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The Partial Molal Volumes of Electrolytes in 0.725 m Sodium Chloride Solutions at 25 °C

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The apparent molal volumes of 29 electrolytes have been determined in the medium 0.725 m NaCl from precise density measurements at 25 °C. The values of ϕ_V have been extrapolated to infinite dilution by using a least-squares fit of the data and by using Young's rule. The two methods yield values of $\bar{V}^{*0}$ in 0.725 m NaCl that agree to within 0.2 cm³ mol⁻¹. The experimentally determined values of $\bar{V}^{*0}$ are compared to those predicted from binary solution data by using the ionic strength principle, Young's rule, and the specific interaction model. The values of $\bar{V}^{*0}$ predicted by using the specific interaction model and Young's rule are similar and in better agreement (±0.3 cm³ mol⁻¹) with the experimental results than those predicted by using the ionic strength principle (±0.4 cm³ mol⁻¹). For electrolytes without a common cation (Na⁺) or anion (Cl⁻), the specific interaction model gives the best estimates. The volumes of mixing the electrolytes with a common cation (NaX + NaCl) and anion (MCl + NaCl) at I = 0.725 determined from our results correlate very well with the enthalpies of mixing and various properties of the uncommon ion (M⁺ and X⁻).

Introduction

In recent years a number of workers have developed[1-5] and used[6-11] various ionic interaction models to estimate the activity coefficients of electrolytes in various ionic media (e.g., seawater). Progress has also been made in using these models to estimate the effect of pressure on the activity coefficients or the partial molal volumes of electrolytes in ionic media.[12-17] Owen and Brinkley[12] estimated the partial molal volumes ($\bar{V}$) of electrolytes in seawater by assuming the $\bar{V}$'s were equivalent to the values in binary solutions at the ionic strength of seawater (~0.725 m). They defined 0.725 m NaCl as being equivalent to "sea salt" and estimated the $\bar{V}$ of electrolytes in sea salt from the measurements of Wirth.[18] In recent years, we have examined the $\bar{V}$'s of electrolytes in 0.725 m NaCl[13-15] and seawater,[13-15] by using a simple hydration model.[13] We have interpreted the deviations from this model in terms of ion pairing.[13-15] Lee[19] has measured the $\bar{V}$'s of electrolytes in NaCl solutions and also showed how Young's rule[23,24] could be used to estimate the partial molal volumes. Leyendekkers[17] has recently used these methods to estimate the partial molal volumes of electrolytes in seawater. In a recent paper, we have used the specific interaction model[16] to estimate the $\bar{V}$ of electrolytes in NaCl and seawater solutions. At present it is difficult to state with certainty which of these methods gives the most reliable estimates for the partial molal volumes of electrolytes in an ionic media because of the paucity of reliable experimental data.

In the present paper we will present our experimental results for measurements of 29 electrolytes in 0.725 m NaCl. We will use these experimental results to examine the most reliable method that can be used to estimate the partial molal volumes of electrolytes in an ionic media.

Experimental Section

The density measurements were made with a vibrating densimeter that is described in detail elsewhere.[25] The densimeter measures the relative densities of aqueous solutions ($d - d^0$) to a precision of ±3 × 10⁻⁶ g cm⁻³.[25,26] The densimeter was calibrated by using ion-exchanged water and dry nitrogen. The reliability of the densimeter was checked by measuring the densities of standard

seawater solutions weight evaporated or diluted with water. The measured densities agree on the average to ±2 ppm[26] with the values calculated from the equation of state of seawater.[27]

The temperature of the densimeter is controlled to ±0.001 °C and set to ±0.005 °C with a platinum resistance thermometer (calibrated by the National Bureau of Standards on the 1968 IPTS temperature scale) and a G-2 Mueller bridge.

All of the salts used were Baker reagent grade. The salts that did not decompose were heated in vacuo at 110 °C for at least 1 h. Stock solutions of these salts (KBr, LiCl, RbCl, CsCl, NaI, KI, NaBr, KCl, NaNO₃, KNO₃, Na₂CO₃, K₂CO₃, Na₂SO₄, K₂SO₄, NaF, KHCO₃, NaHCO₃, NH₄Cl, and NH₄Br) were made by weight in 0.725 m NaCl. Approximately 1 m stock solutions of the electrolytes that could not be dried (HCl, NaOH, KOH, KF, MgCl₂, CaCl₂, SrCl₂, and BaCl₂) were made. The molalities of these solutions were determined by measuring the density (HCl, NaOH, KOH, MgSO₄, and KF) or by titrating with AgNO₃ (MgCl₂, CaCl₂, SrCl₂, and BaCl₂). The NaCl was added to these solutions to make them 0.725 m NaCl. Dilute solutions of the salt mixtures (salt and NaCl) were prepared by adding a weighted amount of 0.725 m NaCl.

Duplicate density measurements were made on most of the solutions. The two measurements agreed on the average to ±3.5 ppm which represents the precision of the measurements. The density of the NaCl medium for all of the experiments was 1.025810 ± 0.000002₅ g mL⁻¹. This density is equivalent to a molality of 0.72525 ± 0.00006 mol (kg of H₂O)⁻¹ as determined from the relationship 10³($d - d^0$) = 1.011 + 38.227 m (valid from 0.7 to 0.8 m). The combined error in density was ~6 ppm. This error is equivalent to an error of ±0.006 cm³ mol⁻¹ at 1.0 m and ±0.06 cm³ mol⁻¹ at 0.1 m in the apparent molal volumes of the electrolytes.

Results and Calculations

The densities at 25 °C for the various electrolytes (NaF, KF, HCl, LiCl, NaCl, KCl, RbCl, CsCl, NH₄Cl, MgCl₂, CaCl₂, SrCl₂, BaCl₂, NaBr, KBr, NH₄Br NaI, KI, NaOH, KOH, NaNO₃, KNO₃, NaHCO₃, KHCO₃, Na₂CO₃, K₂CO₃, Na₂SO₄, K₂SO₄, and MgSO₄) at various molalities (m_3) in
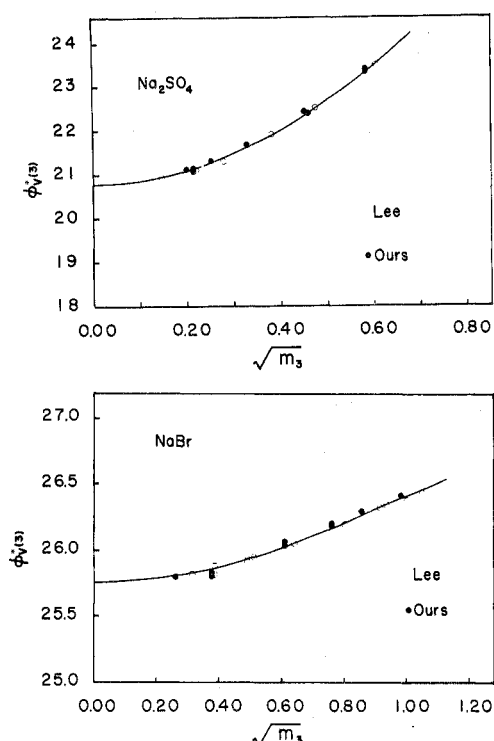
Figure 1. The apparent molal volumes of Na_2SO_4 and NaBr in 0.725 m NaCl at 25 °C plotted vs. the square root of molality.

