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Pressure–Volume–Temperature Properties of Aqueous Mixed Electrolyte Solutions: NaCl + $BaCl_2$ from 25 to 140 °C

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The densities of aqueous electrolyte mixtures of NaCl + $BaCl_2$ have been measured from 25 to 140 °C at constant total ionic strengths of 0.5, 1.0, 2.5, and 4.5 mol kg^{-1}. The mean apparent molal volumes calculated from the experimental density values have been treated using the Pitzer equations, and the ion interaction parameters of mixing have been evaluated. The required apparent molal volumes for the pure aqueous $BaCl_2$ and NaCl have been obtained from our earlier work and that of Rogers and Pitzer, respectively.

Introduction

Pressure–volume–temperature (PVT) properties of aqueous mixed electrolyte solutions are useful for many applications in geology, oil recovery, oceanography, and geothermal brines. They are important in physical chemistry and engineering to develop models to represent the thermodynamic properties of multicomponent electrolyte solutions. These properties are also important in understanding the nature of solute–solute and solute–solvent interactions.

K. S. Pitzer and co-workers (*1–5*) have developed a set of equations which allows the calculation of the thermodynamic properties of single and multicomponent electrolyte solutions not only at high concentrations but also at high temperatures and pressures. These equations contain certain adjustable parameters to be evaluated from the data on single electrolyte systems and simple electrolyte mixtures. Once these parameters are known, the thermodynamic properties of more complex electrolyte solutions can be predicted very easily. Therefore, in our earlier work (*6*) we have reported the PVT properties of aqueous $BaCl_2$ solution from 15 to 140 °C and at pressures from 1 to 200 bar. Now, we are extending our investigation to the PVT properties of the aqueous mixed electrolyte system NaCl + $BaCl_2$ at constant total ionic strengths of 0.5, 1.0, 2.5, and 4.5 mol kg^{-1} and at 25–140 °C. The experiments were carried out at 25–55 °C at a pressure of 1 bar and 80–140 °C at a pressure of 20 bar.

Experimental Section

All solutions were prepared by mass using distilled water which was passed through a NANOPure (Barnstead) ion-exchange apparatus. ACS reagent grade NaCl and $BaCl_2$ were obtained from Fisher Scientific and Aldrich, respectively, and used without further purification. The prepared solutions were then filtered using a millipore 0.45-μm filter to remove any insoluble contaminants. The concentrations of the stock solutions were determined to within ±0.03% by gravimetric analysis for chloride.

The solution densities were measured over the temperature ranges 25–55 and 80–140 °C by a vibrating-tube densimeter, Mettler/Paar DMA 60, with a DMA 602 remote glass cell and a DMA 512 remote stainless steel cell, respectively. The temperature of the densimeter cell was measured with a Leeds and Northrup platinum resistance thermometer and a Muller bridge connected to a Leeds and Northrup dc null detector (model 9828). The experimental temperature was maintained constant over the temperature range from 25 to 55 °C to ±0.005 °C and from 80 to 140 °C to ±0.01 °C. The pressure was maintained with a Circle Seal back-pressure regulator and measured with an in-line Heise gauge to a precision of ±1 bar.

The relative densities were calculated using the equation given below:

$$\Delta d = d - d_0 = B(\tau^2 - \tau_0^2) \tag{1}$$

where d and d_0 are the densities of the unknown and reference solutions. τ and τ_0 are the periods of vibrational frequency of the tube containing the unknown and the reference solution, respectively. Water densities at the experimental temperatures and pressures were calculated using the equation of state of water from the work of Haar et al. (*7*). The calibration of the instrument constant, B, at each temperature and pressure was obtained from the known concentrations of NaCl solutions using the density data of Millero et al. (*8, 9*) and a comprehensive review of aqueous NaCl data by Rogers et al. (*10*). This procedure is the same for the low-temperature DMA 602 cell and the high-temperature DMA 512 cell.

The stock solutions were diluted by mass with deionized water to an appropriate concentration for the preparation of the equal ionic strength NaCl and $BaCl_2$ solutions. The mixture solution at constant total ionic strength is made by mixing different compositions (ionic strength fractions) of aqueous NaCl and $BaCl_2$ solutions. The ionic strength fraction of $BaCl_2$ solution is given by

$$y_B = \frac{3m_B}{m_A + 3m_B} \tag{2}$$

where m_A and m_B are the molalities of NaCl and $BaCl_2$ solutions, respectively. The experimental relative densities (Δd) calculated from eq 1 at given ionic strength fractions of aqueous $BaCl_2$ solution are summarized in Table 1 at constant total ionic strengths of 0.5, 1.0, 2.5, and 4.5 mol kg^{-1} from 25 to 55 °C at a pressure of 1 bar and from 80 to 140 °C at a pressure of 20 bar.

