defined and expressed on the basis of 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 $\beta^{(2)}$ has been adopted for other alkaline-earth metal chlorides including MgCl$_2$(aq) in a similar treatment (Holmes and Mesmer, 1996) 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.

Initially, the heat of dilution data at 573.15 K were fitted to eqs 14 and 15, but the number of data and the range of molality covered are not sufficient to unambiguously determine all four parameters, $\beta^{(0)L}_{Mg,Cl}$, $\beta^{(1)L}_{Mg,Cl}$, $\beta^{(2)L}_{Mg,Cl}$, and $C^{(0)L}_{Mg,Cl}$. A simultaneous fit of both the heat of dilution and heat of mixing data gave satisfactory agreement between the calculated and the experimental data for six parameters (${}^{s}\theta^{L}_{Na,Mg}$, $\psi^{L}_{Na,Mg,Cl}$, $\beta^{(0)L}_{Mg,Cl}$, $\beta^{(1)L}_{Mg,Cl}$, $\beta^{(2)L}_{Mg,Cl}$, $C^{(0)L}_{Mg,Cl}$) with values shown in Table 4. In this treatment, parameters for NaCl(aq), $\beta^{(0)L}_{Na,Cl}$, $\beta^{(1)L}_{Na,Cl}$, $C^{(0)L}_{Na,Cl}$, and $C^{(1)L}_{Na,Cl}$, were calculated from Archer's equation. The standard values α_1 =

