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Experimental Sound Speeds and Derived Compressibilities of the KCl (1) + $CaCl_2$ (2) + Water (3) and KCl (1) + $MgCl_2$ (2) + Water (3) Systems up to an Ionic Strength of 4 mol kg^{-1} at 298.15 K

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The experimental sound velocities of mixtures composed of KCl + $CaCl_2$ + water and KCl + $MgCl_2$ + water are reported at 298.15 K at several ionic strengths in the full mixture composition range. These sound velocities, in conjunction with the earlier published densities, have been employed to estimate the mean apparent molal compressibilities of the mixtures. These mean apparent molal compressibilities of the mixtures have been analyzed by the Pitzer equations without and with binary interaction parameters. The calculated properties with the help of binary interaction parameters show good agreement with those obtained from the experiments. The excess compressibilities examined in light of the Friedman equation have been correlated with excess volumes and enthalpies.

Introduction

Though the experimental volume data on aqueous mixed electrolyte systems have been collected (Kumar et al., 1982; Kumar and Atkinson, 1983; Kumar, 1988; Kumar, 1989a; Kumar, 1989b) with a view to analyze the specific interaction theory of Pitzer (1973), compressibility data for the concentrated mixtures are scarce in the literature. As a part of our research plan we had published the densities and resultant molal volumes for the aqueous KCl + $CaCl_2$ and KCl + $MgCl_2$ systems up to an ionic strength of 4.5 mol kg^{-1} (Kumar, 1986; Kumar, 1989a). The volumetric Pitzer equations were tested for aqueous KCl + $CaCl_2$ mixtures with excellent accuracy. The volumetric data for aqueous KCl + $MgCl_2$, however, were analyzed in light of Young's rule (Young, 1951), and the deviations in volumes from ideal mixing were treated by the Cluster expansion theory of Friedman (Friedman, 1962). To gain a complete picture of the volumetric behavior, we now present the sound speeds *U* for the systems composed of KCl (1) + $CaCl_2$ (2) + water (3) and KCl (1) + $MgCl_2$ (2) + water (3) at 298.15 K in the concentration range extending up to 4 mol kg^{-1}. The estimated mean apparent molal compressibilities and excess properties are treated with the Pitzer equations (Pitzer, 1973; Kumar and Atkinson, 1983).

Experimental Section

KCl and $CaCl_2$ (A. R. grade Loba Chemicals) were used without further purification. $MgCl_2$ (Loba Chemicals) was recrystallized from its solution in water. Concentrations of solutions were determined volumetrically using silver nitrate. The molar concentrations were converted into molal using the densities of the solutions (Gucker et al., 1975; Millero, 1982; Kumar et al., 1982). The sound speeds were measured with an ultrasonic interferometer (Mittal enterprises) with an accuracy of 0.05%. The interferometer was calibrated against the sound speed of the aqueous sodium chloride solution at 298.15 K (Millero et al., 1982). The precision of the measurements is 0.02%. The temperature was kept constant to ±0.01 K using a constant-temperature bath (Julabo). The concentrations are accurate to $\pm 2 \times 10^{-4}$ mol·kg^{-1}.

Results and Discussion

Increments in the sound speeds of the mixtures over that of pure water ΔU ($\Delta U = U - U_0$; U and U_0 are the sound speeds of the solution and pure water, respectively) are listed in Table 1 together with the molalities of the salts m_J. The ionic strength of the mixture I is given by $I = 0.5\sum m_i Z_i^2$, Z being the ionic charge. The ionic strength fraction y_2 of component 2 is defined by $y_2 = 3m_2/(m_1 + 3m_2)$, where 1 and 2 refer to KCl and $CaCl_2$ or $MgCl_2$, respectively.

The *U* values for both the systems were fitted to an equation of the form

$$U = (q_{11} + q_{12}I + q_{13}I^2) + (q_{21} + q_{22}I + q_{23}I^2)y_2 + (q_{31} + q_{32}I + q_{33}I^2)y_2^2 \quad (1)$$

The adjustable parameters q_{ij} together with the uncertainties of the above equation are listed in Table 2. For the purpose of illustration we show in Figure 1 the variation in ΔU with y_2 at different ionic strengths for the KCl + $CaCl_2$ + water and KCl + $MgCl_2$ + water systems. An examination of Figure 1 shows a monotonic change in ΔU with respect to y_2 and ionic strength.