The relative densities from duplicate measurements were found to be precise to ±10 ppm at lower temperatures (25–55 °C) and ±40 ppm at higher temperatures (80–140 °C).

Results and Discussion

The Pitzer expression for the excess volume of the mixture (*11*) is the pressure derivative of the excess Gibbs energy at

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Table 1. Relative Densities of Aqueous NaCl + $BaCl_2$ from 25 to 140 °C (from 80 to 140 °C at a Pressure of 20 bar)

	$10^3(d - d_0)/(\text{g cm}^{-3})$							
y_B	25 °C	35 °C	45 °C	55 °C	80 °C	100 °C	120 °C	140 °C
				I = 0.5 mol kg^{-1}				
0.0000	20.047	19.699	19.412	19.268	19.122	19.290	19.588	20.138
0.1002	21.057	20.724	20.434	20.301	20.143	20.279	20.527	21.041
0.2004	22.069	21.748	21.459	21.336	21.162	21.266	21.468	21.943
0.3001	23.076	22.766	22.478	22.363	22.179	22.249	22.405	22.841
0.4001	24.085	23.788	23.502	23.395	23.200	23.236	23.345	23.741
0.5021	25.116	24.828	24.546	24.447	24.242	24.241	24.306	24.658
0.5996	26.102	25.822	25.545	24.454	25.239	25.203	25.223	25.537
0.6991	27.106	26.838	26.564	26.481	26.254	26.184	26.161	26.432
0.7986	28.109	27.855	27.582	27.508	27.273	27.170	27.099	27.331
0.8998	29.127	28.889	28.617	28.554	28.306	28.167	28.051	28.243
1.0000	30.137	29.914	29.643	29.592	29.330	29.160	28.994	29.149
				I = 1.0 mol kg^{-1}				
0.0000	39.093	38.528	37.964	37.642	37.274	37.603	38.118	39.067
0.0999	41.134	40.580	40.006	39.709	39.324	39.579	40.014	40.882
0.2001	43.181	42.639	42.058	41.783	41.380	41.564	41.915	42.707
0.3000	45.225	44.693	44.107	43.855	43.436	43.547	43.816	44.531
0.4002	47.278	46.755	46.165	45.933	45.499	45.541	45.724	46.359
0.4999	49.326	48.811	48.215	48.004	47.555	47.526	47.624	48.183
0.5999	51.379	50.871	50.273	50.086	49.617	49.521	49.531	50.019
0.6999	53.434	52.937	52.336	52.170	51.686	51.517	51.442	51.852
0.7999	55.489	55.006	54.399	54.258	53.758	53.517	53.357	53.689
0.9001	57.552	57.081	56.466	56.335	55.839	55.523	55.278	55.531
1.0000	59.610	59.151	58.532	58.447	57.915	57.524	57.198	57.371
				I = 2.5 mol kg^{-1}				
0.0000	92.312	91.001	89.706	89.156	88.387	88.777	89.901	91.737
0.1000	97.543	96.236	94.945	94.389	93.553	93.835	94.776	96.460
0.1997	102.768	101.474	100.178	99.622	98.708	98.900	99.646	101.186
0.3000	108.038	106.758	105.455	104.906	103.920	104.008	104.559	105.956
0.4001	113.309	112.042	110.739	110.195	109.135	109.124	109.479	110.731
0.5001	118.583	117.337	116.025	115.492	114.355	114.254	114.406	115.521
0.6001	123.873	122.647	121.330	120.809	119.595	119.399	119.531	120.323
0.6999	129.161	127.960	126.639	126.132	124.836	124.548	124.297	125.128
0.8001	134.486	133.305	131.983	131.485	130.121	129.732	129.281	129.965
0.9001	139.811	138.649	137.332	136.844	135.408	134.922	134.272	134.807
1.0000	145.147	143.998	142.695	142.209	140.712	140.117	139.275	139.655
				I = 4.5 mol kg^{-1}				
0.0000	154.953	153.090	151.114	150.234	148.828	149.857	151.163	153.884
0.1000	164.476	162.580	160.533	159.643	158.123	158.882	159.773	162.379
0.2001	174.051	172.144	170.029	169.132	167.482	167.989	168.428	170.952
0.3002	183.676	181.764	179.571	178.682	176.902	177.158	177.160	179.584
0.3999	193.317	191.400	189.134	188.260	186.352	186.352	185.894	188.241
0.5001	203.045	201.150	198.801	197.943	195.900	195.656	194.739	197.011
0.6000	212.794	210.926	208.488	207.670	205.490	205.005	203.606	205.807
0.7000	222.619	220.757	218.243	217.461	215.163	214.428	212.550	214.683
0.8000	232.495	230.643	228.065	227.311	224.900	223.895	221.552	223.610
0.9000	242.419	240.585	237.945	237.223	234.706	233.447	230.614	232.600
1.0000	252.405	250.571	247.894	247.188	244.588	243.044	239.745	241.643