0.725 m NaCl are given in Tables I–XXIX.[28] As with binary solutions, it is convenient to examine the volume properties of ternary electrolyte solutions in terms of the apparent molal volume (ϕ_V). If one of the electrolytes 3 is considered to be dissolving in a solvent of electrolyte 2 in water, one can define the apparent molal volume of 3 in this ionic medium by

$$\phi_V*(3) = [V_{soln} - V_{med}]/n_3 \qquad (1)$$

where V_{soln} and V_{med} are the volumes of the solution and medium, and n_3 is the number of moles of electrolyte 3. For a molal solution the volume of the solution and the medium are given by

$$V_{soln} = [1000 + m_2M_2 + m_3M_3]/d \qquad (2)$$

$$V_{med} = [1000 + m_2M_2]/d_2$$
$$= 1000/d_0 + m_2\phi_V(2) \qquad (3)$$

where m_i is the molality and M_i is the molecular weight of solute i, d is the measured density of the mixed solution, d_2 is the density of the medium, d_0 is the density of water,[29] and ϕ_V (2) is the apparent molal volume of the medium. Substituting eq 2 and 3 into eq 1 gives

$$\phi_V*(3) = \frac{1000(d_2 - d)}{dd_2m_3} + \frac{M_3}{d} + \frac{m_2M_2}{m_3d} - \frac{m_2M_2}{m_3d_2} \qquad (4)$$

The values of $\phi_V*(3)$ determined from eq 4 are given in Tables I–XXIX.[28] The variation of the $\phi_V*(3)$ vs. $m_3^{1/2}$ for a 1–1 electrolyte (NaBr), three 2–1 electrolytes (Na_2SO_4, $CaCl_2$, $MgCl_2$), and the 2–2 electrolyte $MgSO_4$ are shown in Figures 1 and 2 along with the results of Lee.[19] These values of $\phi_V*(3)$ have been fitted to the equation

$$\phi_V*(3) = \phi_V*^0(3) + Am_3^{1/2} + Bm_3 \qquad (5)$$

The values of the coefficients $\phi_V*^0(3) = \bar{V}_3*^0$, the infinite dilution partial molal volume, A and B determined by a weighted least-squares fit of the data are given in Table
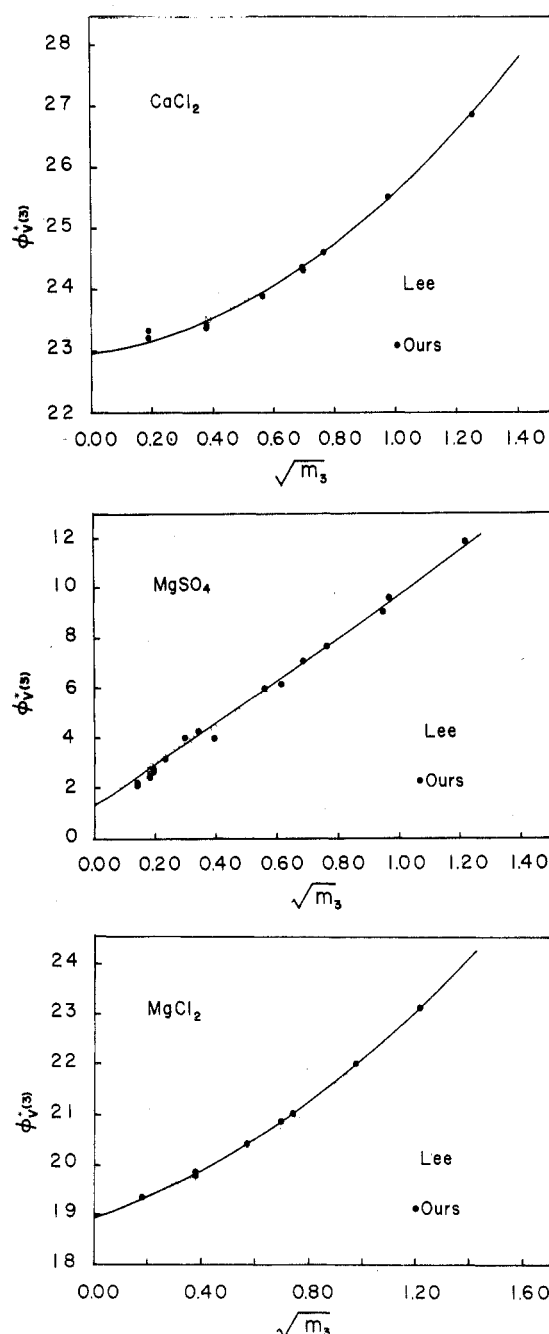
Figure 2. The apparent molal volumes of $CaCl_2$, $MgSO_4$, and $MgCl_2$ in 0.725 m NaCl at 25 °C plotted vs. the square root of molality.

XXX along with the standard deviations.

The partial molal volume of electrolyte 3 in the medium can be determined from

$$\bar{V}_3* = (\partial V_{soln}/\partial m_3) = \phi_V*(3)$$
$$+ m_3[\partial\phi_V*(3)/\partial m_3] \qquad (6)$$

The differentiation of eq 5 gives

$$\bar{V}* = \bar{V}_3*^0 + 1.5Am_3^{1/2} + 2Bm_3 \qquad (7)$$

where $\bar{V}_3*^0$ is the infinite dilution partial molal volume of electrolyte 3 in the medium. Although the $\phi_V*(3)$ data for the electrolytes studied can be fitted to eq 5 with standard deviations less than 0.1 cm^3 mol^{-1}, the errors in $\bar{V}_3*^0$ are slightly larger (as much as ±0.2 cm^3 mol^{-1} for 2–1 and 2–2 electrolytes). To test the extrapolation procedure, we have made volume measurements on solutions formed by adding weighted amounts of NaCl to 0.725 m NaCl. The ex-

TABLE XXX: Coefficients of Eq 5 for Various Electrolytes in 0.725 m NaCl at 25 °C[a]

Electrolyte	ϕ_V*^0	A	B	σ
NaF	0.303	−0.015	1.630	0.02
KF	10.612	0.336	0.883	0.01
HCl	19.606	0.028	0.198	0.01
LiCl	19.192	0.595	−0.178	0.02
NaCl	19.080	0.056	0.701	0.01
KCl	29.343	0.339	0.557	0.01
RbCl	34.654	0.608		0.04
CsCl	41.742	0.758		0.03
NH$_4$Cl	37.905	0.208	0.372	0.02
MgCl$_2$	18.942	1.754	1.408	0.03
CaCl$_2$	22.973	0.689	1.931	0.05
SrCl$_2$	23.169	1.967	1.593	0.03
BaCl$_2$	28.917	1.474	1.959	0.04
NaBr	25.620	0.521	0.299	0.03
KBr	36.165	0.208	0.526	0.03
NH$_4$Br	44.715	0.011	0.295	0.02
NaI	36.917	0.343	0.215	0.02
KI	47.424	0.625		0.03
NaOH	−2.417	0.647	1.178	0.04
KOH	7.896	0.796	0.860	0.04
NaNO$_3$	30.549	0.428	0.567	0.02
KNO$_3$	40.861	0.445	0.501	0.01
NaHCO$_3$	26.772	0.699	1.155	0.02
KHCO$_3$	37.200	0.491	1.310	0.01
Na$_2$CO$_3$	1.945	1.616	1.398	0.03
K$_2$CO$_3$	22.599	1.261	1.188	0.06
Na$_2$SO$_4$	20.794	0.186	2.340	0.05
K$_2$SO$_4$	41.239	2.191	4.739	0.04
MgSO$_4$	1.608	7.081	1.007	0.09

[a] The values of ϕ_V* have the units of cm^3 mol^{-1}. Since the values of ϕ_V* at 1 m are ten times more reliable than at 0.1 m for a given error in density; the values of ϕ_V* have been weighted by the factor 10 m.

trapolated value of $\phi_V*^0 = 18.08$ cm^3 mol^{-1} for NaCl agrees very well with the value of $\bar{V} = 18.06$ cm^3 mol^{-1} at 0.725 m calculated from apparent molal volume data.