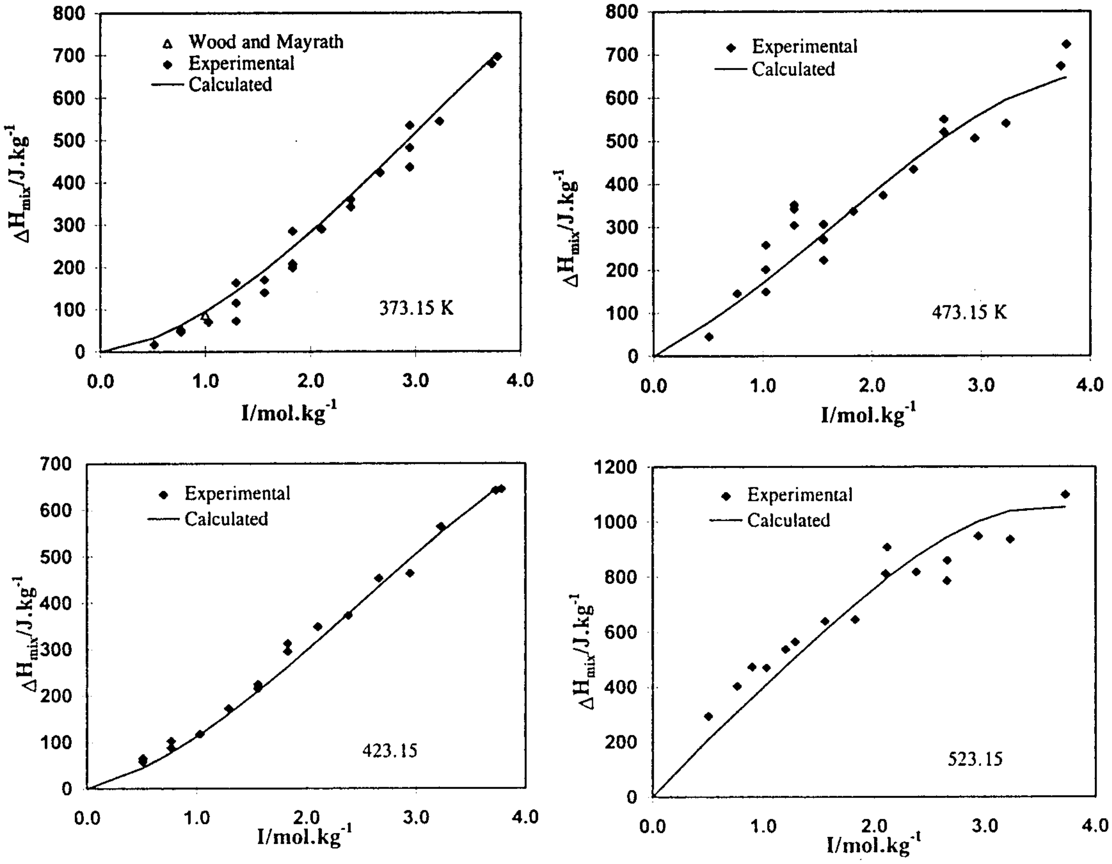

Figure 3. Comparison of the calculated heat of mixing at 373.15, 423.15, 473.15, and 523.15 K with experimental values of this study and those of Wood and Mayrath (1982) at 373.15 K.

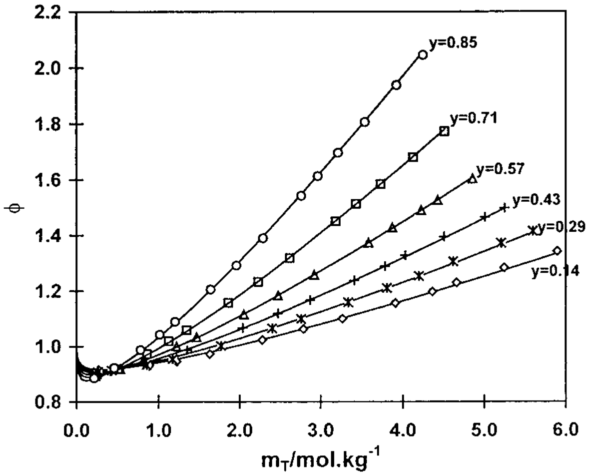

Figure 4. Experimental (symbols, Rard and Miller, 1987) and calculated (curves) osmotic coefficients at various ionic strength fractions, *y*, of $MgCl_2$ at 298.15 K.

2.0 and $\alpha_2 = 12$ were used for $MgCl_2(aq)$. It is probable that there is still considerable uncertainty as to the value of any particular parameter, if all others are freely adjustable. Thus, we do not offer further interpretation at this time.

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 (Clegg *et al.*, 1994) and $InCl_3$ (Pitzer *et al.*, 1997). 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 $MgCl_2^0$, calculations were made under all conditions in our experiments at 573 K. This is discussed below.

Note that the ionic strength *I* is based on complete dissociation of the $MgCl_2$ for the experimental results in Tables 1 and 2 and in all equations above. Only in formulation II below and in the Appendix is *I* based on $MgCl^+$, Cl^-.

(b) Formulation II. The assumption of complete ion association to $MgCl^+$ is clearly a very great oversimplification, but it is informative. Now the initial ionic strength of $MgCl_2(aq)$ before mixing is only one-third of that of the NaCl(aq), and the Debye–Huckel term for mixing is substantial. Equations for the heat of mixing of NaCl(aq) with $MgCl_2(aq)$ and the heat of dilution of $MgCl_2(aq)$ with $MgCl_2(aq)$ being a 1–1 electrolyte are given by eqs A1–A5 in the Appendix. Here the unsymmetrical mixing term ${}^{E}\theta^{L}$ disappears, $\beta^{(0)L}$ and $\beta^{(1)L}$ are the second-order parameters representing interactions between $MgCl^+$ and Cl^-, and the mixing parameters, ${}^{S}\theta^{L}$ and ψ^{L}, account for interactions between $MgCl^+$ and Na^+ and $MgCl^+$, Na^+, and Cl^-, respectively. To minimize the number of parameters, $\beta^{(2)L}$ is not included but α_1 for $MgCl_2(aq)$ is adjusted and the value of 3.5 was optimum. Statistical adjustment of the parameters in eqs A1 and A5 to fit simultaneously the heat of mixing and the heat of dilution data at 573 K yields the parameters in Table 4, together with those obtained on the basis of formulation I.