constant temperature [$V^{ex} = (\mathrm{d}G^{ex}/\mathrm{d}P)_T$] and is given by

$$V^{ex}/(wRT) = \frac{A_v}{RT}\left(\frac{I}{b}\right)\ln(1 + b\sqrt{I}) + 2\Sigma_c\Sigma_a m_c m_a[B^v_{ca} + (\Sigma m_c z_c)C^v_{ca}] + \Sigma_c\Sigma_{c'} m_c m_{c'}[2\theta^v_{cc'} + \Sigma_a m_a \psi^v_{cc'a}] + \Sigma_a\Sigma_{a'} m_a m_{a'}[2\theta^v_{aa'} + \Sigma_c m_c \psi^v_{aa'c}] \quad (3)$$

where w is the number of kilograms of water, I is the ionic strength of the electrolyte mixture, R is the gas constant (83.1441 cm^3 bar mol^{-1} K^{-1}), A_v is the Pitzer–Debye–Huckel parameter for the apparent molal volumes and $C^v = C^{\phi v}/(2|Z_M Z_X|^{1/2})$. The parameter b is a constant whose value is 1.2 kg$^{1/2}$ mol$^{-1/2}$ for all types of 1–1, 1–2, 2–1, 2–2, and 1–3 electrolytes and assumed to be independent of pressure and temperature. The parameters B^v and C^v are temperature- and pressure-dependent terms. B^v is a function of ionic strength and is given by

$$B^v = \beta^{(0)v} + 2\beta^{(1)v}\{1 - (1 + \alpha\sqrt{I})\exp(-\alpha\sqrt{I})\}/(\alpha^2 I) \quad (4)$$

where α is a constant equal to 2 kg$^{1/2}$ mol$^{-1/2}$ and assumed to be independent of temperature and pressure. $\beta^{(0)v}$, $\beta^{(1)v}$, and C^v are adjustable parameters specific to each electrolyte and can be evaluated from pure electrolyte data only. The parameters θ^v and ψ^v are the differences of the interactions between like charged species and can be obtained from common ion mixtures. The molalities of a cation and anion are m_c and m_a, respectively. For a single electrolyte solution eq 3 reduces to

$$V^{ex}/(wRT) = \frac{A_v}{RT}\left(\frac{I}{b}\right)\ln(1 + b\sqrt{I}) + 2(\nu_M\nu_X)m^2\left\{B^v_{MX} + \frac{m}{2}(\nu_M\nu_X)^{1/2}C^{\phi v}_{MX}\right\} \quad (5)$$

where ν_M and ν_X are the stoichiometric parameters of M and X ions, respectively, and $\nu = \nu_M + \nu_X$.

Data Treatment for Aqueous $BaCl_2$ Solution. The total volume of a molal solution is given by

$$V = 1000v_w + m\bar{V}^\circ_{MX} + V^{ex} \quad (6)$$

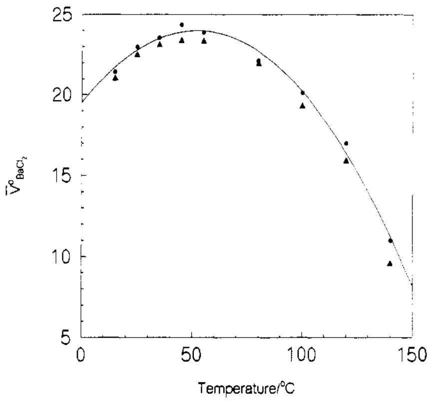

Figure 1. Variation of $\bar{V}^{\circ}_{BaCl_2}$ with temperature: ▲, Redlich–Meyer equation; ●, according to eq 10.