The volume properties of these ternary electrolyte solutions can also be examined in terms of the mean apparent molal volume defined by

$$\Phi_V(2,3) = [V_{soln} - V_{H_2O}]/(m_2 + m_3) \tag{8}$$

where $V_{H_2O} = 1000/d_0$ is the volume of water in the solution and $m_2 + m_3$ is the total molality of electrolytes in solution. Substitution of eq 2 into eq 8 gives

$$\Phi_V(2,3) = \frac{1000(d_0 - d)}{d_0 d(m_2 + m_3)} + \frac{m_2 M_2 + m_3 M_3}{(m_2 + m_3)d} \tag{9}$$

This equation can be simplified by defining the total molality, $m_T = m_2 + m_3$ and mean molecular weight, $M_T = (m_2 M_2 + m_3 M_3)/(m_2 + m_3)$

$$\Phi_V(2,3) = \frac{1000(d_0 - d)}{d_0 d m_T} + \frac{M_T}{d} \tag{10}$$

The values of $\Phi_V(2,3)$ for the various electrolyte mixtures calculated from eq 9 at various molalities are also given in Tables I–XXIX.[28] The variation of the $\Phi_V(2,3)$ vs. m_3 for a 1–1 electrolyte (NaBr), three 2–1 electrolytes (Na$_2$SO$_4$, MgCl$_2$, CaCl$_2$), and the 2–2 electrolyte MgSO$_4$ are shown in Figures 3 and 4 along with the results of Lee.[19]

From the two definitions of $\phi_V*(3)$ and $\Phi_V(2,3)$, one can relate these two quantities by

$$\Phi_V*(3) = \frac{m_2 + m_3}{m_3} \Phi_V(2,3) - \frac{m_2}{m_3} \phi_V(2) \tag{11}$$

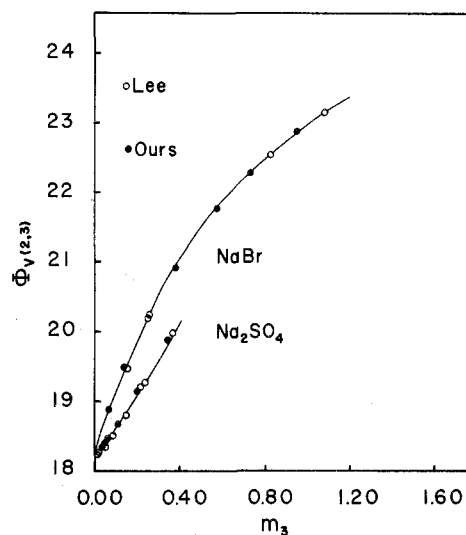$$\Phi_V(2,3) = \frac{m_2}{m_2 + m_3} \phi_V(2) + \frac{m_3}{m_2 + m_3} \phi_V*(3) \tag{12}$$

Figure 3. The mean apparent molal volumes of NaBr and Na$_2$SO$_4$ in 0.725 m NaCl at 25 °C plotted vs. molality.
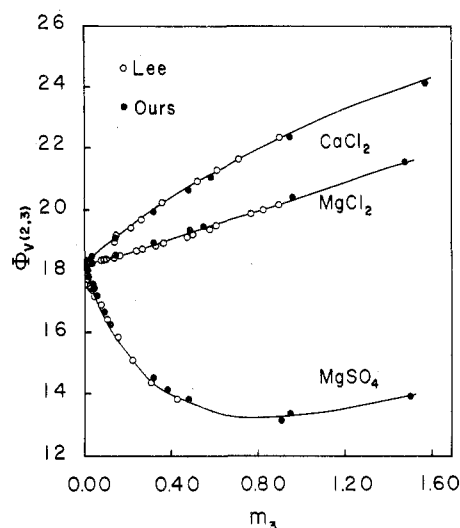

Figure 4. The mean apparent molal volumes of CaCl$_2$, MgCl$_2$, and MgSO$_4$ in 0.725 m NaCl at 25 °C plotted vs. molality.

The $\bar{V}_3*$ can also be determined from the concentration dependency of $\Phi_V(2,3)$. By differentiating eq 11 with respect to m_3 and substituting into eq 6, we have

$$\bar{V}_3* = \Phi_V(2,3) + (m_2 + m_3)[\partial \phi_V(2,3)/\partial m_3] \tag{13}$$

Since $\Phi_V(2,3) = \phi_V(2)$ and $(m_2 + m_3) = m_3$ at $m_3 = 0$, the limiting partial molal volume $\bar{V}_3*^0$ is given by

$$\bar{V}_3*^0 = \phi_V(2) + m_2[\partial \Phi_V(2,3)/\partial m_3]_{m_3=0} \tag{14}$$

The derivative $\partial \Phi_V(2,3)/\partial m_3$ can be obtained[19] from the concentration dependence of $\Phi_V(2,3)$

$$\Phi_V(2,3) = \phi_V(2) + A'm_3 + B'm_3^2 + \ldots \tag{15}$$

At $m_3 = 0$ the derivative of $\partial \Phi_V(2,3)/\partial m_3$ equals A', and the partial molal volume is given by

$$\bar{V}_3*^0 = \phi_V(2) + m_2 A' \tag{16}$$

The values of $\bar{V}_3*^0$ calculated from eq 16 are not very reliable[19] because the value determined for A' is quite dependent upon the degree used to fit the data and reliable values of $\Phi_V(2,3)$ in dilute solutions are not available.

TABLE XXXI: Coefficients for Eq 21 for Various Electrolytes in Water at 25 °C

Electrolyte	$\phi_V{}^0(i)$	A_i	B_i	σ	Ref
NaF	−2.371	1.839	0.561	0.02	30, 31, 32
KF	7.844	1.724	0.509	0.03	31, 33, 34
HCl	17.854	1.460	−0.307	0.02	18b, 35–37
LiCl	16.961	1.700	−0.198	0.02	31, 33, 38–40
NaCl	16.613	1.811	0.094	0.02	18b, 19, 38, 40–43
KCl	26.850	1.839	0.087	0.02	18a, 31, 38, 41, 44–45
RbCl	31.940	1.818	0.191	0.02	31, 38
CsCl	39.166	1.843	0.162	0.02	31, 38
NH$_4$Cl	35.815	1.717	−0.147	0.02	40
MgCl$_2$	14.522	3.155	0.106	0.03	19, 36, 40, 46
CaCl$_2$	17.858	3.611	−0.117	0.03	19, 36, 40, 41, 46
SrCl$_2$	17.975	3.941	−0.038	0.05	40, 46, 47
BaCl$_2$	23.208	4.576	−0.360	0.04	36, 40, 41, 46
NaBr	23.504	1.689	0.076	0.02	19, 31, 32, 39, 48, 49
KBr	33.725	1.403	0.480	0.02	31, 39, 41
NH$_4$Br	42.521	1.965	−0.498	0.02	40, 48
NaI	35.018	1.593	−0.126	0.03	31, 39, 49
KI	45.229	1.645	0.044	0.02	31, 39, 41
NaOH	−5.246	2.048	0.984	0.05	31, 50
KOH	4.929	1.809	0.987	0.05	40
NaNO$_3$	27.805	2.586	−0.292	0.05	40, 51
KNO$_3$	37.979	3.103	−0.712	0.05	36, 40
NaHCO$_3$	23.118	3.662	−0.115	0.05	40, 52
KHCO$_3$	33.427	3.691	−0.024	0.07	40
Na$_2$CO$_3$	−6.195	7.710	−0.383	0.05	40, 44, 52
K$_2$CO$_3$	14.526	5.525	0.371	0.05	40
Na$_2$SO$_4$	11.559	6.750	0.087	0.03	19, 36, 44
K$_2$SO$_4$	32.024	7.464	−0.285	0.03	18a, 36, 40
MgSO$_4{}^a$	−7.198	17.765	−18.462	0.05	19, 40

^{a} For MgSO$_4$ the terms $12.316I^{3/2} - 3.054I^2$ must be added to eq 21 to fit the data.