Comparisons of the experimental and calculated heat of dilution and heat of mixing at 573.15 K are shown in Figures 5 and 6, respectively, where *I* is the ionic strength assuming complete dissociation of $MgCl_2$ to Mg^{2+} and $2Cl^-$. The dashed curves are calculated on the basis of the complete association of Mg^{2+} and Cl^- to $MgCl^+$. The agreement is about equally good for the heat of dilution in two cases. A slightly better result is obtained for heat of

Table 4. Parameters for the NaCl + MgCl$_2$ + H$_2$O System at 573.15 K

formulation I (Mg^{2+}, Na^+, Cl^-)		formulation II ($MgCl^+$, Na^+, Cl^-)	
$\beta^{(0)L}_{Mg,Cl}$/kg·mol^{-1}·K^{-1}	$7.592\ 18 \times 10^{-4}$	$\beta^{(0)L}_{MgCl,Cl}$/kg·mol^{-1}·K^{-1}	$-1.938\ 26 \times 10^{-3}$
$\beta^{(1)L}_{Mg,Cl}$/kg·mol^{-1}·K^{-1}	$2.451\ 90 \times 10^{-2}$	$\beta^{(1)L}_{MgCl,Cl}$/kg·mol^{-1}·K^{-1}	$-4.172\ 88 \times 10^{-2}$
$\beta^{(2)L}_{Mg,Cl}$/kg·mol^{-1}·K^{-1}	$-0.4257\ 49$		
$C^{L}_{Mg,Cl}$/kg^2·mol^{-2}·K^{-1}	$-3.458\ 82 \times 10^{-5}$	$C^{L}_{MgCl,Cl}$/kg^2·mol^{-2}·K^{-1}	0.0
$^{S}\theta^{L}_{Na,Mg}$/kg·mol^{-1}·K^{-1}	$2.588\ 57 \times 10^{-4}$	$^{S}\theta^{L}_{MgCl,Na}$/kg·mol^{-1}·K^{-1}	$3.842\ 43 \times 10^{-4}$
$\psi^{L}_{Na,Mg,Cl}$/kg^2·mol^{-2}·K^{-1}	$4.166\ 92 \times 10^{-5}$	$\psi^{L}_{MgCl,Na,Cl}$/kg^2·mol^{-2}·K^{-1}	$4.987\ 70 \times 10^{-4}$
α_1/kg$^{1/2}$·mol$^{-1/2}$	2.0	α_1/kg$^{1/2}$·mol$^{-1/2}$	3.5
α_2/kg$^{1/2}$·mol$^{-1/2}$	12.0		

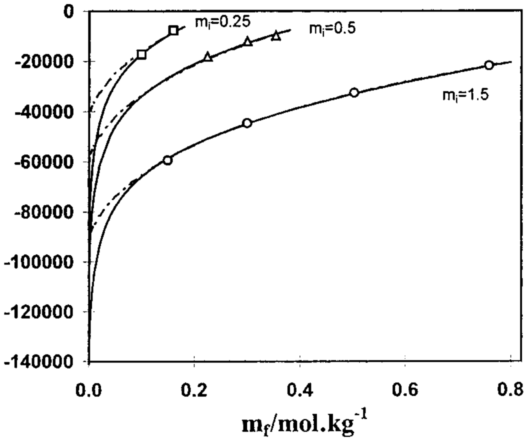

Figure 5. Experimental (symbols) and calculated (curves) heat of dilution of MgCl$_2$(aq) at 573.15 K. Solid and dashed curves are based on formulations I and II, respectively.

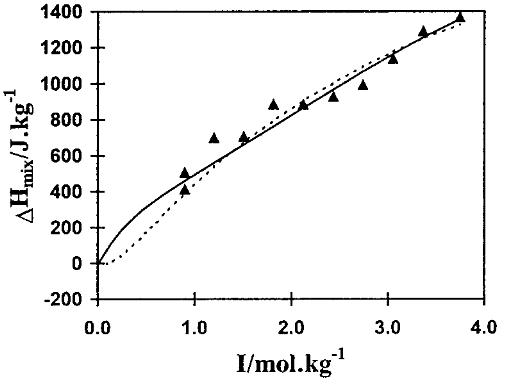

Figure 6. Experimental (symbols) and calculated (curves) heat of mixing of MgCl$_2$(aq) with NaCl(aq) at 573.15 K. Solid and dashed curves are based on formulations I and II, respectively. The ionic strength I is based on the complete dissociation of MgCl$_2$ to Mg^{2+} and $2Cl^-$.

