Apparent Molar Heat Capacities and Volumes of Mixed Electrolytes: [NaCl(aq) + $CaCl_2$(aq)], [NaCl(aq) + $MgCl_2$(aq)], and [$CaCl_2$(aq) + $MgCl_2$(aq)]

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Heat capacities and densities of aqueous solutions containing mixtures of simple electrolytes, [NaCl(aq) + $CaCl_2$(aq)], [NaCl(aq) + $MgCl_2$(aq)], and [$CaCl_2$(aq) + $MgCl_2$(aq)], have been measured from 298.15 to 373.15 K at 0.6 MPa. For each system, values were obtained for full ranges of mixture compositions for total ionic strengths of approximately 3 and 5 mol·kg^{-1}. Measurements for NaCl(aq) (0.11–5.95 mol·kg^{-1}), $MgCl_2$(aq) (0.44–5.19 mol·kg^{-1}), and $CaCl_2$(aq) (1.46–5.54 mol·kg^{-1}) are also reported. The measurements were done using a flow differential heat capacity calorimeter in series with a vibrating-tube densimeter. Values for the apparent molar heat capacities and volumes are reported and compared to literature values and to values predicted by both Young's rule and Pitzer's theory.

Introduction

Most natural and industrial aqueous systems are mixtures of electrolytes, and there have been many studies of osmotic coefficients of mixed electrolyte solutions (Pytkowicz, 1979; Pitzer, 1993). Methods to calculate these coefficients using values from single-electrolyte systems and simple interaction parameters are relatively well established. Generally, two approaches have been taken to analyze the thermodynamic properties of aqueous mixtures of electrolytes: the Pitzer treatment (Pitzer and Kim, 1974; Pabalan and Pitzer, 1987, 1988) and Young's rule (Young and Smith, 1954). Both of these treatments have their strengths and weaknesses, but each offers some insight into the solution properties of mixed-electrolyte systems, especially at relatively high ionic strengths.

Although the Pitzer treatment is a semiemperical approach, the dependence of the interaction parameters on temperature or ionic strength provides some insight into ion–ion and ion–solvent short-range interactions. However, the mathematical treatment is quite sophisticated and is not readily applicable to all systems. On the other hand, a Young's rule approach, being mathematically simpler, has been more widely applied. Recently, it has been used in the investigation of apparent molar volumes and heat capacities for species that are related by associative equilibria (Woolley and Hepler, 1977; Barbero et al., 1983; Hovey and Hepler, 1990).

Past treatments of mixed aqueous electrolyte solutions were primarily based on isopiestic measurements. However, data relating to other properties such as volumes and heat capacities have been less thoroughly analyzed. This is particularly true for mixtures containing unsymmetrical electrolytes and for temperatures other than 298.15 K. Conti et al. (1986, 1989) have reported heat capacity values (333–493 K) for the aqueous $K^+/Na^+/Cl^-/SO_4^{2-}$ system and analyzed the data using Pitzer's equations (Pitzer and Kim, 1974). Oakes et al. (1990) have reported density data for the [NaCl(aq) + $CaCl_2$(aq)] system and compared them to the earlier work of Kumar et al. (1982) and Kumar and Atkinson (1983).

Recently we presented a preliminary set of heat capacity and density data for the systems [NaCl(aq) + KBr(aq)] at 298.15 and 333.15 K and [NaCl(aq) + $MgCl_2$(aq)] at 348.15 K (Lemire et al., 1993). In the present paper we report results of measurements of the heat capacities and densities of aqueous solutions containing mixtures of simple electrolytes, [NaCl(aq) + $CaCl_2$(aq)], [NaCl(aq) + $MgCl_2$(aq)], and [$CaCl_2$(aq) + $MgCl_2$(aq)] from 298.15 to 373.15 K at 0.6 MPa. For each system, values were obtained for full ranges of mixture compositions for total ionic strengths of approximately 3 and 5 mol·kg^{-1}. Measurements were also made to augment the available apparent molar heat capacity values for the simple electrolytes NaCl(aq), $MgCl_2$(aq), and $CaCl_2$(aq). Such experiments permit an evaluation of the uncertainties introduced in using single-electrolyte heat capacities in calculations for mixed-electrolyte systems and in using data from mixed-electrolyte systems to estimate single-electrolyte properties [e.g., as was done in the papers of Hepler and co-workers (Woolley and Hepler, 1977; Barbero et al., 1983; Hovey and Hepler, 1990)].

Experimental Section

The flow heat capacity microcalorimeter, the flow vibrating-tube densimeter system, and the procedures used for the measurements have been described in detail elsewhere (Saluja et al., 1986a, 1987, 1992). The calorimeter and densimeter were operated in series, and the temperature rise during the heat capacity measurements (twice the difference between the temperatures of these measurements) varied from 2.2 to 2.7 K, depending on the temperature of the measurement. The temperatures were stable within ±0.003 K, but the accuracy of the temperatures, measured by comparison with a calibrated quartz thermometer, is probably only ±0.05 K. The pressures are accurate within ±50 kPa. The overall precision in c_p is estimated to be ±4 mJ·K^{-1}·g^{-1}. The uncertainties in the experimental density measurements are estimated to be $\pm 1 \times 10^{-5}$ g·cm^{-3}. This estimate is based on an uncertainty of 1×10^{-9} s in the difference between the vibrational periods of the densimeter tube containing an electrolyte solution and pure water at the same operating temperature and pressure.

The solutions were prepared from reagent grade $CaCl_2 \cdot 2H_2O$ (Baker or Ventron), $MgCl_2 \cdot 6H_2O$ (Baker or

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Table 1. Experimental Values of the Quantities[a] $[(c_p\varrho/c^*_{p,1}\varrho^*_1) - 1]$, $(\varrho - \varrho^*_1)$, $C_{p,2,\phi}$, and $V_{2,\phi}$ for the Binary Solutions NaCl(aq), $MgCl_2$(aq), and $CaCl_2$(aq) at 0.6 MPa

m(NaCl)/ ($mol \cdot kg^{-1}$)	$10^2 \times [(c_p\varrho/c^*_{p,1}\varrho^*_1) - 1]$	$C_{p,2,\phi}$/ ($J \cdot K^{-1} \cdot mol^{-1}$)	$(\varrho - \varrho^*_1)$/ ($kg \cdot m^{-3}$)	$V_{2,\phi}$/ ($cm^3 \cdot mol^{-1}$)	m/(NaCl)/ ($mol \cdot kg^{-1}$)	$10^2 \times [(c_p\varrho/c^*_{p,1}/\varrho^*_1) - 1]$	$C_{p,2,\phi}$/ ($J \cdot K^{-1} \cdot mol^{-1}$)	$(\varrho - \varrho^*_1)$/ ($kg \cdot m^{-3}$)	$V_{2,\phi}$/ ($cm^3 \cdot mol^{-1}$)
	298.15 K		297.05 K			348.15 K		346.90 K	
0.1076	−0.3682	−73.86	4.4545	16.91	0.1076	−0.3124	−45.95	4.2094	18.73
0.2023	−0.6732	−67.30	8.2720	17.35	0.2023	−0.5690	−41.05	7.8629	18.92
0.3013	−0.9699	−62.48	12.2628	17.47	0.3013	−0.8243	−37.29	11.6371	19.10
0.5182	−1.5748	−53.90	20.8226	17.83	0.5182	−1.3514	−31.96	19.8873	19.20
0.6942	−2.0209	−47.99	27.6544	18.05	0.6942	−1.7518	−27.66	26.3766	19.46
1.0186	−2.7393	−37.85	39.9857	18.40	1.0186	−2.4389	−21.48	38.1410	19.79
1.9898	−4.3559	−14.85	75.0587	19.23	1.9898	−4.1292	−7.03	71.9428	20.42
3.9874	−5.9193	18.12	139.9628	20.44	3.9874	−6.2127	16.90	134.6785	21.46
5.9477	−6.0737	40.57	196.1662	21.26	5.9477	−7.0189	34.88	189.0578	22.21
	323.15 K		321.97 K			373.15 K		371.82 K	
0.1076	−0.3181	−45.81	4.2213	18.90	0.1076	−0.3431	−61.98	4.2418	18.01
0.2023	−0.5725	−41.32	7.9518	18.75	0.2023	−0.6134	−54.36	7.9051	18.32
0.3013	−0.8381	−39.01	11.7851	18.87	0.3013	−0.8912	−50.72	11.7036	18.49
0.5182	−1.3664	−33.03	20.1459	18.96	0.5182	−1.4539	−44.05	19.9706	18.66
0.6942	−1.7675	−28.10	26.6534	19.31	0.6942	−1.8767	−39.18	26.5271	18.88
1.0186	−2.4455	−21.71	38.6575	19.52	1.0186	−2.6168	−32.63	38.3473	19.25
1.9898	−4.0464	−4.81	72.7126	20.24	1.9898	−4.4108	−16.49	72.3033	19.94
3.9874	−5.8630	21.20	136.1161	21.26	3.9874	−6.7522	8.23	135.0668	21.14
5.9477	−6.3562	40.32	191.1964	21.98	5.9477	−7.8029	26.60	189.3363	21.99