Another method that can be used to determine the $\bar{V}_3{}^{*0}$ of the electrolytes in the medium is to use Young's rule[23,24]

$$\Phi_V(2,3) = \frac{m_2}{m_2 + m_3}\phi_V{}'(2)$$
$$+ \frac{m_3}{m_2 + m_3}\phi_V{}'(3) + \frac{\Delta V_m}{m_2 + m_3} \quad (17)$$

where $\phi_V{}'(2)$ and $\phi_V{}'(3)$ are the apparent molal volumes of electrolytes (2) and (3) in binary solutions at the ionic strength of the mixture ($I = w_2 m_2 + w_3 m_3$, where w_i is a valence factor equal to 1.0, 3.0, and 4.0, respectively, for 1–1, 2–1, and 2–2 electrolytes) and ΔV_m is the volume of mixing the two electrolyte solutions at the same ionic strength. By combining eq 12 and 17, we obtain

$$\phi_V{}^*(3) = (m_2/m_3)[\phi_V{}'(2) - \phi_V(2)]$$
$$+ \phi_V{}'(3) + (\Delta V_m/m_3) \quad (18)$$

The partial molal volume of electrolyte (3) can be obtained from eq 18 by differentiation and substitution into eq 6

$$\bar{V}_3{}^* = \phi_V{}'(3) + m_3\left[\frac{\partial \phi_V{}'(3)}{\partial m_3}\right]$$
$$+ m_2\left[\frac{\partial \phi_V{}'(2)}{\partial m_3}\right] + \left(\frac{\partial \Delta V_m}{\partial m_3}\right) \quad (19)$$

The value of $\bar{V}_3{}^*$ at $m_3 = 0$ can be evaluated from

$$\bar{V}_3{}^{*0} = [\phi_V{}'(3)]_{m_3=0} + m_2\left[\frac{\partial \phi_V{}'(2)}{\partial m_3}\right]_{m_3=0}$$
$$+ \left[\frac{\partial \Delta V_m}{\partial m_3}\right]_{m_3=0} \quad (20)$$

To evaluate $\bar{V}_3{}^*$ as well as calculate ΔV_m from eq 17, the apparent molal volumes of the electrolytes studied in pure

water[18,19,30-52] (from 0 to 1 m) were fitted to equations of the form

$$\phi_V{}'(i) = \phi_V{}^0(i) + A_i I^{1/2} + B_i I \quad (21)$$

The values of $\phi_V{}^0(i)$, A_i, and B_i for the various electrolytes are given in Table XXXI. The first two terms of eq 20 are given by

$$[\phi_V{}'(3)]_{m_3=0} = \phi_V{}^0(3) + A_3 m_2{}^{1/2} + B_3 m_2 \quad (22)$$

$$m_2\left[\frac{\partial \phi_V{}'(2)}{\partial m_3}\right]_{m_3=0} = w_3\left[B_2 m_2 + \frac{A_2}{2}m_2{}^{1/2}\right] \quad (23)$$

The value of $\phi_V{}'(3)$ at $m_3 = 0$ is just the value of $\phi_V(3)$ in itself at the ionic strength of the NaCl medium (0.725 m). The value of $m_2[\partial\phi_V{}'(2)/\partial m_3]$ at $m_3 = 0$ is simply equal to $\bar{V}_2 - \phi_V(2) = m_2[\partial\phi_v(2)/\partial m_2]$ for NaCl (0.839) at 0.725 m times the valence factor w_3 for the added solute. If $\Delta V_m = 0$, the $\bar{V}_3{}^{*0}$ is simply given by

$$\bar{V}_3{}^{*0} = \phi_V{}^0(3) + A_3 m_2{}^{1/2} + B_3 m_2 + w_3[B_2 m_2$$
$$+ (A_2/2)m_2{}^{1/2}] \quad (24)$$

To calculate $(\partial\Delta V_m/\partial m_3)_{m_3=0}$, one must examine the concentration dependence of ΔV_m. The volume of mixing electrolyte solutions at a constant ionic strength have been studied by a number of workers.[53-57] For the mixing of two 1–1 electrolytes at a constant ionic strength, the ΔV_m is given by

$$\Delta V_m = y_3(1 - y_3)[v_0 + v_1(1 - 2y_3)] \quad (25)$$

where $y_3 = m_3/(m_2 + m_3)$, $(1 - y_3) = y_2 = m_2/(m_2 + m_3)$, and v_0 and v_1 are adjustable parameters related to ionic interactions. The differentiation of eq 25 with respect to m_3, evaluated at $m_3 = 0$ gives

$$\left[\frac{\partial\Delta V_m}{\partial m_3}\right]_{m_3=0} = \frac{v_0}{m_2} + \frac{v_1}{m_2} \quad (26)$$

Since the measurements made in this study were made at

TABLE XXXII: Values of $(\partial \Delta V_m / \partial m_3)$ at $m_3 = 0$ for Mixing Various Electrolytes with NaCl at 25 °C and $I = 0.725\ m$

Electrolyte	$(\partial \Delta V_m / \partial m_3)_{m_3=0}$	Electrolyte	$(\partial \Delta V_m / \partial m_3)_{m_3=0}$
NaF	-0.18	NH_4Br	-0.02_3
KF	0.17	NaI	-0.13
HCl	-0.04_2	KI	-0.07_9
LiCl	-0.02_5	NaOH	0.39
NaCl	0.00	KOH	0.11
KCl	0.02_7	$NaNO_3$	-0.01_0
RbCl	0.16	KNO_3	-0.01_8
CsCl	0.11	$NaHCO_3$	-0.12
NH_4Cl	-0.07_3	$KHCO_3$	-0.13
$MgCl_2$	-0.64	Na_2CO_3	-0.66
$CaCl_2$	-0.45	K_2CO_3	0.68
$SrCl_2$	-0.66	Na_2SO_4	0.82
$BaCl_2$	-0.42	K_2SO_4	0.73
NaBr	-0.07_0	$MgSO_4$	-2.26
KBr	0.10		

changing ionic strengths, it is not possible to fit the values of ΔV_m calculated from eq 17 to eq 25. We have subsequently fitted the values of ΔV_m calculated from

$$\Delta V_m = (m_2 + m_3)[\Phi_V(2,3) - y_2\phi_V{}'(2) - y_3\phi_V{}'(3)] \quad (27)$$

to equations of the form

$$\Delta V_m = A + Bm_3 + Cm_3{}^2 + \ldots \quad (28)$$

The values of $(\partial \Delta V_m / \partial m_3)$ at $m_3 = 0$ (B in eq 28) evaluated from the experimental results are given in Table XXXII. It should be pointed out that the values of $(\partial \Delta V_m / \partial m_3)$ at $m_3 = 0$ are equal to $(v_0 + v_1)/m_2$. For most of the 1–1 electrolytes studied $(\partial \Delta V_m / \partial m_3)_{m_3=0}$ is less than 0.2 cm³ mol⁻¹; while for the 2–1 electrolytes the values are less than 0.7 cm³ mol⁻¹. The value of $(\partial \Delta V_m / \partial m_3)_{m_3=0}$ for $MgSO_4$ is quite large, probably due to ion pairing effects.[58]

The values of $\bar{V}^{*0}$ calculated from eq 20 using the values of $\Delta \partial V_m / \partial m_3$ at $m_3 = 0$ are given in Table XXXIII along with those obtained from eq 7. The results of $\bar{V}^{*0}$ obtained by the two methods agree to within 0.2 cm³ mol⁻¹ for all of the electrolytes studied (which we feel is the maximum error). We will use the average values of $\bar{V}^{*0}$ obtained by these two methods in all of our further calculations.