In the literature are reported the sound speeds of pure aqueous KCl, $CaCl_2$, and $MgCl_2$ at 298.15 K. The experimental ΔU values obtained in the current investigation when appropriately interpolated agree well (average agreement of 0.045% in *U* computed for pure components) with the literature values (Gucker et al., 1975; Kumar et al., 1982; Millero et al., 1982). In the case of the densities, our results at reported concentrations are in good agreement (0.61%) with those reported by Saluja et al. (1995).

The ΔU values when combined with the densities ρ of the solutions can yield adiabatic compressibilities β of the mixture by $\beta = U^{-2}\rho^{-1}$. The densities of these mixtures

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Table 1. Increments in Sound Velocities ΔU, Ionic Strengths, and Molalities m_1 and m_2 for the KCl + $CaCl_2$ + Water and KCl + $MgCl_2$ + Water Systems at 298.15 K

m_1/(mol kg^{-1})	m_2/(mol kg^{-1})	I/(mol kg^{-1})	ΔU/(m s^{-1})	m_1/(mol kg^{-1})	m_2/(mol kg^{-1})	I/(mol kg^{-1})	ΔU/(m s^{-1})
			KCl + $CaCl_2$ + Water				
0.0000	0.2596	0.7788	25.5	0.0000	0.9930	2.9790	82.9
0.1997	0.2074	0.8219	21.7	0.6143	0.7910	2.9874	89.3
0.4016	0.1554	0.8678	24.1	1.2515	0.5908	3.0239	100.6
0.6059	0.1035	0.9164	29.7	1.9137	0.3923	3.0905	109.5
0.8127	0.0517	0.9678	34.0	2.6036	0.1954	3.1897	120.6
1.0221	0.0000	1.0221	50.5	3.3239	0.0000	3.3239	141.6
0.0000	0.6133	1.8399	53.2	0.0000	1.4188	4.2564	116.3
0.3915	0.4894	1.8597	58.5	0.7739	1.1280	4.1580	119.3
0.7920	0.3661	1.8904	64.1	1.5845	0.8408	4.1070	126.5
1.2022	0.2436	1.9329	72.9	2.4364	0.5573	4.1083	140.6
1.6226	0.1215	1.9870	79.3	3.3353	0.2771	4.1666	154.0
2.0538	0.0000	2.0538	94.3	4.2875	0.0000	4.2875	172.3
			KCl + $MgCl_2$ + Water				
0.0000	0.3598	1.0795	40.3	0.0000	1.2238	3.6714	126.3
0.2037	0.2874	1.0660	31.3	0.6142	0.9729	3.5329	103.3
0.4098	0.2152	1.0555	35.3	1.2512	0.7254	3.4274	119.3
0.5138	0.1793	1.0516	39.3	1.5790	0.6028	3.3875	129.3
0.6184	0.1434	1.0485	43.3	1.9133	0.4810	3.3563	139.3
0.8295	0.0716	1.0442	47.3	2.6030	0.2393	3.3209	143.3
1.0433	0.0000	1.0433	51.3	3.3232	0.0000	3.3232	141.6
0.0000	0.7357	2.2069	79.2	0.0000	1.4251	4.2754	145.3
0.4057	0.5866	2.1655	71.3	0.8086	1.1314	4.2029	131.3
0.8211	0.4385	2.1367	75.3	1.6576	0.8426	4.1854	140.3
1.0327	0.3649	2.1275	81.3	2.0987	0.6999	4.1983	147.3
1.2469	0.2915	2.1213	85.3	2.5520	0.5581	4.2262	151.3
1.6838	0.1453	2.1196	87.3	3.4986	0.2774	4.3308	161.3
2.1325	0.0000	2.1325	97.8	4.5443	0.0000	4.5443	178.7

Table 2. Values of Adjustable Parameters in Eq 1 for KCl + $CaCl_2$ + Water and KCl + $MgCl_2$ + Water

parameter	KCl + $CaCl_2$ + water	KCl + $MgCl_2$ + water
q_{11}/(m s^{-1})	1497	1497
q_{12}/(m s^{-1} mol^{-1} kg)	57.5 ± 1.6	51.4 ± 3.5
q_{13}/(m s^{-1} mol^{-2} kg^2)	−3.9 ± 0.4	−2.2 ± 0.9
q_{21}/(m s^{-1})	−84.3 ± 7.9	−87.4 ± 10.3
q_{22}/(m s^{-1} mol^{-1} kg)	7.3 ± 7.3	54.9 ± 9.0
q_{23}/(m s^{-1} mol^{-2} kg^2)	−2.8 ± 1.4	−12.9 ± 1.7
q_{31}/(m s^{-1})	84.3 ± 5.0	70.4 ± 7.3
q_{32}/(m s^{-1} mol^{-1} kg)	−36.88 ± 4.65	−51.6 ± 6.4
q_{33}/(m s^{-1} mol^{-2} kg^2)	6.58 ± 0.90	11.1 ± 1.2