The apparent molal volume of the binary solution is

$$\phi_v = \frac{(V - 1000v_w)}{m} \quad (7)$$

where v_w is the specific volume of water ($cm^3\ g^{-1}$). Substitution of eqs 5 and 6 into eq 7 gives

$$\phi_v = \bar{V}^{\circ}{}_{MX} + \nu|Z_M Z_X|\frac{A_v}{2b}\ln(1 + b\sqrt{I}) + 2(\nu_M\nu_X)RTm\left\{B^v_{MX} + \frac{m}{2}(\nu_M\nu_X)^{1/2}C^{\phi v}_{MX}\right\} \quad (8)$$

According to Rogers and Pitzer (*10*), to obtain reliable adjustable parameters, it is necessary to evaluate the coefficients using the specific volume (v) form of the equation

$$v = \{1000v_w/(1000 + Mm)\} + m\phi_v/(1000 + Mm) \quad (9)$$

Substitution of eq 8 into eq 9 gives $v - [1000v_w/(1000 + Mm)] - m(\mathrm{DHT})/(1000 + Mm) =$

$$\frac{m}{1000 + Mm}\{\bar{V}^{\circ}{}_{MX} + f(1)\beta^{(0)v} + f(2)\beta^{(1)v} + f(3)C^{\phi v}\} \quad (10)$$

where

$$\mathrm{DHT} = \nu|Z_M Z_X|\frac{A_v}{2b}\ln(1 + b\sqrt{I})$$

$$f(1) = 2RT(\nu_M\nu_X)m$$

$$f(2) = 4RT(\nu_M\nu_X)m\{1 - (1 + \alpha\sqrt{I})\exp(-\alpha\sqrt{I})\}/(\alpha^2 I)$$

$$f(3) = (\nu_M\nu_X)^{3/2}m^2RT$$

The A_v values under given experimental conditions were calculated from the equations of Bradley and Pitzer (*12*). The adjustable parameter $\beta^{(1)v}$ is very sensitive to the accuracy of the experimental data. If the accuracy is lower than ±25 ppm, the $\beta^{(1)v}$ term cannot be evaluated from experimental data accurately. Rogers and Pitzer (*10*) also found that, in preliminary isothermal and isobaric calculations, this term could not be evaluated from the volumetric data. Therefore, in our calculations we set $\beta^{(1)v} = 0$. The remaining parameters $\bar{V}^{\circ}$, $\beta^{(0)v}$, and $C^{\phi v}$ were evaluated by a procedure using a weighted nonlinear least-squares method for each set of experimental data from 15 to 140 °C and from 1 to 200 bar of pressure. The $\bar{V}^{\circ}$ parameters evaluated using this method are in fair agreement with the values evaluated from the Redlich–Meyer equation. The $\bar{V}^{\circ}$ values evaluated using the Redlich–Meyer equation were taken from our earlier work (*6*). Figure 1 shows the comparison between $\bar{V}^{\circ}$ values calculated from eq 10 and those calculated from the Redlich–Meyer equation. The partial molal volumes of aqueous $BaCl_2$ solution at infinite dilution, $\bar{V}^{\circ}$, go through a maximum between 40 and 60 °C and rapidly decrease at higher temperatures. This is due to the increasing importance of the electrostriction contribution at higher temperatures due to the breakdown of the water structure. The parameters $\beta^{(0)v}$ and $C^{\phi v}$ obtained at each experimental temperature and pressure are fitted to the equations given below:

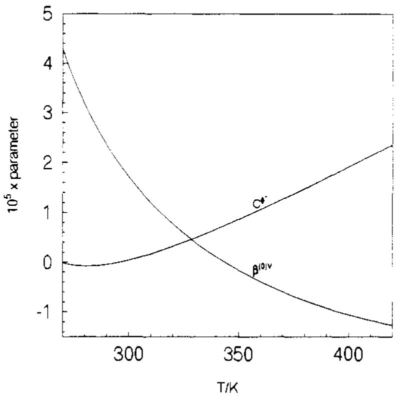

Figure 2. Variation of the Pitzer parameters ($\beta^{(0)v}$ and $C^{\phi v}$) for aqueous $BaCl_2$ solution from 25 to 140 °C.