The reliability and internal consistency of our values of $\bar{V}^{*0}$ can be determined by examining the additivity of the various salt pairs. For the difference between Na^+ and K^+, our results give $\bar{V}^{*0}(Na^+) - \bar{V}^{*0}(K^+) = -10.36 \pm 0.07$ cm³ mol⁻¹ from the salt pairs NaCl–KCl, NaF–KF, NaBr–KBr, NaI–KI, NaOH–KOH, $NaNO_3$–KNO_3, $NaHCO_3$–$KHCO_3$, $^1/_2Na_2CO_3$–$^1/_2K_2CO_3$, and $^1/_2Na_2SO_4$–$^1/_2K_2SO_4$ (the maximum difference was 0.13 cm³ mol⁻¹). The difference between Cl^- and the various anions obtained from our results are: $\bar{V}^{*0}(Cl^-) - \bar{V}^{*0}(F^-) = 18.74 \pm 0.04$ cm³ mol⁻¹, $\bar{V}^{*0}(Cl^-) - \bar{V}^{*0}(Br^-) = -6.75 \pm 0.11$ cm³ mol⁻¹; $\bar{V}^{*0}(Cl^-) - \bar{V}^{*0}(I^-) = -17.99 \pm 0.10$ cm³ mol⁻¹; $\bar{V}^{*0}(Cl^-) - \bar{V}^{*0}(NO_3^-) = -11.54 \pm 0.01$ cm³ mol⁻¹; $\bar{V}^{*0}(Cl^-) - \bar{V}^{*0}(OH^-) = 21.43_5 \pm 0.01$ cm³ mol⁻¹; $\bar{V}^{*0}(Cl^-) - \bar{V}^*(HCO_3^-) = -7.83 \pm 0.07$ cm³ mol⁻¹; $\bar{V}^{*0}(Cl^-) - ^1/_2\bar{V}^{*0}(CO_3^{2-}) = 18.05 \pm 0.03$ cm³ mol⁻¹; and $\bar{V}^{*0}(Cl^-) - ^1/_2\bar{V}^{*0}(SO_4^{2-}) = -8.68 \pm 0.02$ cm³ mol⁻¹.

These differences can be used along with the values of $\bar{V}^{*0}$ for the various electrolytes to obtain reliable values for various ions. To divide the values of $\bar{V}^{*0}$ for the electrolytes into ionic values, it is necessary to assign a value to one ion. We have selected a value of $\bar{V}^{*0}(Na^+) = -4.50$ cm³ mol⁻¹ which is obtained from the specific interaction model.[16] The values of $\bar{V}^{*0}$ for various ions in 0.725 m NaCl obtained by using this value of $\bar{V}^{*0}(Na^+)$ are given in Table XXXIV.

TABLE XXXIII: Comparison of the Values of $\bar{V}^{*0}$ for Various Electrolytes in 0.725 m NaCl Obtained by Extrapolation and by Using Young's Rule

	$\bar{V}^{*0}$, cm³ mol⁻¹		
Electrolyte	Extrapolation[a]	Young's full equation[b]	Δ[c]
NaF	0.30	0.26	0.04
KF	10.61	10.69	-0.08
HCl	19.61	19.67	-0.06
LiCl	19.19	19.08	0.11
NaCl	19.08	19.06	0.02
KCl	29.34	29.35	-0.01
RbCl	34.65	34.63	0.02
CsCl	41.74	41.80	-0.06
NH_4Cl	37.91	37.94	-0.03
$MgCl_2$	18.94	19.16	-0.22
$CaCl_2$	22.97	22.92	0.05
$SrCl_2$	23.17	23.16	0.01
$BaCl_2$	28.92	28.94	-0.02
NaBr	25.62	25.77	-0.15
KBr	36.17	36.21	-0.04
NH_4Br	44.57	44.65	-0.08
NaI	36.92	36.99	-0.07
KI	47.42	47.42	0.00
NaOH	-2.42	-2.34	-0.08
KOH	7.90	7.92	-0.02
$NaNO_3$	30.55	30.62	-0.07
KNO_3	40.86	40.93	-0.07
$NaHCO_3$	26.77	26.87	-0.10
$KHCO_3$	37.20	37.26	-0.06
Na_2CO_3	1.95	1.95	0.00
K_2CO_3	22.60	22.70	-0.10
Na_2SO_4	20.79	20.71	0.08
K_2SO_4	41.24	41.42	-0.18
$MgSO_4$	1.57	1.66	-0.09

[a] Extrapolated from the $\phi_V^*(3)$ data by using eq 7 (Table XXX). [b] Calculated from Young's full equation (eq 20) using the values of $\phi_V{}^0$, A_i, and B_i given in Table XXXI and $(\partial \Delta V_m / \partial m_3)$ at $m_3 = 0$ given in Table XXXII. [c] $\Delta = \bar{V}^{*0}$(extrapolated) $- \bar{V}^{*0}$(Young's full equation).

TABLE XXXIV: The Partial Molal Volumes of Various Ions in 0.725 m NaCl at 25 °C

Ion	$\bar{V}^0(M^{n-})$, cm³ mol⁻¹	Ion	$\bar{V}^0(X^{n-})$, cm³ mol⁻¹
H^+	-3.92	F^-	4.82
Li^+	-4.39	Cl^-	23.56
Na^+	-4.50	Br^-	30.31
K^+	5.78	I^-	41.55
Rb^+	11.08	OH^-	2.12
Cs^+	18.21	NO_3^-	35.10
NH_4^+	14.33	HCO_3^-	31.39
Mg^{2+}	-28.07	CO_3^{2-}	11.02
Ca^{2+}	-24.17	SO_4^{2-}	29.76
Sr^{2+}	-23.96		
Ba^{2+}	-18.19		

Discussion

A comparison of the partial molal volumes of electrolytes in 0.725 m NaCl determined in this study and by other workers is shown in Table XXXV. Our volume results agree very well (to within ±0.26 cm³ mol⁻¹) with the work of Wirth[18] and Lee.[19] The larger errors for $MgCl_2$ and $MgSO_4$ are due to the methods used by Lee in extrapolating the $\phi_V^*(3)$ data. The value of $\bar{V}^{*0}$ for $MgCl_2$ obtained by fitting Lee's results to eq 5 are in good agreement with our results and also yield an additivity value for $MgSO_4$ that agrees with our results. The disagreement between our values of $\bar{V}^{*0}$ for Na_2CO_3 and K_2CO_3 and the results of Duedall[20] is related to expansibility effects (his measurements were made at 20 °C). Duedall's results for K_2CO_3 and Na_2CO_3 yield differences for the $\bar{V}^*(K^+)$ –