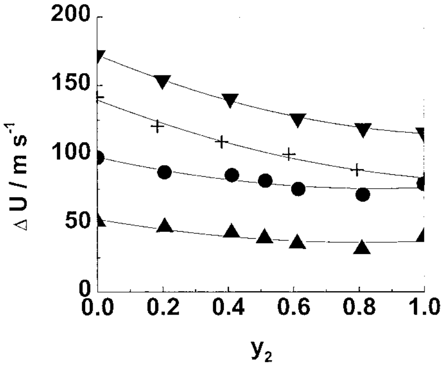

Figure 1. Plots of ΔU versus y_2 at 298.15 K: KCl + $CaCl_2$ + water at I = 3 (+) and I = 4 (▼) and KCl + $MgCl_2$ + water at I = 1 (▲) and I = 2 (●).

were taken from our earlier work (Kumar, 1986, 1989b) at the desired y_2 using the appropriate interpolation function.

The mean apparent molal compressibilities of mixtures ϕ_k^* were then calculated by

$$\phi_k^* = [1000(\rho_0\beta - \rho\beta_0)/(\rho_0\rho\sum_J m_J) + (\beta\sum_J M_J m_J/\rho\sum_J m_J)] \qquad (2)$$

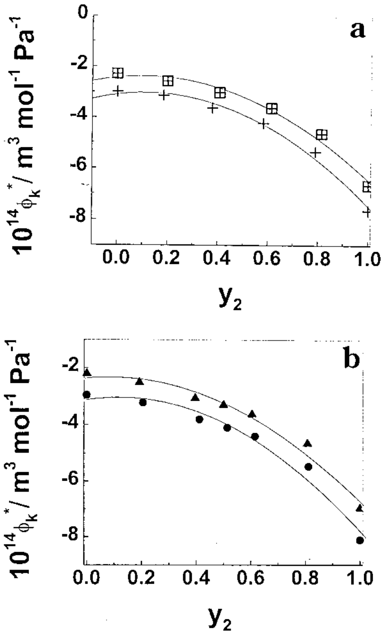

Figure 2. Plot of variations of $\phi_k{}^*{}_{exp}$ with y_2 at different ionic strengths: (a) KCl + $CaCl_2$ + water at I = 3 (+) and I = 4 (⊞); (b) KCl + $MgCl_2$ + water at I = 3 (●) and I = 4 (▲).

where β_0 and ρ_0 are the adiabatic compressibility and density, respectively, of pure water at 298.15 K. The values of U_0 (1496.69 m s^{-1}) and ρ_0 (997.046 kg m^{-3}) and β_0 were taken from the report of Millero et al. (1982). The molar mass of the Jth salt is denoted by M_J.

In Figure 2 we plot the variations of ϕ_k^* against y_2 and I for KCl + $CaCl_2$ + water and KCl + $MgCl_2$ + water, respectively. The ϕ_k^* in these mixtures can be analyzed using the Pitzer equations, in which the interactions between cation and anion can be coupled with those between ions with like charges. The Pitzer equations employ three parameters for describing the short-range interaction forces, while the long-range interaction forces are calculated from the modified Debye–Huckel expression. Since all three pure salts have been analyzed in the past for their compressibilities, we do not herein elaborate on the pure salt fitting. Using our earlier work (Kumar and Atkinson, 1983), it is convenient to write an expression describing the apparent molal compressibility of the ion ϕ_{ki} in the mixture by

$$\phi_{ki} = \phi_{ki}^{\circ} + Zi^2 A_k \ln(1 + bI^{1/2})/2b + RT\sum_j B_{ij} m_j + RT\sum_j C_{ij} m_j^{2} |Z_j|^{1/2}/2|Z_i|^{1/2} \tag{3}$$

with

$$B_{ij} = (\partial^2\beta^{(0)}/\partial P^2)_T + (\partial^2\beta^{(1)}/\partial P^2)_T(2/\alpha^2 I) \times [1 - (1 + \alpha I^{1/2})] \exp(-\alpha I^{1/2}) \tag{4}$$

$$C_{ij} = (\partial^2 c^{\varphi}/\partial P^2)_T/2 \tag{5}$$

where $(\partial^2\beta^{(0)}/\partial P^2)_T$, $(\partial^2\beta^{(1)}/\partial P^2)_T$, and $(\partial^2 c^{\varphi}/\partial P^2)_T$, the second pressure derivatives, are the adjustable parameters of the pure electrolytes (Kumar and Atkinson, 1983). α and b are set to 2.0 (kg mol^{-1})$^{1/2}$ and 1.2 (kg mol^{-1})$^{1/2}$, respectively. A_k is the Pitzer Debye–Huckel limiting slope (Anathaswamy and Atkinson, 1984).