Table 2. Values of the Adjustable Parameters of Equations 11 and 12

B_1	$8.670\ 239 \times 10^{-5}$	C_1	$-8.240\ 557 \times 10^{-5}$
B_2	$2.154\ 935 \times 10^{-3}$	C_2	$7.142\ 877 \times 10^{-4}$
B_3	$-4.977\ 946 \times 10^{-7}$	C_3	$2.433\ 938 \times 10^{-7}$
B_4	$5.583\ 802 \times 10^{-10}$	C_4	-1.0253×10^{-5}
B_5	$8.880\ 197 \times 10^{-6}$	C_5	$3.241\ 308 \times 10^{-4}$
B_6	$-2.432\ 534 \times 10^{-8}$	C_6	$2.072\ 931 \times 10^{-6}$

$$\beta^{(0)v} = B_1 + B_2/(T - 227) + B_3T + B_4T^2 + (P - P_0)\{B_5 + B_6T\} \quad (11)$$

$$C^{\phi v} = C_1 + C_2/(T - 227) + C_3T + (P - P_0)\{C_4 + C_5/(T - 227) + C_6T\} \quad (12)$$

where T is the temperature in kelvins, P is the pressure in bars, and $P_0 = 1.013\ 25$ bar. The plots of $\beta^{(0)v}$ and $C^{\phi v}$ *vs* temperature are shown in Figure 2. $\beta^{(0)v}$ decreases with increasing temperature while $C^{\phi v}$ increases with temperature. This behavior is normal for most electrolytes. The experimental density data at 1 atm of pressure cover from 25 to 55 °C. The data from 80 to 140 °C were obtained at 20, 100, and 200 bar of pressure only. So the data from 80 to 140 °C are lacking at 1 atm of pressure, and the data from 25 to 55 °C are lacking at higher pressures. Therefore, the experimental data from 15 to 55 °C at 1 bar of pressure and from 80 to 140 °C at 20 bar of pressure were only treated using eqs 11 and 12. The fitting values B_1 to B_6 and C_1 to C_6 are given in Table 2. Using these values, the experimental densities are reproduced with an uncertainty of ±150 ppm. If the entire data set is treated using the above eqs 11 and 12, the reproducibility in experimental densities is ±358 ppm. But the reproducibility in experimental density data sets at a given temperature and pressure with individual $\beta^{(0)v}$ and $C^{\phi v}$ values evaluated using eq 10 is ±22 ppm. The large differences in the reproducibility in experimental data and those obtained from the adjustable parameters (B_1 to B_6 and C_1 to C_6) were due to a lack of density measurements in the entire range of temperature and pressure. It is also important to use these equations within the experimental temperature and pressure ranges only. This is because extrapolated values may not give correct density estimations.

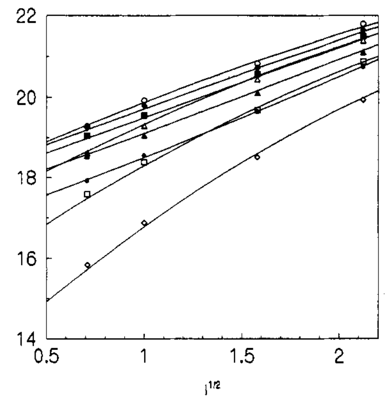

Figure 3. Variation of apparent molal volumes of aqueous NaCl solution from 25 to 140 °C: ●, 25; ▲, 35; ■, 45; ◆, 55; ○, 80; △, 100; □, 120; ◇, 140 °C.

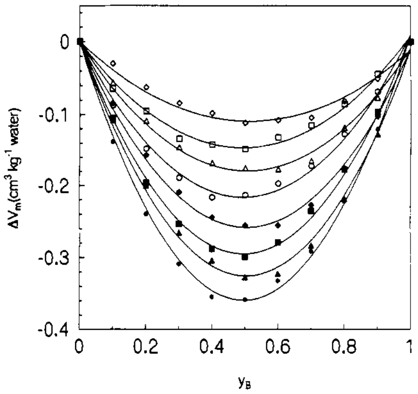

Figure 4. Variation of the volume of mixing for the system NaCl + $BaCl_2$ + H_2O from 25 to 140 °C with I = 4.5 mol kg^{-1}: ●, 25; ▲, 35; ■, 45; ◆, 55; ○, 80; △, 100; □, 120; ◇, 140 °C.