TABLE XXXV: Comparison of the Partial Molal Volumes of Electrolytes in 0.725 m NaCl Obtained in this Study and Those Obtained by Other Workers at 25 °C

Electrolyte	$\bar{V}*^0$, cm³ mol⁻¹ Our results	Lit.	Δ
HCl	19.64	19.64[a]	0.00
NaCl	19.06	19.05[a,b]	0.01
KCl	29.34	29.32[c]	0.02
NaBr	25.70	25.79[b]	−0.09
KBr	36.19	36.34[c]	−0.15
Na₂SO₄	20.75	20.65[b]	0.10
K₂SO₄	41.33	41.31[c]	0.02
MgCl₂	19.05	19.31[b]	−0.26
		(19.09)[b]	(−0.04)
CaCl₂	22.97	23.08[b]	−0.11
MgSO₄	1.62	1.88[b]	−0.25
		(1.64)[b]	(−0.02)
Na₂CO₃	1.95	1.70[d]	0.25
K₂CO₃	22.65	23.20[d]	−0.55

[a] Wirth,[18b] estimated by interpolation. [b] Lee.[19] The value for MgSO₄ was obtained by additivity [ϕ_V*^0(Mg-SO₄) = ϕ_V*^0(MgCl₂) + ϕ_V*^0(Na₂SO₄) − 2ϕ_V*^0(NaCl)]. The values given in parentheses were calculated from Lee's values of ϕ_V*(3) by using eq 7. [c] Wirth,[18a] estimated by interpolation. [d] Duedall[20] at 20 °C.

$\bar{V}*$(Na⁺) = 10.75 cm³ mol⁻¹ which is ~0.4 cm³ mol⁻¹ larger than found in this study. Since the differences in the expansibilities of Na⁺ and K⁺ are small at an ionic strength of 0.725 m, this comparison indicates that Duedall's $\bar{V}*^0$ for K₂CO₃ at 20 °C may be too high. To summarize, these comparisons indicate that our values of $\bar{V}*^0$ are reliable to ±0.1 cm³ mol⁻¹ for 1–1 electrolytes and ±0.2 cm³ mol⁻¹ for 2–1 electrolytes.

The partial molal volume of an electrolyte in an ionic medium can be estimated by a number of methods.[12-17] Most of the methods are based on various models for ionic interactions.[1-10,59] The most direct method is the use of the ionic strength principle.[12] This method essentially states that the partial molal volume of an electrolyte in an ionic medium is equal to the value in pure water at the ionic strength of the medium. The method is related to Harned's rule[2] for the trace activity coefficient of an electrolyte (γ_3) in a mixed electrolyte solution

$$\log \gamma_3 = \log \gamma_3' + \alpha_{23} m_2 \tag{29}$$

where γ_3' is the value of γ_3 in pure water at the ionic strength of the mixture of molality m_2 and α_{23} is an interaction coefficient. By assuming the Harned coefficient α_{23} is independent of pressure, we obtain

$$\bar{V}_3*^0 = \bar{V}_3' = \phi_V^0(3) + 1.5A_3 m_2^{1/2} + 2B_3 m_2 \tag{30}$$

The partial molal volumes of electrolytes determined in this study are compared in Table XXXVI with those calculated from eq 30.

For electrolytes with a common anion (Cl⁻), the ionic strength principle predicts values for $\bar{V}*^0$ that agree on the average to ±0.23 cm³ mol⁻¹ (maximum difference of 0.58 cm³ mol⁻¹). For electrolytes with a common cation (Na⁺) the deviations are larger ±0.48 cm³ mol⁻¹ (maximum difference of 1.18 cm³ mol⁻¹). For electrolytes without a common cation or anion the predicted values agree with the measured values on the average to ±0.41 cm³ mol⁻¹ (maximum difference of 1.29 cm³ mol⁻¹). The values of $\bar{V}*^0$ for various ions estimated by using the ionic strength principle (from the values for electrolytes with a common cation or anion) are compared with the measured values in Table XXXVII. For cations the predicted $\bar{V}*^0$'s agree with the measured values to ±0.22 cm³ mol⁻¹ and for anions

TABLE XXXVI: Comparisons of the Measured and Calculated Values of $\bar{V}*^0$ of Electrolytes in 0.725 m NaCl at 25 °C

Electrolyte	Ionic strength	$\bar{V}*^0$(measd) − $\bar{V}*^0$(calcd), cm³ mol⁻¹ Young's rule	Specific interaction
HCl	0.37	−0.07	−0.13
LiCl	0.33	0.05	0.05
NaCl	0.00	0.00	0.00
KCl	0.02	0.02	0.03
RbCl	0.10	0.17	0.20
CsCl	0.02	0.08	0.09
NH₄Cl	0.13	−0.09	−0.04
MgCl₂	0.35	−0.75	−0.75
CaCl₂	0.58	−0.49	−0.41
SrCl₂	0.21	−0.66	−0.67
BaCl₂	0.40	−0.43	−0.38
	±0.23	±0.26	±0.25
NaF	−0.51	−0.16	−0.15
NaCl	0.00	0.00	0.00
NaBr	−0.07	−0.14	−0.16
NaI	0.08	−0.17	−0.21
NaOH	−1.18	−0.43	−0.37
NaNO₃	−0.09	−0.04	0.13
NaHCO₃	−0.81	−0.17	0.23
Na₂CO₃	−1.15	−0.66	−0.99
Na₂SO₄	0.44	0.86	0.51
	±0.48	±0.29	±0.31
NH₄Br	0.30	−0.06	−0.15
KF	−0.13	0.13	−0.03
KBr	−0.02	0.08	0.08
KI	0.03	−0.08	0.01
KOH	−0.76	−0.11	−0.33
KNO₃	0.02	−0.05	0.18
KHCO₃	−0.88	−0.16	0.39
K₂CO₃	0.49	0.59	−0.83
K₂SO₄	0.20	0.65	0.60
MgSO₄	−1.29	−2.30	−0.27
	±0.41	±0.42	±0.29

TABLE XXXVII: Comparison of the Measured and Calculated Values of $\bar{V}*^0$ of Ions in 0.725 m NaCl at 25 °C

Ion	Ionic strength	$\bar{V}*^0$(measd) − $\bar{V}*^0$(calcd), cm³ mol⁻¹ Young's rule	Specific interaction
H⁺	0.37	0.07	−0.13
Li⁺	0.32	0.07	0.05
Na⁺	0.00	0.00	0.00
K⁺	0.01	0.02	0.03
Rb⁺	0.10	0.17	0.20
Cs⁺	0.01	0.08	0.09
NH₄⁺	0.09	−0.12	−0.07
Mg²⁺	0.34	−0.75	−0.72
Ca²⁺	0.58	−0.49	−0.34
Sr²⁺	0.21	−0.66	−0.67
Ba²⁺	0.40	−0.43	−0.38
	±0.22	±0.26	±0.24
F⁻	0.46	−0.11	−0.11
Cl⁻	0.00	0.00	0.00
Br⁻	0.04	−0.03	−0.05
I⁻	0.18	−0.07	−0.11
OH⁻	−1.18	−0.43	−0.37
NO₃⁻	−0.08	−0.03	0.14
HCO₃⁻	−0.74	−0.10	0.30
CO₃²⁻	−1.10	−0.61	−0.92
SO₄²⁻	0.46	0.88	0.52
	±0.47	±0.25	±0.28

the predicted $\bar{V}*^0$'s agree with the measured values to ±0.47 cm³ mol⁻¹. The better agreement for cations is

related to the fact that most cations do not have strong interactions with Cl⁻ ions. The larger deviations for the anions can be related to the volume changes for the formation of various ion pairs with Na⁺.[16]

The use of Young's rule to estimate the $\bar{V}*^0$ was discussed earlier. The method assumes that the volume of mixing two electrolyte solutions is zero. The partial molal volumes of electrolytes and ions determined in this study are compared with those calculated from eq 24 in Tables XXXVI and XXXVII. For electrolytes with a common anion, the differences are ±0.26 cm³ mol⁻¹; for electrolytes with a common cation, the differences are ±0.29 cm³ mol⁻¹; and for electrolytes with uncommon ions, the differences are ±0.42 cm³ mol⁻¹. The predicted values for cations and anions agree, respectively, on the average to ±0.26 and ±0.25 cm³ mol⁻¹. Overall, the predicted values of $\bar{V}*^0$ using Young's rule are better than using the ionic strength principle.