$m(MgCl_2)$/ ($mol \cdot kg^{-1}$)	$10^2 \times [(c_p\varrho/c^*_{p,1}\varrho^*_1) - 1]$	$C_{p,2,\phi}$/ ($J \cdot K^{-1} \cdot mol^{-1}$)	$(\varrho - \varrho^*_1)$/ ($kg \cdot m^{-3}$)	$V_{2,\phi}$/ ($cm^3 \cdot mol^{-1}$)	$m(MgCl_2)$/ ($mol \cdot kg^{-1}$)	$10^2 \times [(c_p\varrho/c^*_{p,1}\varrho^*_1) - 1]$	$C_{p,2,\phi}$/ ($J \cdot K^{-1} \cdot mol^{-1}$)	$(\varrho - \varrho^*_1)$/ ($kg \cdot m^{-3}$)	$V_{2,\phi}$/ ($cm^3 \cdot mol^{-1}$)
	298.15 K		297.05 K			348.15 K		346.90 K	
0.4422	−2.9405	−205.7	33.8625	17.88	0.4422	−2.4950	−173.8	34.2163	15.76
0.8530	−5.2727	−182.3	63.5860	19.30	0.8530	−4.4988	−153.4	64.2358	17.34
1.1273	−6.7033	−170.9	82.7845	19.99	1.1273	−5.6824	−141.3	83.5428	18.19
1.6716	−9.1753	−148.8	119.0526	21.33	1.6716	−7.8759	−123.6	120.1714	19.65
2.1596	−11.0629	−131.5	149.9746	22.30	2.1596	−9.4977	−107.1	151.0151	20.90
3.5806	−15.2599	−90.85	231.5156	24.73	3.5806	−13.3038	−72.75	233.6312	23.44
5.1885	−18.6772	−60.20	312.1836	26.64	5.1885	−16.2135	−43.21	314.5267	25.64
	323.15 K		321.97 K			373.15 K		371.82 K	
0.4422	−2.6462	−179.3	33.7352	17.66	0.4422	−2.5392	−193.4	35.1540	12.43
0.8530	−4.7217	−156.1	63.3053	19.16	0.8530	−4.5071	−167.8	65.9152	14.32
1.1273	−6.0293	−147.0	82.5440	19.75	1.1273	−5.7044	−153.9	85.3052	15.65
1.6716	−8.3215	−128.6	118.8769	21.02	1.6716	−7.6562	−130.1	123.3005	16.94
2.1596	−10.1247	−114.3	149.7506	22.03	2.1596	−9.3310	−114.8	154.7229	18.44
3.5806	−14.0815	−77.65	231.4230	24.46	3.5806	−12.7263	−73.51	237.9254	21.68
5.1885	−17.2710	−48.95	312.2098	26.41	5.1885	−14.9783	−38.71	319.9636	24.18

$m(CaCl_2)$/ ($mol \cdot kg^{-1}$)	$10^2 \times [(c_p\varrho/c^*_{p,1}\varrho^*_1) - 1]$	$C_{p,2,\phi}$/ ($J \cdot K^{-1} \cdot mol^{-1}$)	$(\varrho - \varrho^*_1)$/ ($kg \cdot m^{-3}$)	$V_{2,\phi}$/ ($cm^3 \cdot mol^{-1}$)	$m(CaCl_2)$/ ($mol \cdot kg^{-1}$)	$10^2 \times [(c_p\varrho/c^*_{p,1}\varrho^*_1) - 1]$	$C_{p,2,\phi}$/ ($J \cdot K^{-1} \cdot mol^{-1}$)	$(\varrho - \varrho^*_1)$/ ($kg \cdot m^{-3}$)	$V_{2,\phi}$/ ($cm^3 \cdot mol^{-1}$)
	298.15 K		297.05 K			348.15 K		346.90 K	
1.4585	−8.4381	−144.0	119.7541	25.67	1.4585	−7.1457	−108.6	118.2091	25.53
1.9069	−10.2117	−124.1	152.7361	26.68	1.9069	−8.6038	−89.65	150.6594	26.65
2.8113	−12.8214	−87.32	214.5428	28.45	2.8113	−10.7111	−55.32	211.2589	28.62
3.5691	−14.0893	−58.67	261.9341	29.71	3.5691	−11.5941	−27.64	257.4460	30.06
4.7967	−14.8315	−17.46	330.8592	31.50	4.7967	−11.9346	11.19	324.1334	32.11
5.5407	−14.7778	3.78	368.4193	32.45	5.5407	−12.0696	27.98	360.1400	33.22
	323.15 K		321.97 K			373.15 K		371.82 K	
1.4585	−7.6321	−118.9	118.2489	26.19	1.4585	−6.9179	−110.1	119.1668	23.95
1.9069	−9.2534	−101.1	150.9062	27.16	1.9069	−8.2562	−90.09	152.2515	24.99
2.8113	−11.6344	−67.50	211.9816	28.92	2.8113	−10.0349	−50.34	212.1980	27.59
3.5691	−12.7288	−39.89	258.2926	30.31	3.5691	−10.7155	−21.31	258.2779	29.21
4.7967	−13.2473	−0.30	325.9506	32.14	4.7967	−11.0908	15.71	324.4888	31.53
5.5407	−13.2714	21.04	358.3712	33.83	5.5407	−11.3642	30.81	360.1716	32.77

[a] $(c_p\varrho/c^*_{p,1}\varrho^*_1)$ is the ratio of the volume heat capacity of the solution to that of water; $(\varrho - \varrho^*_1)$ is the difference between the density of the solution and that of water; $C_{p,2,\phi}/(J \cdot K^{-1} \cdot mol^{-1})$ is the apparent molar heat capacity; $V_{2,\phi}/(cm^3 \cdot mol^{-1})$ is the apparent molar volume.

Fisher), and NaCl (Baker). The solids were dried (at room temperature) under vacuum prior to preparation of the solutions by weight. Solutions prepared from the same solids were analyzed for chloride using the Mohr method (Vogel, 1961). Thus, the extent of hydration of the alkaline earth chlorides was determined. EDTA analyses (Vogel, 1961) were used to confirm the concentrations of $MgCl_2$(aq) and $CaCl_2$(aq), and agreement within 2% of the values from the chloride analyses was found. However, only the results of the more accurate chloride analyses (±0.5%) were used to calculate the solution concentrations.

Results and Discussion

Binary Solutions. Experimentally determined values of the quantities $\{(c_p\varrho/c^*_{p,1}\varrho^*_1) - 1\}$ and $(\varrho - \varrho^*_1)$ for the binary solutions NaCl(aq), $MgCl_2$(aq), and $CaCl_2$(aq) at 0.6 MPa are reported in Table 1 [ϱ is the solution density, ϱ^*_1 is the density of the pure solvent (water) at the temperature and pressure of the experiment, c_p is the specific heat capacity of the solution, and $c^*_{p,1}$ is the specific heat capacity of the pure solvent at the temperature and pressure of the experiment]. Values of the apparent molar heat capacity,

Table 2. Pitzer-Equation Fitting Parameters for Apparent Molar Heat Capacities (at P = 0.6 MPa)[a]

	NaCl(aq)	$MgCl_2$(aq)	$CaCl_2$(aq)
$10^{-5}p_1$/(J·mol^{-1})	−5.67378	−3.92360	14.24773
	(−6.32780)	(−4.30823)	(14.32424)
$10^{-3}p_2$/(J·K^{-1}·mol^{-1})	3.30305	1.00650	16.9394
	(3.70844)	(1.46808)	(−16.6666)
p_3/(J·K^{-2}·mol^{-1})	−4.98341	1.63661	61.73393
	(−5.60219)	(0.31385)	(59.89560)
10^2p_4/(J·K^{-3}·mol^{-1})	0	0	−7.324035
	(0)	(0)	(−7.041939)
10^5p_5/(J·K^{-4}·mol^{-1})	0	−1.66647	0
	(0)	(−1.40736)	(0)
10^2p_6/(K^{-1}·kg·mol^{-1})	−5.60469	−3.17140	−2.701822
	(−12.5992)	(−6.21455)	(−9.50646)
10^4p_7/(K^{-2}·kg·mol^{-1})	3.10963	1.69654	1.317303
	(7.05594)	(3.37135)	(5.38466)
10^7p_8/(K^{-3}·kg·mol^{-1})	−4.38847	−2.30979	−1.678444
	(−9.96596)	(−4.60905)	(−7.694386)
$10p_9$/(K^{-1}·kg·mol^{-1})	−0.580369	−4.48537	−10.51800
	(−0.256946)	(−0.92726)	(−3.49549)
10^3p_{10}/(K^{-2}·kg·mol^{-1})	0.163252	2.66028	6.289511
	(0.077317)	(0.70206)	(2.091627)
10^6p_{11}/(K^{-3}·kg·mol^{-1})	0	−3.72356	−9.126241
	(0)	(−1.03521)	(−2.917350)
10^3p_{12}/(K^{-1}·kg^2·mol^{-2})	(5.91194)	(2.43634)	(5.17068)
10^5p_{13}/(K^{-2}·kg^2·mol^{-2})	(−3.390152)	(−1.34085)	(−3.08994)
10^8p_{14}/(K^{-3}·kg^2·mol^{-2})	(4.86021)	(1.84078)	(4.56945)

[a] Values in parentheses are those obtained if terms for C^J_{MX} are included in the fit to eq 3.