The parameters $(\partial^2\beta^{(0)}/\partial P^2)_T$, $(\partial^2\beta^{(1)}/\partial P^2)_T$, and $(\partial^2 c^{\varphi}/\partial P^2)_T$ are derived from the isothermal ϕ_k versus m fits. The ϕ_{ki} values with appropriate stoichiometric combinations give rise to the calculated mean apparent molal compressibilities of the mixture $\phi_k{}^*{}_{+-}$. The $\phi_k{}^*{}_{+-}$ values are calculated from the interactions between ions of opposite charges. In addition to the interactions between opposite charges, the interactions between ions with like charges, namely K^+ and Ca^{2+}, and K^+ and Mg^{2+}, can be described by a binary mixing parameter, θ_{++}. The θ_{++} parameter is calculated from the differences of $\phi_k{}^*{}_{\mathrm{exp}}$ and $\phi_k{}^*{}_{+-}$. The relevant equations for obtaining the apparent molal compressibility of the Jth salt in the mixture are

$$\phi_{kJ} = \sum_J \upsilon_i \phi_{ki} \tag{6}$$

$$\phi_k{}^*{}_{\mathrm{cal}} = \sum_J m_J \phi_{kJ} / \sum_J m_J \tag{7}$$

In eq 6, ϕ_{ki} is calculated with θ_{++} by using the following expression:

$$\phi_{ki} = \text{R. H. S. of eq 3} + RT\sum_k \theta_{ik} m_k \tag{8}$$

In eqs 3 and 8 summations over j are over ions of opposite charge and summations over k are over ions of the same charge.

The θ_{++} values are calculated by

$$\theta_{++} = (\phi_k{}^*{}_{\mathrm{exp}} - \phi_k{}^*{}_{+-})(m_1 + m_2)/(2RTm_1 m_2) \tag{9}$$

Table 3. Adjustable Parameters $\phi_k{}^{\circ}$, $(\partial^2\beta^{(0)}/\partial P^2)_T$, $(\partial^2\beta^{(1)}/\partial P^2)_T$, $(\partial^2 c^{\varphi}/\partial P^2)_T$ for Pure Electrolytes Used in the Calculations for the KCl + $CaCl_2$ + Water and KCl + $MgCl_2$ + Water Systems at 298.15 K[a]

salt	$-10^{15}\phi_k{}^{\circ}$/ (m^3 mol^{-1} Pa^{-1})	10^{18}-$(\partial^2\beta^{(0)}/\partial P^2)_T$/ (m^3 mol^{-1} Pa^{-2})	10^{18}-$(\partial^2\beta^{(1)}/\partial P^2)_T$/ (m^3 mol^{-1} Pa^{-2})	10^{19}-$(\partial^2 c^{\varphi}/\partial P^2)_T$/ (m^3 mol^{-1} Pa^{-2})
KCl	35.63	1.7941	−3.2804	−3.208
$CaCl_2$	72.30	1.4813	15.0	1.0276
$MgCl_2$	96.30	5.8366	71.16	−19.71

[a] $A_k = -3.778 \times 10^{-15}$ m^3 kg$^{1/2}$ mol$^{-3/2}$ Pa^{-1}.

Table 4. Standard Deviations in ϕ_k* and *U* forKCl + $CaCl_2$ + Water and KCl + $MgCl_2$ + Water

	KCl + $CaCl_2$ + water		KCl + $MgCl_2$ + water	
	$\sigma_{+,-}$[a]	$\sigma_{\theta++}$[b]	$\sigma_{+,-}$[a]	$\sigma_{\theta++}$[b]
$10^{14}\phi_k$*/(m^3 mol^{-1} Pa^{-1})	0.30	0.04	9.72	0.028
U/(m s^{-1})	19.8	1.2	22.4	1.3

[a] Without θ_{++}. [b] With θ_{++}.