The use of the specific interaction model to estimate the $\bar{V}*^0$ of electrolytes and ions in ionic media has been discussed elsewhere.[16] In using the specific interaction model one asumes that specific short-range interactions in solutions of constant ionic strength are limited to ions of opposite charge only.[59] The partial molal volumes of electrolytes in water are represented by[16]

$$\bar{V}(MX) = \bar{V}°(MX) + \frac{S_V I^{1/2}}{1 + I^{1/2}}$$
$$+ 2\nu_M \nu_X B_{MX}[MX] \tag{31}$$

where S_V is the Debye–Hückel limiting slope (=2.802w at 25 °C), ν_M is the number of cations and ν_X is the number of anions formed when MX completely dissociates, [MX] is the molality of MX, and B_{MX} is the volume specific interaction parameter which is a function of ionic strength.[16] The partial molal volumes of electrolytes and ions are predicted by using the equations[16]

$$\bar{V}*(MX) = \bar{V}°(MX) + \frac{2.802w I^{1/2}}{1 + I^{1/2}}$$
$$+ \nu_M \sum_X B_{MX}[X] + \nu_X \sum_M B_{MX}[M] \tag{32}$$

$$\bar{V}*(M^+) = \bar{V}°(M^+) + \frac{2.802w I^{1/2}}{1 + I^{1/2}} + \sum_X B_{MX}[X] \tag{33}$$

$$\bar{V}*(X^-) = \bar{V}°(X^-) + \frac{2.802w' I^{1/2}}{1 + I^{1/2}} + \sum_M B_{MX}[M] \tag{34}$$

where the interaction coefficients B_{MX} are at the ionic strength of the mixture and $w' = Z^{1/2}$ (0.5 for $Z = ±1$ and 2.0 for $Z = ±2$). In a 0.725 m NaCl solution the values of $\bar{V}*(MX)$, $\bar{V}*(M^+)$, and $\bar{V}*(X^-)$ are determined from

$$\bar{V}*(MX) = \bar{V}°(MX) + 1.289w$$
$$+ \nu_M B_{MCl}(0.725) + \nu_X B_{NaX}(0.725) \tag{35}$$

$$\bar{V}*(M^+) = \bar{V}°(M^+) + 1.289w' + B_{MCl}(0.725) \tag{36}$$

$$\bar{V}*(X^-) = \bar{V}°(X^-) + 1.289w' + B_{NaX}(0.725) \tag{37}$$

The values of $\bar{V}*^0$ for various electrolytes and ions calculated from eq 35–37 are compared with the measured values in Tables XXXVI and XXXVII. For electrolytes with a common anion, the predicted values agree on the average to ±0.25 cm³ mol⁻¹; with a common cation, the differences are ±0.31 cm³ mol⁻¹; and with both uncommon cations and anions, the differences are ±0.29 cm³ mol⁻¹. The values of $\bar{V}*^0$ predicted from the specific interaction model are much better than those estimated by using the

TABLE XXXVIII: Comparison of the Values of v_0 with the Values of RTh_0 for Common Cation and Anion Mixing of Electrolytes with NaCl

	v_0	RTh_0
Common Cation	Cl–X Interactions	
F	-0.13	
Cl	0.00	0.0
Br	-0.05	3.2[60,61,62]
I	-0.09	
OH	-0.28	
NO₃	-0.07	12.4[60,61,62]
HCO₃	-0.09	
CO₃	-0.48	
SO₄	0.59	-27[60,61,67]
Common Anion	Na–M Interactions	
H	-0.03	124[60,69]
Li	-0.02	84[60,61,62,65,68]
Na	0.00	0.0
K	0.02	-38[60,61,62,68]
Rb	0.12	-50[60,61]
Cs	0.08	-35[60,61]
NH₄	-0.05	
Mg	-0.46	172[63]
Ca	-0.33	137[66]
Sr	-0.48	
Ba	-0.30	85.3[66]

ionic strength principle and slightly better than those estimated by using Young's rule. If MgSO₄ is eliminated from the comparisons, the specific interaction model and Young's rule are nearly equivalent. This is clearly demonstrated by examining the estimates for the values of $\bar{V}*^0$ (Table XXXVII) for cations and anions. In summary, these comparisons indicate that the specific interaction model and Young's rule (without ΔV_m) predict better values of $\bar{V}*^0$ in 0.725 m NaCl than the ionic strength principle.

The failure of Young's rule and the specific interaction model to predict more reliable values is due to the fact that the interactions between like charged ions are not considered. To improve these estimations, one must have some knowledge of the volume of mixing the various electrolyte solutions with NaCl at an ionic strength of 0.725. Since the values of $\bar{V}*^0$ are additive, only the volumes of mixing various electrolytes with a common cation (Na⁺) and anion (Cl⁻) need to be considered. Although the values of $v_0 \simeq m_2(\partial \Delta v_m/\partial m_3)_{m_3=0}$ determined from our results have large errors, it is possible to examine how the values of v_0 are related to other excess thermodynamic properties for the same systems. The enthalpies of mixing electrolytes containing a common cation and anion with NaCl at $I = 1.0$ have been studied by Young and co-workers,[60,61] Wood and co-workers,[62-67] and Stern and co-workers.[68,69] A comparison of our estimated values of v_0 and the enthalpy interaction[1] term RTh_0 (at $I = 0$) is given in Table XXXVIII and Figure 5. As is quite apparent from these comparisons, the values of v_0 correlate very well with RTh_0. As found in enthalpy studies by other workers[60,61] for common anion mixtures, the cations can be divided into two groups (H⁺, Li⁺, NH₄⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺), and (K⁺, Rb⁺, Cs⁺). The mixing of Na⁺ with the so-called "structure making" cations (H⁺, Li⁺, NH₄⁺, Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺) produces a decrease in volume; while the mixing with the "structure breaking" cations (K⁺, Rb⁺, and Cs⁺) produces an increase in volume.