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 treatment appear to arise from the Debye–Huckel term in eq A1, which yields negative values in the whole concentration range of our study but is absent in the eq 13 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 cannot give a clear confirmation of the ΔH_{mix} values in the dilute region.

Heats of dilution for MgCl$_2$(aq) at temperatures from 523 to 598 K were measured by Gillespie *et al.* (1992). Their measurements were at 10.3 MPa for 523 K and at 11.0 MPa for 573 K. Pressure effects on the heat of dilution were estimated using the volumetric data for MgCl$_2$(aq) reported by Pepinov *et al.* (1992). In the concentration range of our experiments, enthalpies of dilution of MgCl$_2$(aq) at 10 MPa are estimated to be 10% more negative than those at 20 MPa at 523 K, and this difference increases somewhat at 573 K. With these pressure corrections being accounted for, there is a systematic difference of about 10–15% between our data and those of Gillespie *et al.* at 523 and 573 K, with our values being more negative. A similar difference in the heat of dilution of CaCl$_2$(aq) was shown by Holmes *et al.* (1994) between values calculated from their model and from the experimental results of these authors at 523.15 K. Part of these differences may arise due to the addition of a small amount of hydrochloric acid in the chloride solutions in the measurements by Gillespie *et al.*

Discussion

It is interesting to note that the heat of mixing at each ionic strength reaches a minimum value in the temperature range of this study (Figure 7). Equation 13 for the heat of mixing can be rewritten as

$$\Delta H_{mix} = \Delta H_{PE} + \Delta H_{Cl} \tag{20}$$

where

$$\Delta H_{PE} = y(1-y)RT^2I^2\left[\frac{2}{3}B^{L}_{MX} - \frac{2}{9}B^{L}_{NX} + \frac{2}{9}(6-y)IC^{L}_{MX} - \frac{2}{27}(5-y)IC^{L}_{NX}\right] \tag{21}$$

$$\Delta H_{CI} = y(1-y)RT^2I^2\left[-\frac{2}{3}{}^{E}\theta^{L}_{MN} - \frac{2}{3}{}^{S}\theta^{L}_{MN} - \frac{1}{9}(3-y)I\psi^{L}_{MNX}\right] \tag{22}$$

with ΔH_{PE} and ΔH_{CI} being the contributions to the heat of mixing from (1) the two salts as *pure electrolytes* at constant ionic strength due to binary MX and NX interactions and (2) from the MN and MNX *cation interactions*, respectively. Variations of these two quantities with temperature at different ionic strengths are shown in Figure 8. At 298 K, the heat of mixing is primarily contributed by the pure electrolyte terms in eq 21; only a minor contribution to the heat of mixing is from the cation interaction terms in eq 22. At this temperature, the heat of mixing of the two electrolytes can be approximated using only the properties of pure electrolytes. As temperature increases, the pure electrolyte term ΔH_{PE} decreases, while ΔH_{CI} does not change appreciably with temperature at $T < 373$ K. It has been found that the term in eq 22 involving the electrostatic

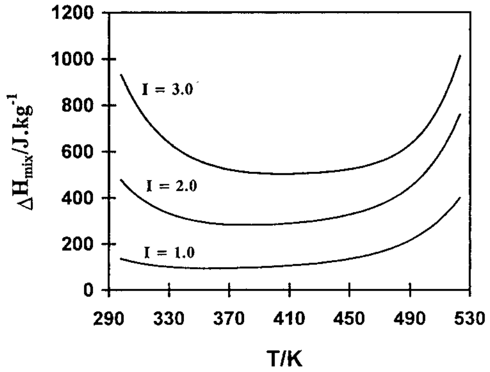

Figure 7. Heat of mixing for $MgCl_2$(aq) with NaCl(aq) at various ionic strengths as a function of temperature. The unit for the ionic strength I is mol·kg^{-1}.