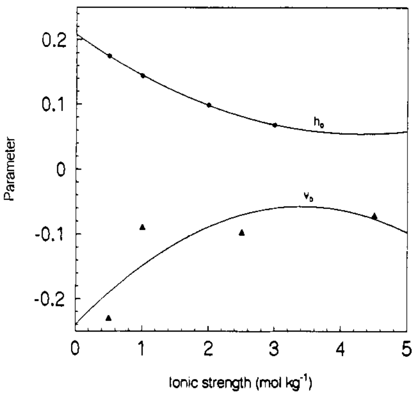

Figure 5. Variation of interaction parameters (h_0 and v_0) with ionic strength for the system NaCl + $BaCl_2$ + H_2O at 25 °C ($h_0 = 0.208 - 0.071I + 0.008I^2$, $v_0 = -0.240 + 0.107I - 0.016I^2$).

The densities and apparent molal volumes of aqueous NaCl solution from 25 to 140 °C were obtained from the work of Rogers and Pitzer. At $y_B = 0$ the concentration of aqueous $BaCl_2$ is zero. Therefore, the density values obtained are those of pure aqueous NaCl solution. The apparent molal values calculated from the density measurements are shown in Figure 3. The smooth lines are the apparent molal volumes of aqueous NaCl solution obtained from the equations of Rogers and Pitzer (*10*). This figure clearly shows good agreement between our work and that of Rogers and Pitzer.

Data Treatment for Mixed Electrolyte Solution. The mean apparent molal volumes, $\phi_{v(mix)}$, of the ternary mixture are given by

$$\phi_{v(mix)} = \frac{M_T}{d} - \frac{1000(d - d_0)}{d d_0 m_T} \tag{13}$$

where $m_T = m_A + m_B$, $M_T = (M_A m_A + M_B m_B)/m_T$, and m_A, M_A, m_B, and M_B are the molalities and formula weights of electrolytes A and B, respectively.

The volume changes for mixing of the electrolytes A and B were calculated from the apparent molal volumes of the mixture and pure electrolytes using the relation given below:

$$\Delta V_m = m_T \phi_{v(mix)} - m_A \phi_v^{(A)} - m_B \phi_v^{(B)} \tag{14}$$

The volume changes for mixing of aqueous NaCl and $BaCl_2$ solutions at low ionic strengths (0.5 and 1.0 mol kg^{-1}) are very small. They are also negative at all the ionic strengths and temperatures studied in the present investigation. Desnoyers et al. (*13*) used the Gurney (*14*) cosphere model to explain ion–water interactions in electrolyte mixtures. According to them, when two structure makers (aqueous NaCl and $BaCl_2$) are mixed, a repulsion results with a resulting decrease in volume. This is true in the present system, and the volume change is found to be negative at all the ionic strengths and temperatures. The volume change increases in magnitude with increasing ionic strength of the mixture. It is also clear that increasing the concentration of the electrolyte mixture increases the nonideality of the electrolyte solution. The largest negative values were obtained at an ionic strength of 4.5 mol kg^{-1}. These negative values are due to cation–cation interactions between Na^+ and Ba^{2+} ions taking place in the mixed electrolyte solution. The volume change is gradually decreased in magnitude with increasing temperature. This means the relative interaction between Na^+ and Ba^{2+} ions decreases with increasing temperature. As an example, the variation of the volume change for mixing at a constant total ionic strength of 4.5 mol kg^{-1} with temperature is shown in Figure 4. The volume of mixing is very sensitive to the temperature. This kind of behavior was also noticed in the aqueous system NaCl + $MgCl_2$ in the work of Connaughton et al. (*15*).

In most of Millero's papers, the volume change for mixing the major sea salts was fitted to the equation $\Delta V_m = y(1 - y)I^2[\nu_0 + \nu_1(1 - 2y)]$, and the ν_0 and ν_1 parameters were evaluated. These parameters are related to the interaction of like charged ions. A similar equation was used for heats of mixing by Wood and Ghamkhar (*16*) as $\Delta H_m = RTI^2 y(1 - y)[h_0 + h_1(1 - 2y)]$. The heat of mixing values for the present system were also reported by these researchers at 25 °C. The parameter h_0 is a measure of the magnitude of the interaction between Na^+ and Ba^{2+} ions in the mixed electrolyte solution. In the present study, we have plotted ν_0 and h_0 *vs* the ionic strength of the system at 25 °C in Figure 5. The ν_0 values gradually increase with increasing ionic strength whereas h_0 values gradually decrease with increasing ionic strength. These two parameters are symmetrically related to each other along the abscissa. The parameter h_0 is the temperature derivative of the free energy of the system whereas ν_0 is the pressure derivative.