$C_{p,2,\phi}$, are calculated from the experimental specific heat capacity measurements according to

$$C_{p,2,\phi}(T,m) = M_2c_p(T,m) + [c_p(T,m) - c^*_{p,1}(T)]/m \quad (1)$$

where M_2 is the molar mass of the solute, m is the molality of the solute (mol·kg^{-1}), and the standard molality is m° = 1 mol·kg^{-1}. The apparent molar volumes ($V_{2,\phi}$/m^3·mol^{-1}) are calculated from the density data using the equation

$$V_{2,\phi}(T,m) = M_2/\varrho(T,m) - [\varrho(T,m) - \varrho^*_1(T)]/[m\varrho^*_1(T)\varrho(T,m)] \quad (2)$$

The reference values for pure water, $c^*_{p,1}$ and ϱ^*_1, are calculated from the equations and computer program of Haar et al. (1983).

The values of the apparent molar heat capacities for NaCl(aq) differ only slightly (≤1.0 J·K^{-1}·mol^{-1} for 298.15 K and ≤4.6 J·K^{-1}·mol^{-1} for 373.15 K) from those based on the assessment of Archer (1992). The differences in $C_{p,2,\phi}$ are systematic, being mainly positive for temperatures ≤348.15 K and negative at 373.15 K. In general, the molar volumes are within 0.1 cm^3·mol^{-1} of the assessed values. The experimental apparent molar volumes of the $MgCl_2$(aq) and $CaCl_2$(aq) for 298.15 K are very similar to the fitted values of Monnin (1987); however, the experimental values for $CaCl_2$(aq) at 323.15 K are lower than the fitted values.

The array of $C_{p,2\phi}$ for all experimental temperatures and molalities for each simple electrolyte [including values for $MgCl_2$(aq) and $CaCl_2$(aq) reported previously by Saluja and LeBlanc (1987)] was used to fit Pitzer-type equations (Saluja et al., 1986b; Phutela et al., 1987) of the form

$$C_{p,2,\phi} = C^\infty_{p,2} + (\nu_{MX}|Z_MZ_X|A_J/2b)\ln(1 + bI^{1/2}) - 2\nu_M\nu_XRT^2m[\beta^{(0)J} + 2\beta^{(1)J}[1 - (1 + \alpha I^{1/2}) \times \exp(-\alpha I^{1/2})]/\alpha^2I] - 4\nu_M\nu_XRT^2m^2C^J \quad (3)$$

where

$$C^\infty_{p,2}(T)/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = p_1(\mathrm{K}/T) + p_2 + p_3(T/\mathrm{K}) + p_4(T/\mathrm{K})^2 + p_5(T/\mathrm{K})^3 \quad (4)$$

$$\beta^{(0)J}(T)/(\mathrm{kg\cdot mol^{-1}\cdot K^{-2}}) = p_6(\mathrm{K}/T) + p_7 + p_8(T/\mathrm{K}) \quad (5)$$

$$\beta^{(1)J}(T)/(\mathrm{kg\cdot mol^{-1}\cdot K^{-2}}) = p_9(\mathrm{K}/T) + p_{10} + p_{11}(T/\mathrm{K}) \quad (6)$$

$$C^J_{MX}(\mathrm{T})/(\mathrm{kg^2\cdot mol^{-2}\cdot K^{-2}}) = p_{12}(\mathrm{K}/T) + p_{13} + p_{14}(T/\mathrm{K}) \quad (7)$$

and obtain the parameters p_i. The parameters Z_M and Z_X

Table 3. Pitzer-Equation Fitting Parameters for Apparent Molar Volumes (at P = 0.6 MPa)[a]

	NaCl(aq)	$MgCl_2$(aq)	$CaCl_2$(aq)
$10^{-5}q_1$/(cm^3·K·mol^{-1})	−0.337401	0.0461413	2.165664
	(−0.354192)	(−0.3078636)	(2.053687)
$10^{-3}q_2$/(cm^3·mol^{-1})	0.218081	−1.81694	−1.853244
	(0.228374)	(0.141122)	(−1.786730)
q_3/(cm^3·K^{-1}·mol^{-1})	−0.296460	1.13617	4.54661
	(−0.311810)	(0.164067)	(4.44830)
10^3q_4/(cm^3·K^{-2}·mol^{-1})	0	−1.77934	0
	(0)	(−0.809971)	(0)
10^6q_5/(cm^3·K^{-3}·mol^{-1})	0	0	−7.891186
	(0)	(0)	(−7.888403)
q_6/(K·MPa^{-1}·kg·mol^{-1})	0.445998	0.266537	−5.09554
	(1.040162)	(2.579438)	(−2.04001)
10^3q_7/(MPa^{-1}·kg·mol^{-1})	−2.51718	−1.37968	49.73197
	(−5.96882)	(−22.08057)	(28.19189)
10^5q_8/(K^{-1}·MPa^{-1}·kg·mol^{-1})	0.367492	0.197283	−15.90828
	(0.879578)	(6.42521)	(−11.33624)
10^7q_9/(K^{-2}·MPa^{-1}·kg·mol^{-1})	0	0	1.677198
	(0)	(−0.626479)	(0.733918)
q_{10}/(K·MPa^{-1}·kg·mol^{-1})	1.02648	2.60616	0.8398230
	(0.90868)	(1.90295)	(1.593366)
10^3q_{11}/(MPa^{-1}·kg·mol^{-1})	−3.22226	−9.33690	−3.863747
	(−3.09954)	(−7.64325)	(−6.136556)
10^2q_{12}/(K·MPa^{-1}·kg^2·mol^{-2})	(−5.10160)	(0.1736267)	(−20.4985)
10^4q_{13}/(MPa^{-1}·kg^2·mol^{-2})	(2.99523)	(−0.2785783)	(12.5095)
10^7q_{14}/(K^{-1}·MPa^{-1}·kg^2·mol^{-2})	(−4.45397)	(−0.5897875)	(−18.9530)

[a] Values in parentheses are those obtained if terms for V^J_{MX} are included in the fit to eq 8.

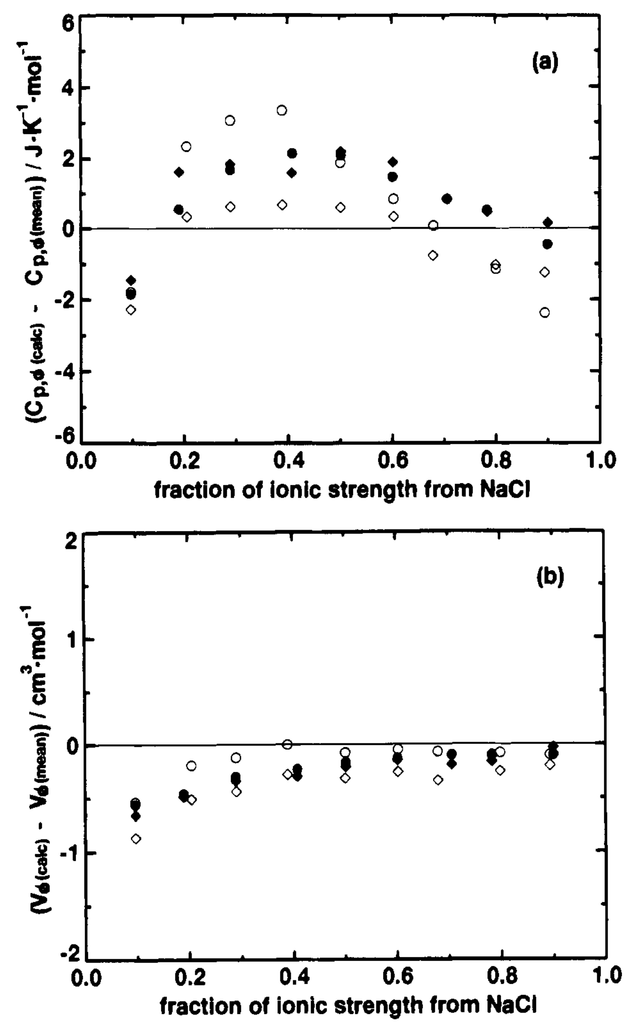

Figure 1. Differences between values of Y_ϕ(calc), based on Young's rule (eq 16), and experimentally determined values of Y_ϕ(mean) for the system [$MgCl_2$(aq) + NaCl(aq)] as a function of solution composition: (a) apparent molar heat capacities at 298.15 (circles) and 373.15 K (diamonds); (b) apparent molar volumes at 296.02 (circles) and 371.82 K (diamonds). The open symbols are for solutions with $I \approx 3$ mol·kg^{-1}; the solid symbols are for solutions with $I \approx 5$ mol·kg^{-1}.