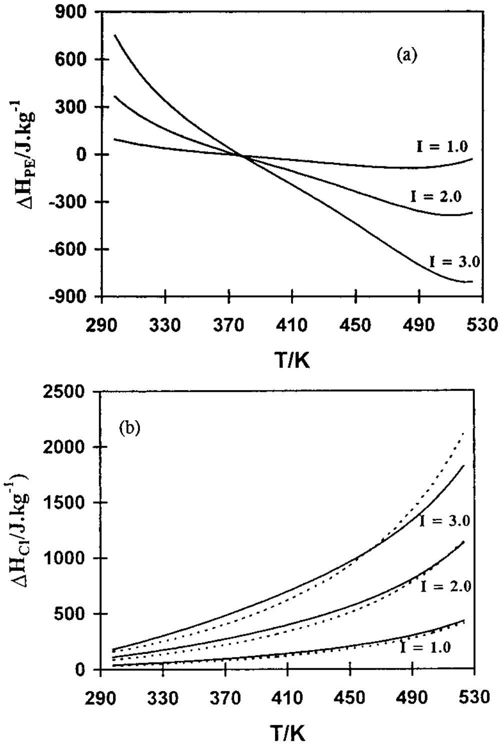

Figure 8. Contributions to the heat of mixing, ΔH_{mix}, from (a) ΔH_{PE} and (b) ΔH_{Cl} (see text). Dashed lines in (b) are calculated from the electrostatic unsymmetrical mixing term, $-^2/_3y(1-y)RT^2I^2\,{}^E\theta^L_{MN}$. The unit for the ionic strength I is mol·kg^{-1}.

unsymmetrical mixing parameter, ${}^E\theta^L_{MN}$, makes the greatest contribution to ΔH_{Cl} among the other two terms in the equation in our model (Figure 8b). This electrostatic term (${}^E\theta^L_{MN}$) varies inversely with the dielectric constant (permittivity) of water and its temperature derivatives (Pitzer, 1975, 1983). In the temperature range $T < 373$ K, ΔH_{Cl} remains relatively small, and the change of ΔH_{mix} is dominated by the change in ΔH_{PE}. Decreased ΔH_{mix} values are observed with increasing temperature. At temperatures above 373 K, ΔH_{Cl} increases rapidly while ΔH_{PE} decreases with increasing temperature. The rapid increases of ΔH_{Cl} with temperature at $T > 373$ K can be ascribed to the sharp changes in the properties of water as noted above. The heat of mixing ΔH_{mix} is dominated by the change in ΔH_{Cl} at higher temperatures where increases in the heat of mixing are observed.

Osmotic coefficients and the mean activity coefficients of NaCl and $MgCl_2$ in the mixtures were calculated at various temperatures at $y = 0.5$ using our model and are shown in Figures 9 and 10. The calculated activity coefficients of NaCl for ionic strengths 0.5–3.0 mol·kg^{-1} were compared with those reported by Rao and Ananthaswamy (1989) and Tishchenko (1991) from 298 to 318 K. The agreement is better than 0.5% in most cases with a maximum deviation of 2.4%. De Lima and Pitzer (1983) have calculated the mean activity coefficients of NaCl in the saturated aqueous mixtures of NaCl(aq) and $MgCl_2$(aq) to 473 K. The mixing parameters, $\theta_{Na,Mg}$ and $\psi_{Na,Mg,Cl}$, were assumed to be equal to zero in their calculations. Thus

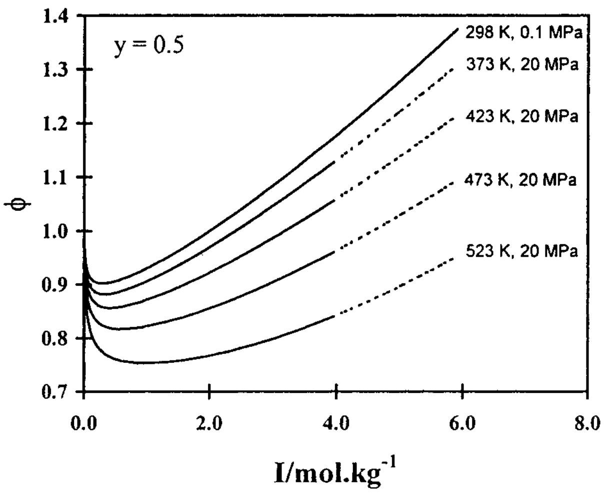

Figure 9. Osmotic coefficients of the aqueous mixtures NaCl + $MgCl_2$ at various temperatures at $y = 0.5$ as a function of ionic strength.