The effect of water structural interactions on ion–ion interactions was first suggested by Frank and Robinson.[70] Gurney[71] with his cosphere model made further developments of these ideas. Desnoyers et al.[31] developed a general rule that relates these ionic structural interactions in terms of the Gurney cospheres. They[31] state that, "two
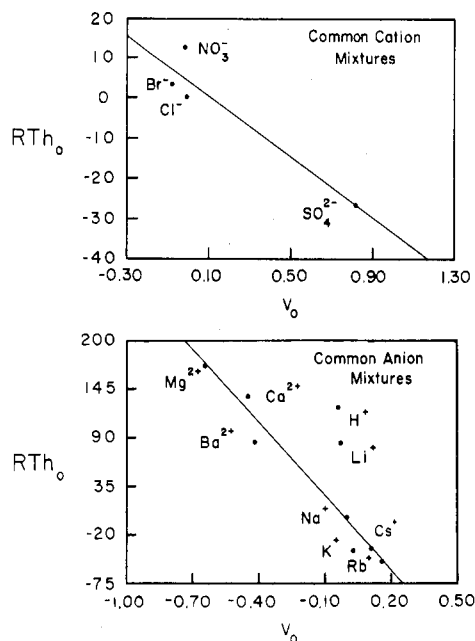
Figure 5. The enthalpy interaction term (RTh_0) plotted vs. the volume interaction term (v_0) for mixing NaCl with electrolytes containing a common cation (NaX) and a common anion (MCl) at 25 °C.
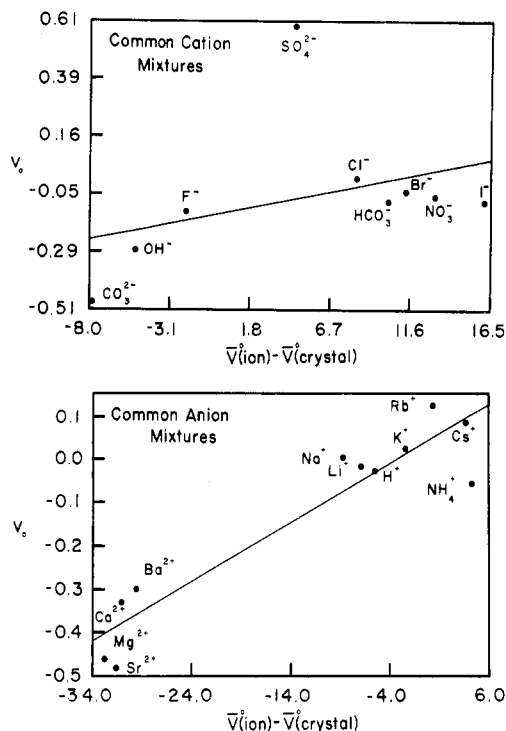

Figure 6. The volume interaction term (v_0) plotted vs. the difference between the partial molal volume of the uncommon ion at infinite dilution, $\bar{V}^0$(ion), and the crystal molal volume, $\bar{V}^0$(cryst).

solutes will attract each other if their structural influences, or their tendencies to orient water molecules, are compatible with each other; conversely, an incompatibility in these structural influences or tendencies will result in repulsive forces". The mixing of two electrolytes of the same structural form (i.e., two "structure making" electrolytes) causes a repulsion with a decrease in volume and an increase in enthalpy. The mixing of two electrolytes of opposite structural forms (i.e., a "structure making" and "structure breaking" electrolyte) causes an attraction with an increase in volume and a decrease in enthalpy. As is clearly demonstrated in the comparisons given in Table XXXVIII and shown in Figure 5, our results are in agreement with the predictions of the structural interaction model of Desnoyers.[31] Although the sign of ΔV_m or v_0 can be predicted from this structural interaction model, it is not possible to predict the magnitude of the volume changes. There also is no unambiguous way of selecting whether an ion is a "structure breaker or maker".[72] If the structural concepts are valid, one might expect a correlation between excess thermodynamic properties with properties related to structure such as molal entropies, volumes, and expansibilities.[73,74] Leyendekkers[17] for example has developed a correlation between $(\partial \Delta V_m/\partial m_3)_{m_3=0}$ and entropy for mixtures of electrolytes in seawater. The functional form[17] of the correlation for anions, however, is quite complex ($\partial \Delta V_m/\partial m_3$ is a cubic function of entropy).

We have attempted to correlate the values of v_0 to various thermodynamic properties of the uncommon ions, such as $\bar{S}^0$, the partial molal entropy; $\bar{E}^0$, the partial molal compressibility; $\bar{K}_S^0$, the partial molal adiabatic compressibility; b_V, the Redlich–Rosenfeld molal volume deviation parameter, and $\bar{V}^0$(ion) – $\bar{V}^0$(cryst), the differences between the partial molal volume of an ion and the crystal molal volume ($2.52r^3$, where r is the crystal radius). The linear correlation of v_0 vs. $\bar{V}^0$(ion) – $\bar{V}^0$(cryst) for the common cations and anions is shown in Figure 6. The values of v_0 for the common anion mixtures show a linear correlation with these thermodynamic properties. [The standard errors in v_0 are 0.10, 0.16, 0.13, 0.07, and 0.07 cm³ mol⁻¹, respectively, for the correlations with $\bar{S}^0$, $\bar{E}^0$, $\bar{K}_S^0$, b_V, and $\bar{V}^0$(ion) – $\bar{V}^0$(cryst).] The values of v_0 for the

common cation mixtures do not correlate as well with the thermodynamic properties of the uncommon anion. [The standard errors in v_0 are 0.27, 0.24, 0.28, 0.28, 0.28, and 0.26 cm³ mol⁻¹, respectively, for linear correlations with $\bar{S}^0$, $\bar{E}^0$, $\bar{K}_S^0$, b_V, and $\bar{V}^0$(ion) – $\bar{V}^0$(cryst).] If the SO₄²⁻–Cl⁻ mixtures are not used, the correlations improve considerably. [The standard errors in v_0 are 0.11, 0.10, 0.07, 0.11, 0.09 cm³ mol⁻¹, respectively, for correlations with $\bar{S}^0$, $\bar{E}^0$, $\bar{K}_S^0$, b_V, and $\bar{V}^0$(ion) – $\bar{V}^0$(cryst).]

Although these correlations may be fortuitous, the results do indicate that the volume of mixing electrolyte solutions with common anions and cations are related to the water–ion interactions of the uncommon ion. In our future work we plan to make direct volume of mixing measurements of NaCl solutions with other electrolytes (with and without a common ion) as a function of ionic strength and temperature in an attempt to elucidate these structural interactions.

Supplementary Material Available: Tables I–XXIX, listings of density, $\phi_V*(3)$, and $\Phi_V(2,3)$ for the various electrolytes studied (29 pages). Ordering information is available on any current masthead page.

References and Notes

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Solubility of Iodine in Mixed Solvents. A Case Study of Preferential Solvation in Nonpolar and Associated Solutions

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The solubilities of iodine have been measured at 288.15, 298.15, and 308.15 K in the following seven binary mixed solvents: n-C_6H_{14} + c-C_6H_{12}, c-C_6H_{12} + C_6H_6, C_6H_6 + $C_6H_5CH_3$, c-C_6H_{12} + EtOH, n-C_7H_{16} + EtOH, C_6H_6 + EtOH, and EtOH + H_2O. The entropy of solution of iodine ΔS_{soln} has been evaluated at 298.15 K as a function of the mole fraction of one solvent x in mixed solvents. A distinct maximum or minimum in the ΔS_{soln} vs. x relation for such associated solutions as EtOH + H_2O or c-C_6H_{12} + EtOH was found to be parallel with the anomalies in the diffusivity of iodine in the same solvent systems. A thermodynamic analysis of the solubility data based primarily on the regular solution theory was given.

Introduction

Our recent studies on the diffusivity of iodine in binary mixed solvents[1-3] have revealed that the temperature reduced isoviscous diffusion coefficient $D_{11}{}^0\eta_{23}/T$ vs. mole fraction of mixed solvents x_2 relation[4,5] deviates negatively from the additivity with respect to x_2, whenever the

difference in the interactions of two solvents with iodine is nonnegligible. Such a relative decrease in diffusivity suggests that the stability of iodine complexes in these mixed solvents might be greater than those in pure solvents. The entropy of solution ΔS_{soln} of iodine which may be obtained from the temperature dependence of the