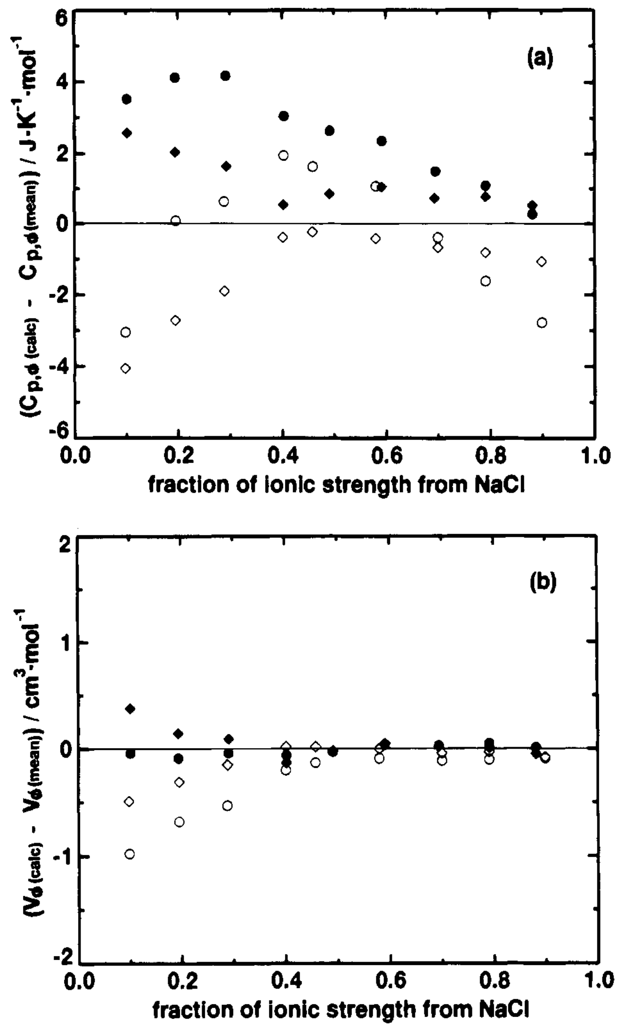

Figure 2. Differences between values of Y_ϕ(calc), based on Young's rule (eq 16), and experimentally determined values of Y_ϕ(mean) for the system [$CaCl_2$(aq) + NaCl(aq)] as a function of solution composition: (a) apparent molar heat capacities at 298.15 (circles) and 373.15 K (diamonds); (b) apparent molar volumes at 296.02 (circles) and 371.82 K (diamonds). The open symbols are for solutions with $I \approx 3$ mol·kg^{-1}; the solid symbols are for solutions with $I \approx 5$ mol·kg^{-1}.

are the algebraic valences of the cation and anion, respectively; ν_M and ν_X denote the amount of cations and anions ($\nu_{MX} \equiv \nu_M + \nu_X$); I is the molal ionic strength; and A_J/(J·kg$^{1/2}$·K^{-1}·mol$^{-3/2}$) is the theoretical limiting Debye–Hückel slope for partial molar heat capacities (Bradley and Pitzer, 1979). The parameters α and b are arbitrary constants in the Pitzer equations and for 1−1 and 1−2 or 2−1 electrolytes are assigned the values of 2.0 kg$^{1/2}$·mol$^{1/2}$ and 1.2 kg$^{1/2}$·mol$^{1/2}$, respectively.

A similar procedure was used for the array of apparent molar volumes where the Pitzer-type equations (Saluja et al., 1986b; Phutela et al., 1987) of the form

$$V_{2,\phi} = V_2^\infty + (\nu_{MX}|Z_M Z_X|A_V/2b)\ln(1 + bI^{1/2}) + 2\nu_M\nu_X RTm[\beta^{(0)V} + \beta^{(1)V}[1 - (1 + \alpha I^{1/2}) \times \exp(-\alpha I^{1/2})]/\alpha^2 I] + 4\nu_M\nu_X RTm^2 C^V \quad (8)$$

where

$$V_2^\infty(T)/(\text{cm}^3\cdot\text{mol}^{-1}) = q_1(\text{K}/T) + q_2 + q_3(T/\text{K}) + q_4(T/\text{K})^2 + q_5(T/\text{K})^3 \quad (9)$$

$$\beta^{(0)V}(T)/(\text{kg}\cdot\text{mol}^{-1}\cdot\text{MPa}^{-1}) = q_6(\text{K}/T) + q_7 + q_8(T/\text{K}) + q_9(T/\text{K})^2 \quad (10)$$

$$\beta^{(1)V}(T)/(\text{kg}\cdot\text{mol}^{-1}\cdot\text{MPa}^{-1}) = q_{10}(\text{K}/T) + q_{11} \quad (11)$$

$$C_{MX}^V(T)/(\text{kg}^2\cdot\text{mol}^{-2}\cdot\text{MPa}^{-1}) = q^{12}(\text{K}/T) + q^{13} + q^{14}(T/\text{K}) \quad (12)$$

were used to obtain the fitting parameters q_i. The parameter A_V/(cm^3·kg$^{1/2}$·mol$^{-3/2}$) is the theoretical limiting Debye–Hückel slope for partial molar volumes (Bradley and Pitzer, 1979).

Fitting parameters for the apparent molar heat capacities and volumes are given in Tables 2 and 3, respectively. It was found previously (Phutela et al., 1987) that terms involving the third virial coefficients, C_{MX}^J (for $C_{p,2,\phi}$) and C_{MX}^V (for $V_{2,\phi}$), representing triple-ion interactions, are not necessary for analyzing experimental results for $CaCl_2$(aq) and $SrCl_2$(aq) for experimental molalities as great as 1 mol·kg^{-1} ($I = 3$ mol·kg^{-1}). In the present work, calculations were done both including and excluding the C_{MX}^J and C_{MX}^V terms. However, the relatively sparse data for temperatures between 320 and 380 K are not adequate to permit physically meaningful values to be obtained for the highly correlated p_i and q_i parameters. For example, for the $C_{p,2,\phi}$ values for $CaCl_2$(aq), the average difference between the experimental and calculated values drops only

Table 4. Experimental Values of the Quantities[a] $[(c_p\varrho/c^*_{p,1}\varrho^*_1) - 1]$, $(\varrho - \varrho^*_1)$, $C_{p,\phi}$(mean), and V_ϕ(mean) for the Ternary Solutions [$MgCl_2$(aq) + NaCl(aq)], [$CaCl_2$(aq) + NaCl(aq)], and [$MgCl_2$(aq) + $CaCl_2$(aq)] at 0.6 MPa

m(NaCl)/(mol·kg^{-1})	m($MgCl_2$)/(mol·kg^{-1})	I^b/(mol·kg^{-1})	$10^2 \times [c_p\varrho/c^*_{p,1}\varrho^*_1 - 1]$	$C_{p,\phi}$(mean)/(J·K^{-1}·mol^{-1})	$(\varrho - \varrho^*_1)$/(kg·m^{-3})	V_ϕ(mean)/(cm^3·mol^{-1})	$10^2 \times [c_p\varrho/c^*_{p,1}\varrho^*_1 - 1]$	$C_{p,\phi}$(mean)/(J·K^{-1}·mol^{-1})	$(\varrho - \varrho^*_1)$/(kg·m^{-3})	V_ϕ(mean)/(cm^3·mol^{-1})
			298.15 K		296.02 K		323.15 K		321.97 K	
0.27673	0.85919	2.854	−5.7407	−132.0	73.2235	20.20	−5.1452	−109.4	72.5377	20.42
0.57650	0.74403	2.809	−5.7230	−103.3	76.2285	19.83	−5.1486	−83.68	75.2157	20.26
0.83121	0.67907	2.868	−5.8208	−83.42	80.7837	19.80	−5.2537	−65.72	79.4549	20.38
1.10605	0.57852	2.842	−5.7477	−64.95	83.4928	19.78	−5.2392	−49.95	81.8823	20.46
1.42384	0.47243	2.841	−5.6944	−47.87	87.3189	19.77	−5.2176	−34.70	85.4152	20.53
1.71500	0.37686	2.846	−5.6273	−34.81	90.9317	19.74	−5.1884	−23.16	88.7374	20.57
1.97659	0.31069	2.909	−5.6489	−25.36	95.3535	19.81	−5.2681	−15.42	92.8986	20.67
2.32142	0.19507	2.907	−5.5408	−14.04	99.3112	19.81	−5.1947	−5.20	96.5741	20.71
2.64920	0.10483	2.964	−5.4878	−5.05	104.2753	19.86	−5.1990	2.47	101.2493	20.79
0.41533	1.28240	4.263	−7.8983	−113.1	106.3609	21.21	−7.2096	−95.62	105.4469	21.39
0.84983	1.20620	4.468	−8.0720	−82.94	115.7071	21.20	−7.4298	−68.93	114.4593	21.49
1.28230	1.05250	4.440	−7.8740	−60.44	120.1015	20.98	−7.3071	−48.76	118.3670	21.45
1.82740	0.88557	4.484	−7.6868	−37.98	126.9845	20.92	−7.2048	−28.79	124.8594	21.46
2.31090	0.76402	4.603	−7.5705	−22.42	134.7045	20.90	−7.1908	−15.27	132.1095	21.53
2.80870	0.61800	4.663	−7.3298	−8.80	141.1963	20.87	−7.0421	−3.28	138.2861	21.53
3.31630	0.46054	4.698	−7.0511	2.76	147.1337	20.86	−6.8827	6.70	143.8320	21.55
3.82160	0.35377	4.883	−6.8811	12.33	155.8756	20.92	−6.8324	14.98	152.0687	21.67
4.43890	0.16500	4.934	−6.4819	22.76	162.8782	20.94	−6.5343	24.32	158.8357	21.67
			348.15 K		346.90 K		373.15 K		371.82 K	
0.27673	0.85919	2.854	−5.0079	−109.5	73.0483	19.40	−5.0562	−122.0	74.6702	17.16
0.57650	0.74403	2.809	−5.0211	−83.52	75.5120	19.56	−5.1168	−95.17	76.8958	17.83
0.83121	0.67907	2.868	−5.1666	−66.38	79.5690	19.88	−5.2709	−76.76	80.8834	18.42
1.10605	0.57852	2.842	−5.1642	−50.57	81.8518	20.12	−5.2853	−59.89	82.9612	18.94
1.42384	0.47243	2.841	−5.1917	−35.82	85.0768	20.38	−5.3875	−45.79	86.1410	19.38
1.71500	0.37686	2.846	−5.2268	−25.22	88.2095	20.54	−5.4526	−34.70	89.1348	19.70
1.97659	0.31069	2.909	−5.3114	−17.39	92.3161	20.67	−5.5537	−25.85	92.8769	20.07
2.32142	0.19507	2.907	−5.3025	−7.75	95.7064	20.83	−5.6008	−16.50	96.2797	20.29
2.64920	0.10483	2.964	−5.3593	−0.56	100.2280	20.95	−5.7123	−9.42	100.7209	20.49
0.41533	1.28240	4.263	−6.9392	−93.94	106.3316	20.36	−6.8732	−102.1	108.6716	18.26
0.84983	1.20620	4.468	−7.1591	−67.46	115.2227	20.70	−7.2406	−77.15	117.3577	19.06
1.28230	1.05250	4.440	−7.1214	−48.76	118.9144	20.85	−7.2300	−57.53	120.8473	19.51
1.82740	0.88557	4.484	−7.1043	−29.62	124.9414	21.12	−7.2742	−37.80	126.5451	20.10
2.31090	0.76402	4.603	−7.1702	−16.96	131.9605	21.30	−7.4240	−25.32	133.4108	20.46
2.80870	0.61800	4.663	−7.1205	−5.84	137.8359	21.42	−7.4489	−14.13	139.0404	20.74
3.31630	0.46054	4.698	−7.0312	3.78	143.0725	21.54	−7.4109	−3.94	143.7901	21.07
3.82160	0.35377	4.883	−7.0540	11.46	151.3003	21.67	−7.4938	4.02	151.6688	21.33
4.43890	0.16500	4.934	−6.8869	20.14	157.5760	21.78	−7.4235	12.19	158.1381	21.44