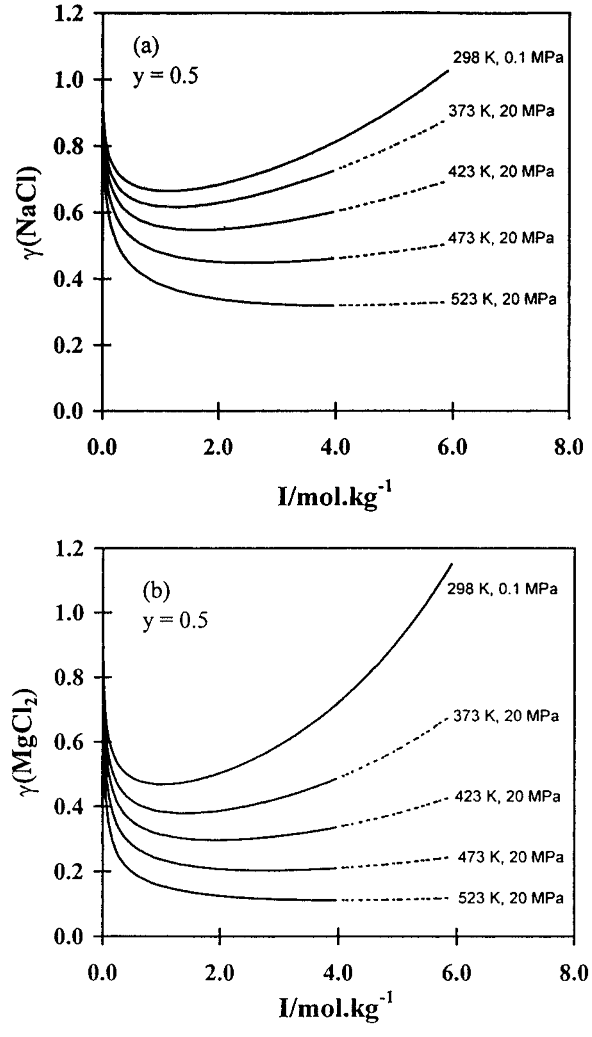

Figure 10. Mean activity coefficients of (a) NaCl (b) $MgCl_2$ in the mixtures at various temperatures at $y = 0.5$ as a function of ionic strength.

the calculated activity coefficients were only from the contribution of the two salts as pure electrolytes. Calculations using our model of the mean activity coefficients of NaCl(aq), $\gamma_{\pm,\mathrm{NaCl}}$, in the mixtures of the concentration range within our experimental measurements indicate that if the mixing terms are ignored the $\gamma_{\pm,\mathrm{NaCl}}$ value is larger by several percent than if these terms are included. This difference increases with temperature and with increasing the ionic strength fraction of $MgCl_2$. Inclusion of the mixing parameters, $\theta_{\mathrm{Na,Mg}}$ and $\psi_{\mathrm{Na,Mg,Cl}}$, in our model certainly gives a better prediction of the thermodynamic properties for the ternary mixtures. The present results will provide parameters not only for the binary and ternary mixtures but also for more complex mixtures. The calculation can also be extended to the solubility limit when new experimental data become available.

Acknowledgment

We thank Dr. H. F. Holmes and Dr. J. M. Simonson for making available the Holmes and Mesmer equation while in press, and for valuable comments.