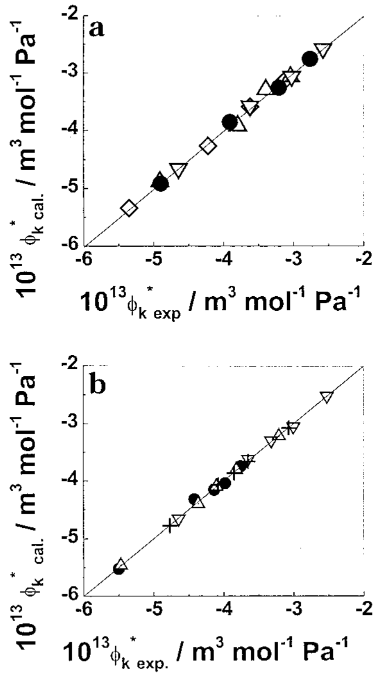

Figure 3. Plot of $\phi_k{}^*{}_{\mathrm{exp}}$ versus $\phi_k{}^*{}_{\mathrm{cal}}$: (a) KCl + $CaCl_2$ + water at 298.15 K at I = 1 (△), I = 2 (◇), I = 3 (●), and I = 4 (▽); (b) KCl + $MgCl_2$ + water at 298.15 K at I = 1 (●), I = 2 (△), I = 3 (+), and I = 4 (▽).

In Table 3 we list the values of adjustable parameters for the pure aqueous KCl, $CaCl_2$, and $MgCl_2$ solutions. The experimental U data were treated both without and with θ_{++}. It is important to note that the calculation of $\phi_k{}^*{}_{+-}$ via eqs 3–6 is essentially an application of Young's rule (Young, 1951), implying that no excess compressibilities exist, when two solutions of equal ionic strength are mixed. Considering the importance of mixing terms in volume properties, it is imperative to employ the same for the compressibilities too. In Table 4 are collected the standard deviations σ for ϕ_k* and U without and with the use of θ_{++}. An examination of Table 4 shows that the calculations of ϕ_k* are improved when the interactions between like charged ions are incorporated in the equations. A contrast of $\phi_k{}^*{}_{\mathrm{exp}}$ with $\phi_k{}^*{}_{\mathrm{cal}}$ is shown in Figure 3a at several concentrations. An examination of Figure 3a strongly emphasizes the necessity of the ionic interactions between like charged species. In the case of KCl + $CaCl_2$ + water, the predictions of ϕ_k* are drastically improved, indicating remarkable reduction of the standard deviation in the U values. A similar observation is noted in Figure 3b for the KCl + $MgCl_2$ + water system. The average standard deviation of 9.72 × 10^{-14} m^3 mol^{-1} Pa^{-1} in ϕ_k* is reduced to 0.028 × 10^{-14} m^3 mol^{-1} Pa^{-1} by the use of θ_{++}. In Figure 4 we opt to demonstrate the deviations ($\partial U = U_{\mathrm{exp}} - U_{\mathrm{cal}}$) in the sound velocities for KCl + $CaCl_2$ + water and KCl

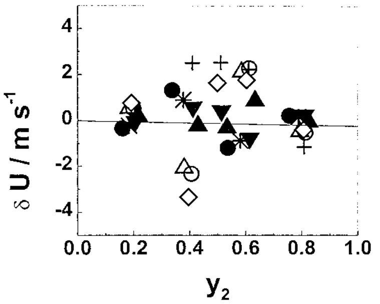

Figure 4. Differences in sound velocities $\delta U = U_{\exp} - U_{\mathrm{cal}}$ as a function of y_2: KCl + $CaCl_2$ + water at 298.15 K at $I = 1$ (●), $I = 2$ (∗), $I = 3$ (△), and $I = 4$ (○); KCl + $MgCl_2$ + water at 298.15 K at $I = 1$ (+), $I = 2$ (▼), $I = 3$ (▲), and $I = 4$ (◇).

Table 5. Values of Parameters for Eq 10 for Representing the Concentration Dependence of θ_{++}

I/(mol kg^{-1})	$10^8\theta_0$	$10^8\theta_1$	$10^9\theta_2$
	KCl + $CaCl_2$ + Water		
1	53.02	−109.8	979.0
2	8.02	−10.46	112.5
3	0.171	6.15	−3.81
4	−3.68	14.83	−71.3
	KCl + $MgCl_2$ + Water		
1	13.92	−17.22	6.87
2	6.46	−13.59	2.55
3	−3.94	9.44	0.152
4	−5.50	19.77	−1.37

+ $MgCl_2$ + water as a function of y_2 at different ionic strengths. The deviations are random throughout the compositions for both the systems, emphasizing the effective role of the mixing parameters.