m(NaCl)/(mol·kg^{-1})	m($CaCl_2$)/(mol·kg^{-1})	I^b/(mol·kg^{-1})	10^2·$[c_p\varrho/c^*_{p,1}\varrho^*_1 - 1]$	$C_{p,\phi}$(mean)/(J·K^{-1}·mol^{-1})	$(\varrho - \varrho^*_1)$/(kg·m^{-3})	V_ϕ(mean)/(cm^3·mol^{-1})	10^2·$[c_p\varrho/c^*_{p,1}\varrho^*_1 - 1]$	$C_{p,\phi}$(mean)/(J·K^{-1}·mol^{-1})	$(\varrho - \varrho^*_1)$/(kg·m^{-3})	V_ϕ(mean)/(cm^3·mol^{-1})
			298.15 K		296.02 K		323.15 K		321.97 K	
0.2879	0.8863	2.947	−6.0883	−121.8	84.1438	24.28	−5.4658	−96.10	82.5049	25.24
0.5896	0.8111	3.023	−6.2158	−94.83	88.9399	23.21	−5.5957	−72.69	87.0236	24.20
0.8655	0.7109	2.998	−6.1293	−74.80	90.7692	22.44	−5.5232	−55.01	88.6517	23.45
1.2023	0.6675	3.205	−6.3709	−57.36	99.3775	21.81	−5.8124	−41.24	96.9378	22.81
1.4514	0.5718	3.167	−6.2396	−45.48	100.5862	21.36	−5.7298	−31.37	98.0154	22.36
1.7590	0.4254	3.035	−5.9668	−32.61	99.8639	20.82	−5.4488	−19.09	97.1555	21.82
2.0666	0.2946	2.950	−5.7308	−21.10	100.2122	20.45	−5.3364	−10.66	97.3751	21.44
2.3763	0.2088	3.003	−5.6587	−11.80	104.0694	20.27	−5.3380	−3.25	101.0319	21.25
2.6621	0.09947	2.961	−5.4768	−4.00	105.3592	20.03	−5.2081	3.38	102.1807	21.00
0.4917	1.4612	4.875	−8.9306	−97.62	135.9896	24.66	−8.1181	−77.01	133.4808	25.51
0.9398	1.3052	4.855	−8.7010	−71.31	138.6158	23.85	−7.9475	−54.05	135.8324	24.72
1.4359	1.1681	4.940	−8.5198	−48.47	144.3294	23.16	−7.8593	−34.77	141.2564	24.03
1.9492	0.9659	4.847	−8.0801	−29.57	145.6802	22.53	−7.5746	−19.37	142.3834	23.39
2.3891	0.8210	4.852	−7.8133	−16.76	148.9663	22.12	−7.3814	−8.28	145.4658	22.97
2.8826	0.6640	4.875	−7.5246	−4.98	153.1457	21.72	−7.1481	2.30	149.3522	22.57
3.3623	0.4942	4.845	−7.1713	5.09	155.7616	21.41	−6.9469	10.25	151.7128	22.26
3.9938	0.3510	5.047	−6.8951	16.10	164.6963	21.24	−6.8186	19.31	160.3703	22.07
4.4528	0.2001	5.053	−6.5699	23.16	167.6371	21.10	−6.5603	25.56	163.2215	21.90
			348.15 K		346.90 K		373.15 K		371.82 K	
0.2879	0.8863	2.947	−5.2188	−89.91	82.2178	24.90	−5.1762	−97.87	83.4955	23.01
0.5896	0.8111	3.023	−5.3721	−68.07	86.6401	23.98	−5.3486	−75.38	87.8710	22.42
0.8655	0.7109	2.998	−5.3453	−51.85	88.1305	23.35	−5.3763	−60.18	89.4968	21.90
1.2023	0.6675	3.205	−5.6573	−39.26	96.4026	22.72	−5.7168	−46.57	97.4762	21.64
1.4514	0.5718	3.167	−5.6303	−30.36	97.2728	22.39	−5.7245	−37.87	98.3438	21.40
1.7590	0.4254	3.035	−5.4552	−20.08	96.3220	21.91	−5.6266	−28.32	97.2737	21.07
2.0666	0.2946	2.950	−5.3429	−11.36	96.4165	21.59	−5.5880	−20.25	97.3137	20.86
2.3763	0.2088	3.003	−5.4252	−5.10	99.9251	21.45	−5.6950	−13.78	100.8581	20.77
2.6621	0.09947	2.961	−5.3442	0.85	101.0732	21.20	−5.7045	−8.34	101.7206	20.68
0.4917	1.4612	4.875	−7.6967	−69.95	132.9092	25.27	−7.4986	−72.69	134.2010	23.90
0.9398	1.3052	4.855	−7.5936	−48.86	135.0382	24.62	−7.4961	−52.99	136.1948	23.52
1.4359	1.1681	4.940	−7.5842	−31.38	140.2480	24.03	−7.5563	−36.01	141.2838	23.14
1.9492	0.9659	4.847	−7.4123	−17.80	141.1793	23.48	−7.4557	−22.42	141.7496	22.86
2.3891	0.8210	4.852	−7.3343	−8.29	144.0905	23.11	−7.4515	−13.86	144.9332	22.48
2.8826	0.6640	4.875	−7.2232	0.82	147.8559	22.74	−7.4603	−5.81	148.7200	22.18
3.3623	0.4942	4.845	−7.0917	8.11	150.1523	22.45	−7.4197	1.07	150.8620	21.98
3.9938	0.3510	5.047	−7.0832	16.31	158.5236	22.30	−7.5317	8.78	159.1215	21.92
4.4528	0.2001	5.053	−6.9353	21.70	161.2850	22.14	−7.5163	13.47	161.7022	21.84

Table 4 (Continued)