Appendix

For the mixing solutions of NaCl(aq) with $MgCl_2$(aq), the latter being a 1−1 electrolyte dissociated only to $MgCl^+$ and Cl^- (formulation II), the heat of mixing per kilogram of water can be expressed as

$$\begin{aligned}\Delta H_{\mathrm{mix}} = \frac{A_{\mathrm{H}}}{b}[I_{\mathrm{m}} \ln(1 + b\sqrt{I_{\mathrm{m}}}) - (1 - y)I^0_{\mathrm{NaCl}} \ln(1 + \\ b\sqrt{I^0_{\mathrm{NaCl}}}) - yI^0_{\mathrm{MgCl_2}} \ln(1 + b\sqrt{I^0_{\mathrm{MgCl_2}}})] - \\ RT^2\{[2m_{\mathrm{NaCl}}(m_{\mathrm{NaCl}} + m_{\mathrm{MgCl_2}}) - 2(1 - \\ y)(m^0_{\mathrm{NaCl}})^2]\beta^{(0)\mathrm{L}}_{\mathrm{Na,Cl}} + [2m_{\mathrm{NaCl}}(m_{\mathrm{NaCl}} + m_{\mathrm{MgCl_2}})g(\alpha\sqrt{I_{\mathrm{m}}}) - \\ 2(1 - y)(m^0_{\mathrm{NaCl}})^2 g(\alpha\sqrt{I^0_{\mathrm{NaCl}}})]\beta^{(1)\mathrm{L}}_{\mathrm{Na,Cl}} + [2m_{\mathrm{NaCl}}(m_{\mathrm{NaCl}} + \\ m_{\mathrm{MgCl_2}})^2 - 2(1 - y)(m^0_{\mathrm{NaCl}})^3]C^{(0)\mathrm{L}}_{\mathrm{Na,Cl}} + [2m_{\mathrm{NaCl}}(m_{\mathrm{NaCl}} + \\ m_{\mathrm{MgCl_2}})^2 h(\alpha_{\mathrm{c}}\sqrt{I_{\mathrm{m}}}) - 2(1 - y) \times \\ (m^0_{\mathrm{NaCl}})^3 h(\alpha_{\mathrm{c}}\sqrt{I^0_{\mathrm{NaCl}}})]C^{(1)\mathrm{L}}_{\mathrm{Na,Cl}} + [2m_{\mathrm{MgCl_2}}(m_{\mathrm{NaCl}} + m_{\mathrm{MgCl_2}}) - \\ 2y(m^0_{\mathrm{MgCl_2}})^2]\beta^{(0)\mathrm{L}}_{\mathrm{MgCl,Cl}} + [2m_{\mathrm{MgCl_2}}(m_{\mathrm{NaCl}} + \\ m_{\mathrm{MgCl_2}})g(\alpha_1\sqrt{I_{\mathrm{m}}}) - 2y(m^0_{\mathrm{MgCl_2}})^2 g(\alpha_1\sqrt{I^0_{\mathrm{MgCl_2}}})]\beta^{(1)\mathrm{L}}_{\mathrm{MgCl,Cl}} + \\ [2m_{\mathrm{MgCl_2}}(m_{\mathrm{NaCl}} + m_{\mathrm{MgCl_2}})^2 - 2y(m^0_{\mathrm{MgCl_2}})^3]C^{(0)\mathrm{L}}_{\mathrm{MgCl,Cl}} + \\ m_{\mathrm{NaCl}}m_{\mathrm{MgCl_2}}\,{}^{\mathrm{S}}\theta^{\mathrm{L}}_{\mathrm{MgCl,Na}} + m_{\mathrm{NaCl}}m_{\mathrm{MgCl_2}}(m_{\mathrm{NaCl}} + \\ m_{\mathrm{MgCl_2}})\psi^{\mathrm{L}}_{\mathrm{MgCl,Na,Cl}}/2\} \quad \text{(A1)}\end{aligned}$$

where $m_{\mathrm{MgCl_2}}$ and m_{NaCl} are the molalities of $MgCl_2$(aq) and NaCl(aq) in the mixture, $m^0_{\mathrm{MgCl_2}}$ and m^0_{NaCl} are the initial molalities of $MgCl_2$(aq) and NaCl(aq) solutions; I_{m} is the ionic strength of the mixture, I^0_{NaCl} and $I^0_{\mathrm{MgCl_2}}$ are the initial ionic strengths of the NaCl(aq) and $MgCl_2$(aq) solutions, and y is the ionic strength fraction of the $MgCl_2$(aq) assuming complete dissociation of $MgCl_2$:

$$I_{\mathrm{m}} = m_{\mathrm{NaCl}} + m_{\mathrm{MgCl_2}}; \quad I^0_{\mathrm{NaCl}} = m^0_{\mathrm{NaCl}}; \quad I^0_{\mathrm{MgCl_2}} = m^0_{\mathrm{MgCl_2}} \quad \text{(A2)}$$

$$g(x) = 2[1 - (1 + x)\exp(-x)]/x^2 \quad \text{(A3)}$$

$$h(x) = 4[6 - (6 + 6x + 3x^2 + x^3)\exp(-x)]/x^4 \quad \text{(A4)}$$

$\alpha = 2.0$, $\alpha_{\mathrm{c}} = 2.5$, $\alpha_1 = 3.5$, and $b = 1.2$. The ion-interaction parameters for NaCl, $\beta^{(0)\mathrm{L}}_{\mathrm{Na,Cl}}$, $\beta^{(1)\mathrm{L}}_{\mathrm{Na,Cl}}$, $C^{(0)\mathrm{L}}_{\mathrm{Na,Cl}}$, and $C^{(1)\mathrm{L}}_{\mathrm{Na,Cl}}$, were calculated from Archer's equation. For the assumed 1−1 electrolyte, $\{MgCl^+, Cl^-\}$, when mixing with another 1−1 electrolyte, NaCl, the higher order unsymmetrical mixing term ${}^{\mathrm{E}}\theta^{\mathrm{L}}$ disappears in the equation. Parameters for $MgCl_2$, $\beta^{(0)\mathrm{L}}_{\mathrm{MgCl,Cl}}$, $\beta^{(1)\mathrm{L}}_{\mathrm{MgCl,Cl}}$, and $C^{(0)\mathrm{L}}_{\mathrm{MgCl,Cl}}$, and for the mixing, ${}^{\mathrm{S}}\theta^{\mathrm{L}}_{\mathrm{MgCl,Na}}$, and $\psi^{\mathrm{L}}_{\mathrm{MgCl,Na,Cl}}$, were obtained by a simultaneous fit of the heat of mixing data to eq A1 and the heat of dilution data to eqs A5 and 14.

$$\begin{aligned}L_\phi = \frac{A_{\mathrm{H}}}{b}\ln(1 + b\sqrt{I}) - 2RT^2[m(\beta^{(0)\mathrm{L}}_{\mathrm{MgCl,Cl}} + \\ \beta^{(1)\mathrm{L}}_{\mathrm{MgCl,Cl}} g(\alpha_1\sqrt{I})) + m^2 C^{(0)\mathrm{L}}_{\mathrm{MgCl,Cl}}] \quad \text{(A5)}\end{aligned}$$

$$\Delta H_{\mathrm{dil}} = L_\phi(m_{\mathrm{f}}) - L_\phi(m_{\mathrm{i}}) \quad (14)$$

where ΔH_{dil} is the molar enthalpy of dilution of the electrolyte solution and L_ϕ is the apparent molar enthalpy at initial and final molalities m_{i} and m_{f}, respectively. Equation A5 was derived from eq 7 for a 1−1 electrolyte $\{MgCl^+, Cl^-\}$. To limit the number of parameters, no $\beta^{(2)}$ has been introduced in the calculation. Alternate values for α_1 were tested. The best fit was obtained with the α_1 value of 3.5, and this value was adopted. Ion-interaction parameters obtained from calculations on the basis of the complete association of Mg^{2+} with Cl^- to $MgCl^+$ (formulation II) are listed in Table 4, together with those obtained on the basis of formulation I with complete dissociation of $MgCl_2$ to Mg^{2+} and Cl^-. The parameter $C^{(0)\mathrm{L}}_{\mathrm{MgCl,Cl}}$, was set to be zero in the fit.

Comparison of the experimental and the calculated heat of mixing and heat of dilution at 573 K (Figures 5 and 6) showed that the two treatments fit the experimental data about equally good with formulation II having two fewer adjustable parameters. A clear choice between the two treatments at 573 K cannot be given from the present data base.

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