Though the Pitzer theory suggests that the binary interaction parameter should be independent of salt concentrations, the experiences from this and other laboratories in the past have shown this to be variable (Kumar and Atkinson, 1983; Saluja et al., 1995). The ionic strength and the mixture composition dependence of θ_{++} can be represented by

$$\theta_{++} = \theta_0 + \theta_1 y_2 + \theta_2 {y_2}^2 \qquad (10)$$

Accordingly, the coefficients for calculating θ_{++} as a function of y_2 and I of both systems (obtained from the least-squares analysis) are recorded in Table 5. Though θ_{++} can be represented by a simple functional form, the numbers of adjustable parameters are quite large.

Friedman (1962) studied the interactions between ions having like charges for symmetric and asymmetric mixing using cluster expansion theory. His equation for describing the excess properties can be written for the excess compressibility of mixing Δk_{m} as

$$\Delta k_{\mathrm{m}} = y_1 y_2 I^2 [k_0 + (1 - 2y_2)k_1] \qquad (11)$$

where k_0 and k_1 indicate binary (K^+, Ca^{2+} and K^+, Mg^{2+}) and ternary (K^+, Ca^{2+}, Cl^- and K^+, Mg^{2+}, Cl^-) interactions, respectively. These values are reported in Table 6 for both the aqueous mixtures.

During the fitting of ϕ_k* by the Pitzer equations it was observed that the involvement of the θ_{++} interaction parameter could fulfill the fitting requirement. No ternary interaction parameters were therefore warranted in the present investigation. In the same way the physical significance of k_1 in the fitting may be noted. The Friedman (eq 11) was employed for the analysis of enthalpy data of aqueous electrolyte mixtures (Wood et al., 1969). The Friedman parameters for enthalpy, RTh_0 and RTh_1 are analogous to k_0 and k_1 in eq 11. It would be of interest to examine the correlations emerging out of volume, compressibility, and enthalpy data. For this purpose in Figure 5a are plotted v_0, k_0, and RTh_0 as a function of I for the KCl + $CaCl_2$ + water system at 298.15 K. Analogous plots for the aqueous KCl + $MgCl_2$ + water system are given in Figure 5b. The trend of variations of v_0, k_0, and RTh_0 confirms the unsymmetric charge mixing (as in the present case) in the limiting ionic concentration range toward infinity. This effect arises out of mixing of the univalent K^+ ion with a bivalent Ca^{2+} or Mg^{2+} species. The curvatures in the low ionic concentration range are the results of the high-order limiting law.

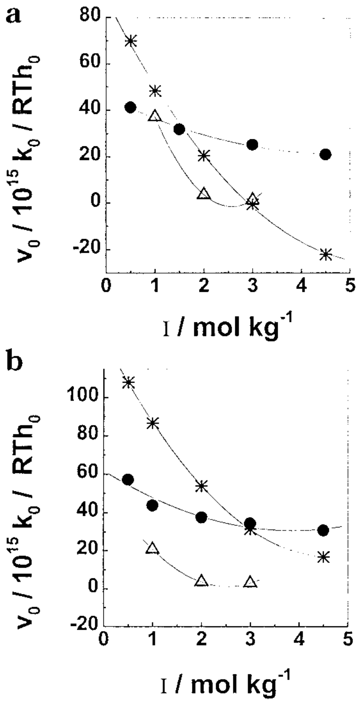

Figure 5. Friedman parameter for compressibility k_0 from eq 11 for (a) KCl + $CaCl_2$ + water and (b) KCl + $MgCl_2$ + water at 298.15 with the corresponding enthalpy RTh_0 and v_0 parameters; see text for details. v_0 (●); k_0 (△); RTh_0 (∗).

Table 6. Friedman Parameters for Eq 11

	KCl + $CaCl_2$ + Water		KCl + $MgCl_2$ + Water	
I/ (mol kg^{-1})	$10^{15}k_0$/ (m^3 mol^{-2} kg Pa^{-1})	$10^{15}k_1$/ (m^3 mol^{-2} kg Pa^{-1})	$10^{15}k_0$/ (m^3 mol^{-2} kg Pa^{-1})	$10^{15}k_1$/ (m^3 mol^{-2} kg Pa^{-1})
1	37.2	12.4	20.8	−21.0
2	3.6	2.0	3.6	−2.8
3	1.3	0.30	0.30	−0.64
$10^{15}\sigma$	3.34		1.64	

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