$m(MgCl_2)$/ ($mol{\cdot}kg^{-1}$)	$m(CaCl_2)$/ ($mol{\cdot}kg^{-1}$)	I^b/ ($mol{\cdot}kg^{-1}$)	$10^2{\cdot}[c_p\varrho/c^*_{p,1}\varrho^*_1 - 1]$	$C_{p,\phi}$(mean)/ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$(\varrho - \varrho^*_1)$/ ($kg{\cdot}m^{-3}$)	V_ϕ(mean)/ ($cm^3{\cdot}mol^{-1}$)	$10^2{\cdot}[c_p\varrho/c^*_{p,1}\varrho^*_1 - 1]$	$C_{p,\phi}$(mean)/ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$(\varrho - \varrho^*_1)$/ ($kg{\cdot}m^{-3}$)	V_ϕ(mean)/ ($cm^3{\cdot}mol^{-1}$)
			298.15 K		296.02 K		323.15 K		321.97 K	
0.09630	0.8777	2.922	−6.0841	−166.1	80.8630	24.30	−5.4550	−136.5	79.6387	25.02
0.1979	0.7906	2.966	−6.1203	−165.6	80.9522	23.86	−5.4915	−136.9	79.8541	24.45
0.2737	0.6568	2.792	−5.7831	−168.5	75.5279	23.28	−5.1936	−140.2	74.5464	23.81
0.3792	0.6233	3.008	−6.1425	−165.6	80.0578	23.17	−5.5043	−137.4	79.0853	23.63
0.4734	0.4725	2.838	−5.8090	−168.8	74.6025	22.41	−5.2205	−141.6	73.7854	22.78
0.5636	0.3960	2.879	−5.8644	−169.0	74.7234	22.07	−5.2509	−141.4	73.9926	22.34
0.6308	0.2767	2.723	−5.5507	−171.3	69.8183	21.45	−4.9804	−144.6	69.2181	21.63
0.7343	0.1857	2.760	−5.5930	−172.0	69.8424	20.89	−5.0280	−146.0	69.2432	21.05
0.8340	0.09200	2.778	−5.5822	−171.1	69.1213	20.58	−5.0259	−146.6	68.7684	20.49
0.1604	1.4451	4.817	−9.0084	−136.0	128.3525	26.00	−8.1950	−112.2	126.4063	26.71
0.2923	1.2591	4.654	−8.7856	−140.1	123.0483	25.44	−7.9835	−115.8	121.1739	26.15
0.4591	1.0946	4.661	−8.7648	−141.0	121.5031	24.96	−7.9820	−117.8	119.8778	25.52
0.5979	0.9587	4.670	−8.7469	−141.6	120.3194	24.55	−7.9469	−118.0	118.7068	25.10
0.7474	0.7648	4.537	−8.5273	−144.7	115.5558	23.89	−7.7520	−122.0	114.2919	24.25
0.8703	0.5907	4.383	−8.2716	−147.6	110.3868	23.33	−7.5139	−124.8	109.2613	23.64
1.0352	0.4429	4.434	−8.3191	−147.8	109.9455	22.91	−7.5678	−125.8	108.9372	23.14
1.1634	0.3025	4.398	−8.2371	−149.2	107.7472	22.42	−7.4988	−127.5	106.7962	22.62
1.3075	0.1411	4.346	−8.1156	−150.2	104.8355	21.95	−7.3901	−129.4	104.2064	21.95
			348.15 K		346.90 K		373.15 K		371.82 K	
0.09630	0.8777	2.922	−5.1726	−129.0	79.7471	24.18	−5.0942	−135.5	80.6680	22.22
0.1979	0.7906	2.966	−5.2198	−130.0	79.9787	23.60	−5.1487	−137.1	80.9818	21.58
0.2737	0.6568	2.792	−4.9378	−133.6	74.7299	22.89	−4.9127	−144.3	76.0559	20.44
0.3792	0.6233	3.008	−5.2479	−132.0	79.3997	22.61	−5.2020	−141.4	80.7541	20.26
0.4734	0.4725	2.838	−4.9763	−136.6	74.1913	21.63	−4.9506	−147.3	75.5767	19.15
0.5636	0.3960	2.879	−5.0430	−138.4	74.4737	21.13	−5.0318	−150.1	75.9659	18.55
0.6308	0.2767	2.723	−4.7819	−141.3	69.6350	20.46	−4.7937	−157.3	71.7744	17.06
0.7343	0.1857	2.760	−4.8281	−143.8	69.9400	19.59	−4.8433	−157.3	71.5025	16.88
0.8340	0.09200	2.778	−4.8376	−145.2	69.5135	18.99	−4.8706	−160.0	71.2145	16.14
0.1604	1.4451	4.817	−7.6217	−100.9	126.5161	26.00	−7.3242	−102.3	128.1983	24.08
0.2923	1.2591	4.654	−7.4387	−104.1	120.9635	25.63	−7.1776	−107.6	123.1195	23.38
0.4591	1.0946	4.661	−7.4389	−107.4	120.2018	24.67	−7.2033	−110.0	121.7193	22.83
0.5979	0.9587	4.670	−7.4471	−109.6	119.3350	24.07	−7.2390	−113.8	121.2182	22.00
0.7474	0.7648	4.537	−7.2905	−113.6	114.6790	23.36	−7.0930	−119.2	116.9551	20.98
0.8703	0.5907	4.383	−7.0823	−117.6	109.9210	22.55	−6.9321	−124.2	112.0579	20.21
1.0352	0.4429	4.434	−7.1692	−120.8	110.0651	21.76	−6.9727	−125.9	112.1397	19.48
1.1634	0.3025	4.398	−7.0943	−122.4	107.9828	21.20	−6.9504	−129.0	110.0677	18.90
1.3075	0.1411	4.346	−7.0249	−125.7	105.5183	20.44	−6.9354	−134.3	107.7664	18.01

[a] $(c_p\varrho/c^*_{p,1}\varrho^*_1)$ is the ratio of the volume heat capacity of the solution to that of water; $(\varrho - \varrho^*_1)$ is the difference between the density of the solution and that of water; $C_{p,\phi}$(mean/($J{\cdot}K^{-1}{\cdot}mol^{-1}$) is the experimental apparent molar heat capacity; V_ϕ(mean)/($cm^3{\cdot}mol^{-1}$) is the experimental apparent molar volume. [b] I/($mol{\cdot}kg^{-1}$) is the ionic strength of the solution.

from ±2.2 to ±2.0 on addition of the extra three coefficients of the C^J_{MX} term. In particular, the coefficients related to $\beta^{(0)Y}$ and C^Y_{MX} are strongly correlated. There are sufficient literature data to determine C^J_{MX} and C^V_{MX} for NaCl(aq) and possibly $CaCl_2$(aq), but a total reanalysis of the reported values is beyond the scope of the present work. As will be shown later, the use of different sets of parameters has only a marginal effect on the calculations involving mixed-electrolyte solutions. For the sake of simplicity, the C^J_{MX} and C^V_{MX} terms are not used in most of the present analysis.

Ternary Solutions. Values of $[(c_p\varrho/c^*_{p,1}p^*_1) - 1]$ and $(\varrho - \varrho^*_1)$ for the mixtures [NaCl(aq) + $CaCl_2$(aq)], [NaCl(aq) + $MgCl_2$(aq)], and [$CaCl_2$(aq) + $MgCl_2$(aq)] at 0.6 MPa are reported in Table 4. Experimental apparent molar heat capacities and volumes Y_ϕ (mean) [this is ${}^\phi Y^{mean}$ as used by Hovey and Hepler (1990)] are calculated from the specific heat capacities and densities according to

$$C_{p,\phi}(\text{mean}) = [c_p(1 + m_2M_2 + m_3M_3) - c^*_{p,1}]/(m_2 + m_3) \quad (13)$$

and

$$V_\phi(\text{mean}) = [(1 + m_2M_2 + m_3M_3)/\varrho - 1/\varrho^*_1]/(m_2 + m_3) \quad (14)$$

[These equations were given incorrectly in Lemire et al. (1993); however, the Y_ϕ(mean) values in that paper were calculated with the correct equations as above.]

For apparent molar heat capacities or volumes of mixed electrolytes, Young's rule (Young and Smith, 1954) can be written

$$Y_{\phi,\Sigma} = \sum_{i=2}^{n}(m_i/\sum_{i=2}^{n}m_i)Y_{\phi,i} + \delta \quad (15)$$

where all $Y_{\phi,i}$ values apply at the total ionic strength of the solution. For apparent molar heat capacities, and to a slightly lesser extent for apparent molar volumes, Young's rule was recently shown to hold with $\delta = 0$—at least for a limited number of ternary (two electrolyte) cases. Therefore, for the systems investigated in the present study, values [Y_ϕ(calc)] are also calculated solely from the values for the pure electrolytes according to

$$Y_\phi(\text{calc}) = [m_2/(m_2 + m_3)]Y_{2,\phi} + [m_3/(m_2 + m_3)Y_{3,\phi}] \quad (16)$$

where $Y_{i,\phi}$ is the extensive property (apparent molar heat capacity or apparent molar volume) for electrolyte i of molar mass M_i and molality m_i. The values of $Y_{i,\phi}$ are those for the total ionic strength of the solution. The differences [Y_ϕ(calcd) − Y_ϕ(mean)] are plotted in Figures 1−3.