The volume changes for mixing the aqueous NaCl and $BaCl_2$ solutions (ΔV_m) were also calculated using the Pitzer equation given below:

$$\Delta V_m = V_{mix}^{ex} - y_A V_A^{ex} - y_B V_B^{ex} \tag{15}$$

Here V_A^{ex} and V_B^{ex} refer to the pure electrolytes NaCl and $BaCl_2$ at the ionic strength of the electrolyte mixture, and y_A and y_B, respectively, are the ionic strength fractions of electrolyte NaCl and $BaCl_2$ solutions in the mixture ($y_A + y_B = 1$).

According to Connaughton et al. (*17*), the volume change could also be obtained by substitution of eqs 3 and 5 into eq fig6

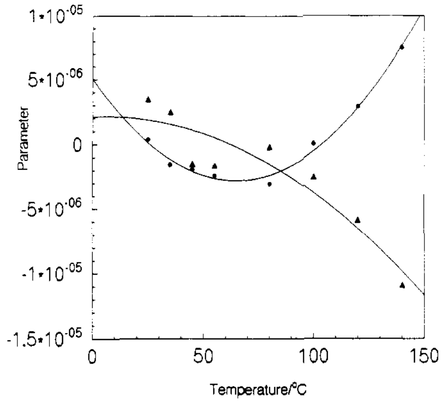

Figure 6. Variation of θ^{v}_{NaBa} and ψ^{v}_{NaBaCl} with temperature: ●, θ^{v}_{NaBa}; ▲, ψ^{v}_{NaBaCl}.

Table 3. Pitzer Mixing Parameters (θ^{v} and ψ^{v}) for the System NaCl + $BaCl_2$ + H_2O

T/°C	$\theta^{v} \times 10^6$	$\psi^{v} \times 10^6$	T/°C	$\theta^{v} \times 10^6$	$\psi^{v} \times 10^6$
25	0.421	3.521	80	−3.005	−0.145
35	−1.506	2.548	100	0.006	−2.512
45	−1.863	−1.454	120	2.911	−5.857
55	−2.386	−1.583	140	7.509	−10.87

15, leading to the following equation in terms of the Pitzer pure and mixed electrolyte parameters:

$$\Delta V_m/(wRTI^2) = y_B(1 - y_B)\{-(2/3)B^{v}_{NaCl} - (2/9)(6 - y_B)IC^{v}_{NaCl} + (2/9)B^{v}_{BaCl_2} + (2/27)(5 - y_B)IC^{v}_{BaCl_2} + (2/3)\theta^{v}_{NaBa} + (1/9)(3 - y_B)I\psi^{v}_{NaBaCl}\} \quad (16)$$

The terms B^{v} and C^{v} are calculated from pure electrolyte data. The remaining terms θ^{v} and ψ^{v} are evalulated from the present work. At low ionic strengths the volume of mixing is very low. In fact, no mixing parameters are needed at the lower ionic strengths. But, at higher ionic strengths (>1 mol kg^{-1}) mixing parameters are definitely needed. To reduce the number of parameters, we have made an attempt to evaluate the mixing parameters independent of ionic strength. For this, the experimental data at all the ionic strengths and at a given temperature were treated using eq 16, and common θ^{v} and ψ^{v} parameters were evaluated. In this case we have tried each set of data at the experimental temperature and pressures (i) without θ^{v} and ψ^{v} terms, (ii) with only the θ^{v} term, and finally (iii) with both terms θ^{v} and ψ^{v}. Inclusion of only the θ^{v} term improved the RMSD values a little bit. But, using both θ^{v} and ψ^{v} terms yields a significant improvement in the fit. The mixing parameters (θ^{v} and ψ^{v}) evalulated at all the temperatures are summarized in Table 3. Figure 6 shows the variation of these mixing parameters (θ^{v} and ψ^{v}) with temperature. The binary mixing parameter θ^{v} first decreases with temperature and then gradually increases. The ternary mixing parameter ψ^{v} just decreases with increasing temperature.

Finally it can be said that the densities of mixed electrolyte solutions are predicted more accurately using the mixed interaction parameters (θ^{v} and ψ^{v}) evalulated from the Pitzer formalism together with the pure electrolyte parameters.

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