The apparent molar heat capacities for the mixtures, as calculated using Young's rule, are generally within 4 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ of the experimentally determined values. As

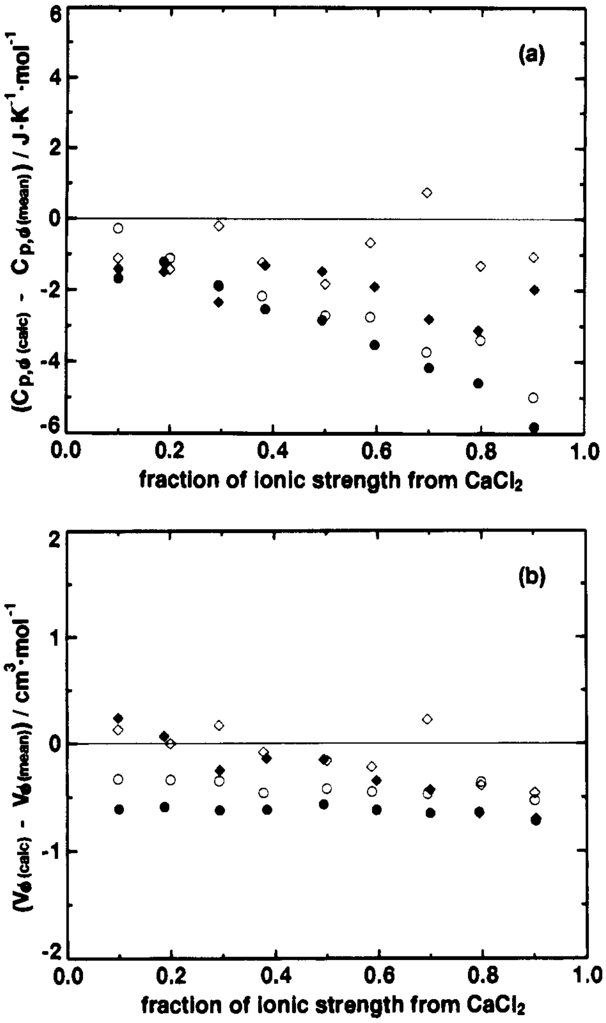

Figure 3. Differences between values of Y_ϕ(calc), based on Young's rule (eq 16), and experimentally determined values of Y_ϕ(mean) for the system [$MgCl_2$(aq) + $CaCl_2$(aq)] as a function of solution composition: (a) apparent molar heat capacities at 298.15 (circles) and 373.15 K (diamonds): (b) apparent molar volumes at 296.02 (circles) and 371.82 K (diamonds). The open symbols are for solutions with $I \approx 3$ mol·kg^{-1}; the solid symbols are for solutions with $I \approx 5$ mol·kg^{-1}.

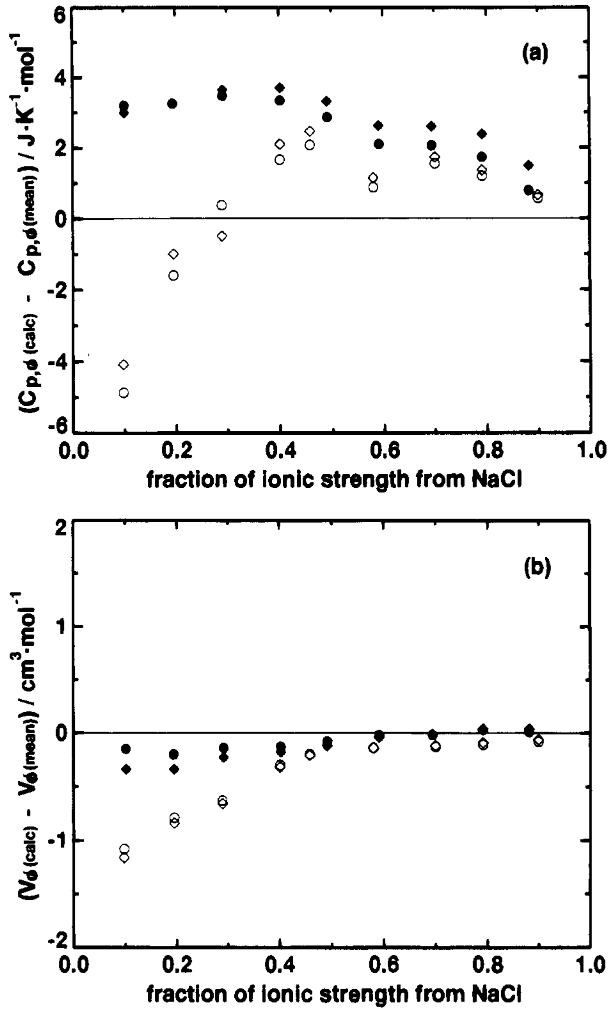

Figure 4. Differences between values of Y_ϕ(calc), based on Young's rule (eq 16), and experimentally determined values of Y_ϕ(mean) for the system [$CaCl_2$(aq) + NaCl(aq)] as a function of solution composition: (a) apparent molar heat capacities at 323.15 K for C^J_{MX} included in the analysis of the binary data (diamonds) and for C^J_{MX} omitted (circles); (b) apparent molar volumes at 321.97 K for C^V_{MX} included (diamonds) and for C^J_{MX} omitted (circles). The open symbols are for solutions with $I \approx 3$ mol·kg^{-1}; the solid symbols are for solutions with $I \approx 5$ mol·kg^{-1}.

the uncertainties in the experimental values are expected to be between ±1 and ±4 J·K^{-1}·mol^{-1} (Saluja et al., 1992), this agreement is satisfactory for most purposes. For the apparent molar volumes, the uncertainties in the experimental values are estimated to be between ±0.05 and ±0.2 cm^3·mol^{-1} (Saluja et al., 1992). As can be seen from Figures 1 to 3, the apparent molar volumes calculated using Young's rule differ significantly from the experimental values. The ternary apparent molar values for $I \approx 3$ and 5 mol·kg^{-1} appear to be equally well estimated from the binary data.

The inclusion of V^J_{MX} and C^J_{MX} terms in the least-squares fitting of the equations to the binary data resulted only in small changes to the [Y_ϕ(calc) − Y_ϕ(mean)] values. Figure 4 shows values for the [$CaCl_2$(aq) + NaCl(aq)] system at 50 °C. The effect of using these terms involving the third virial coefficients is comparable to the effect of selecting different numbers of terms in the expressions for $\beta^{(0)Y}$ and $\beta^{(1)Y}$ (eqs 5, 6, 10, and 11) and is less than the experimental uncertainties.

Alternatively, since these electrolytes have a common anion [Cl^-(aq)], their solution properties can be analyzed using a Pitzer treatment where eqs 3 and 8 now become

$$C_{p,\phi,\Sigma} = \sum_{i=2}^{3} x_i(C^\infty_{p,i} + (\nu_i|Z_M Z_X|A_J/2b)\ln(1 + bI^{1/2}) - 2\nu_M\nu_X RT^2 m_i[\beta_i^{(0)J} + 2\beta_i^{(1)J}[1 - [1 + \alpha I^{1/2}] \times \exp[-\alpha I^{1/2}]]/\alpha^2 I]) - 2RT^2(m_M m_{M'}\theta^J_{MM'} + m_M m_{M'} m_X \psi^J_{MM'X}) \quad (17)$$

and

$$V_{\phi,\Sigma} = \sum_{i=2}^{3} x_i(V_i^\infty + (\nu_i|Z_M Z_X|A_V/2b)\ln(1 + bI^{1/2}) + 2\nu_M\nu_X RT m_{MX}[\beta_i^{(0)V} + \beta_i^{(1)V}[1 - [1 + \alpha I^{1/2}] \times \exp[-\alpha I^{1/2}]]/\alpha^2 I]) + 2RT(m_M m_{M'}\theta^V_{MM'} + m_M m_{M'} m_X \psi^V_{MM'X}) \quad (18)$$

where $\theta^Y_{MM'}$ and $\psi^Y_{MM'X}$ are the binary and ternary interaction parameters for property Y, respectively, M and M′ are the two ions having the same charge, X is the common ion, and $x_i = m_i(m_2 + m_3)$.

The parameters $\theta^Y_{MM'}$ and $\psi^Y_{MM'X}$ can be obtained by assuming that $Y_{\phi,\Sigma} \simeq Y_\phi$(mean) and that the difference

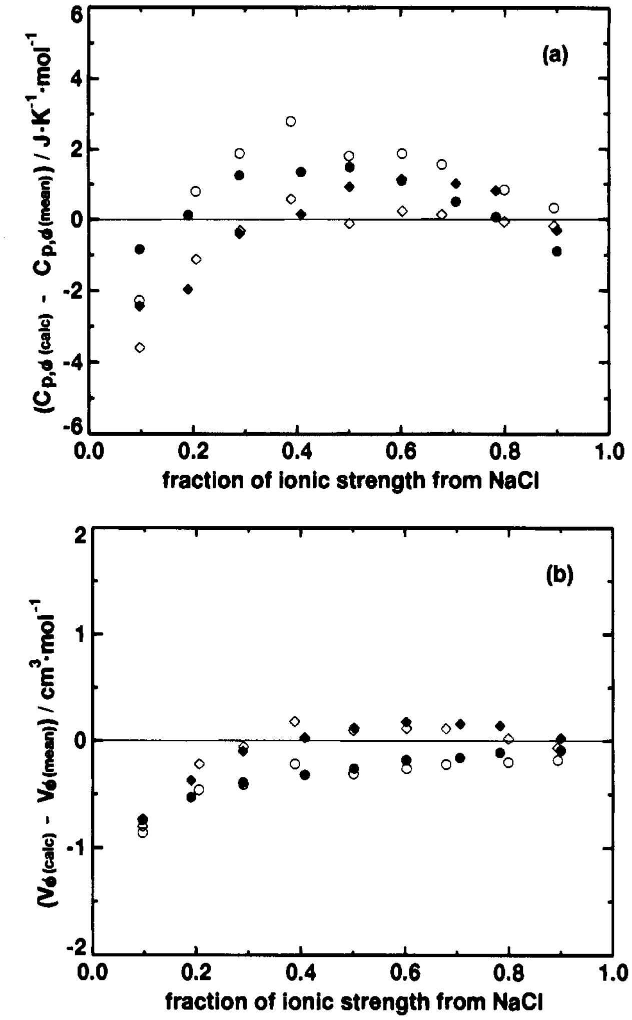

Figure 5. Differences between values of Y_ϕ(calc) and experimentally determined values of Y_ϕ(mean) for the system [$MgCl_2$(aq) + NaCl(aq)] as a function of solution composition and calculated using Young's rule (circles) and Pitzer's equations (diamonds): (a) apparent molar heat capacities at 348.15 K; (b) apparent molar volumes at 346.90 K. The open symbols are for solutions with $I \approx 3$ mol·kg^{-1}; the solid symbols are for solutions with $I \approx 5$ mol·kg^{-1}. For the Pitzer equation treatment Y_ϕ(calc) is $Y_{\phi,\Sigma}$.

between the values predicted by eqs 17 and 18 with the interaction parameters set to zero ($Y^0_{\phi,\Sigma}$) and the experimentally evaluated values is given by eqs 13–15. Thus,

$$[C^0_{p,\phi,\Sigma} - C_{p,\phi}(\text{mean})]/2RT^2 m_M m_{M'} = \theta^J_{MM'} + m_X/2\psi^J_{MM'X} \tag{19}$$

and

$$[V_\phi(\text{mean}) - V^0_{\phi,\Sigma}]/2RTm_M m_{M'} = \theta^V_{MM'} + m_X/2\psi^V_{MM'X} \tag{20}$$

where for the systems in this study $m_X = m[Cl^-(aq)]$. The values obtained for the binary and ternary interaction parameters calculated using eqs 19 and 20 and the mean apparent molar heat capacities and volumes (Table 4) can be found in Tables 5 and 6, respectively. The parameters used to calculate $C^0_{p,\phi,\Sigma}$ and $V^0_{\phi,\Sigma}$ were those given in Tables 2 and 3, respectively. For these systems, the value of $\psi^Y_{MM'X}$ was found to be statistically significant only for the heat capacities and then only for low temperatures.

Since there are few studies on the interaction parameters for the heat capacities and the volumes of mixed-salt systems, a comparison of literature values is limited. In theory, use of an ion interaction model should result in

Table 5. Values for the Pitzer Binary ($\theta^J_{MM'}$) and Ternary ($\psi^J_{MM'}$) Interaction Parameters That Result from Fitting Equation 19 to the Apparent Molar Heat Capacity Data for the Ternary Solutions [$CaCl_2$(aq) + NaCl(aq)] and [$MgCl_2$(aq) + NaCl(aq)] at 0.6 MPa

T/K	$10^5\theta^J_{MM'}$/ (kg·mol^{-1}·K^{-2})	$10^5\psi^J_{MM'X}$/ (kg^2·mol^{-2}·K^{-2})
	$MgCl_2$(aq) + NaCl(aq), I = 3.0 mol·kg^{-1}	
298.15	−4.70	2.38
323.15	−2.37	1.43
348.15	−0.06	
373.15	0.01	
	$CaCl_2$(aq) + NaCl(aq), I = 3.0 mol·kg^{-1}	
298.15	−8.33	4.87
323.15	−5.94	4.01
348.15	−2.18	1.58
373.15	−1.87	1.34
	$MgCl_2$(aq) + NaCl(aq), I = 5.0 mol·kg^{-1}	
298.15	−4.00	1.46
323.15	−1.67	0.48
348.15	−0.14	
373.15	−0.06	
	$CaCl_2$(aq) + NaCl(aq), I = 5.0 mol·kg^{-1}	
298.15	−3.03	0.97
323.15	−1.65	0.34
348.15	−1.11	
373.15	−0.17	

Table 6. Values for the Pitzer Binary Interaction Parameters ($\theta^V_{MM'}$) That Result from Fitting Equation 20 to the Apparent Molar Volume Data for the Ternary Solutions [$CaCl_2$(aq) + NaCl(aq)] and [$MgCl_2$(aq) + NaCl(aq)] at 0.6 MPa

	$10^5\theta^V_{MM'}$/(MPa^{-1}·mol·kg^{-1})			
I/(mol·kg^{-1})	296.02 K	321.97 K	346.90 K	371.82 K
	[$CaCl_2$(aq) + NaCl(aq)]			
3.0	−2.26	−1.01	−0.22	−0.54
5.0	−1.02	−0.43	−0.02	1.53
	[$MgCl_2$(aq) + NaCl(aq)]			
3.0	−2.05	−0.81	−0.63	−0.15
5.0	−1.39	−0.73	−0.36	−0.11

parameters that are independent of ionic strength (Pitzer, 1983). The present data are too limited for a thorough quantitative analysis. However, Tables 5 and 6 show some trends in the values of interaction parameters that can be compared to trends in the interaction parameters obtained through activity or osmotic coefficients. Pitzer (1975) has found that, for activity coefficients at 298.15 K, $\theta_{NaCa} = \theta_{NaMg}$ and $\psi_{NaCa} > \psi_{NaMg}$. Similar features are noted here where at I = 3.0 mol·kg^{-1}, $\theta_{NaCa} < \theta_{NaMg}$, and $\psi_{NaCa} > \psi_{NaMg}$, while at I = 5.0 mol·kg^{-1}, $\theta_{NaCa} \simeq \theta_{NaMg}$ and ψ_{NaMg} is only slightly larger than ψ_{NaCa}. For the H^+(aq)/Ca^{2+}(aq) and H^+(aq)/Mg^{2+}(aq) systems (Khoo, 1986), where the degree of interaction between the ions is greater due to the smaller size of the proton, it is found that $\theta_{HCa} < \theta_{HMg}$ and $\psi_{HCa} > \psi_{HMg}$. Therefore, it appears that Mg^{2+}(aq), being a smaller ion than Ca^{2+}(aq), exerts a stronger influence on the ion–ion binary interactions at the lower temperatures and ionic strengths, while at the higher temperatures or ionic strengths the effect of cation size on the binary and ternary interactions is diminished.

The values for $\theta^J_{MM'X}$ and $\psi^J_{MM'X}$ obtained here are comparable in magnitude and sign to the values obtained by Conti et al. (1986, 1989) for SO_4^{2-}(aq)/Cl^-(aq) interactions. Their studies indicated the ternary mixing parameter for this pair was not statistically significant at these higher temperatures and, at T < 373, $-\theta^J_{MM'}$ for their 2:1 mixture also decreased as the temperature increased. Both of these features also are noted here.

The fits of eq 20 to the apparent molar volume data indicated the ternary mixing parameter was statistically insignificant for both the [$CaCl_2$(aq) + NaCl(aq)] and [$MgCl_2$(aq) + NaCl(aq)] systems. Therefore, Table 6 shows only the binary mixing parameter for these systems at the various temperatures and ionic strengths. The values given here are in general agreement with the values given by Kumar and Atkinson (1983) for θ^V_{NaCa}, but there is one noticeable difference. For their measurements at $I = 5$ mol·kg^{-1}, the value of θ^V_{NaCa} decreases as temperature increases, while at $I = 2$ and 1 mol·kg^{-1} this dependence is reversed. In the present work, θ^V_{NaCa} increases as the temperature increases at $I = 3$ and 5 mol·kg^{-1}, in agreement with the observations of Kumar and Atkinson at the lower ionic strengths. Although in this study and those of Kumar et al. (1982) and Kumar and Atkinson (1983) the higher order electrostatic terms have been neglected, these higher order terms were included in the study of Oakes et al. (1990). Their values of θ^V_{NaCa} are also in general agreement with the values from the present study. Oakes et al. (1990) evaluated their binary mixing parameters using apparent molar volume data obtained over a wide variety of ionic strengths. Therefore, their value of θ_{NaCa} represents an "average" value for this range. This value also increases with increasing temperature.

From this study, we conclude that Young's rule and the Pitzer treatment are able to predict empirically the behavior of the apparent molar volume and apparent molar heat capacity data for mixed-salt systems equally well. The Pitzer treatment is not substantially better than the Young's rule analysis for predicting the apparent molar heat capacities and volumes of ternary electrolyte solutions from data for the binary solutions. For example, as shown in Figure 5 for the [NaCl(aq) + MgCl(aq)] system (apparent molar heat capacities at 323.15 K, apparent molar volumes at 321.97 K), the differences are not identical but do show similar spreads and trends. This is true even though the Y_ϕ(calc) from the Pitzer treatment is identical to $Y_{\phi,\Sigma}$ (i.e., it includes the fitted $\theta^Y_{MM'}$, not just the parameters for the two single-electrolyte systems).

A sensitivity analysis of both the Pitzer expression and Young's rule indicates ionic strength terms dominate in both equations. Therefore, it is not surprising that both Young's rule and Pitzer treatment are in agreement. Given the simplicity of Young's rule, this method would be preferable if one needs only to predict the behavior of these properties for a given system.

Note Added in Proof: A minor calculation error (<0.5% in a concentration value for one of the [$MgCl_2$(aq) + NaCl(aq)] solutions) was discovered during checking of the page proofs, and has been corrected in the tables. Correction of this error results in Young's rule and Pitzer's equation values for $I = 3$ and $x = 0.389$ that are slightly lower than those shown in Figures 1 and 5. There are also minor effects on the positions of all points represented by open diamonds in Figure 5. The trends shown in the figures and the conclusions based on them are not affected.

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