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Densities and Apparent Molal Volumes of Aqueous $BaCl_2$ Solutions from 15 to 140 °C and from 1 to 200 bar

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The densities of aqueous $BaCl_2$ solutions have been measured at concentrations from 0.01 to 1.6 m, in the temperature range from 15 to 140 °C and the pressure range from 1 to 200 bar. The derived apparent molal volumes have been fitted to the Redlich–Meyer equation to obtain the infinite dilution apparent molal volumes, Φ°_v. The effect of temperature and pressure upon Φ°_v values has been discussed. The results have been compared with literature data.

Apparent molar volumes obtained from density measurements are one of the oldest and most extensively investigated properties of electrolyte solutions. The data are used to elucidate the nature of solute–solute and solute–solvent interactions, as well as structural changes in the solvent induced by the solute.

Aqueous solutions of alkaline-earth-metal chlorides are important components of natural brines and are widely used in industrial processes. The volume properties of these solutions at high temperatures and pressures are of special interest as they can be used to understand and predict the effects of temperature and pressure on the thermodynamic properties of these solutions. Measurements have been made on $CaCl_2$, $MgCl_2$, and $SrCl_2$ solutions but only a few at high temperatures and pressures (*1–8*).

There are a few experimental measurements on $BaCl_2$ solutions at low temperature (*9–12*). At elevated temperatures the only measurements are those of Ellis (*2*), and at high pressures there are no measurements.

In this paper we report the results of $BaCl_2$ densities at concentrations from 0.01 m to nearly saturation in the temperature range from 15 to 140 °C and the pressure range 1 to 200 bar.

Experimental Section

NaCl and $BaCl_2$ were Fisher Scientific ACS certified. All solutions were prepared by weight dilution of stock solutions using water which was first distilled, then passed through a Barnstead 18.5 Mohm ion-exchange apparatus, and subsequently filtered with a 10-μm glass filter until its conductivity was less than 0.05 μS cm^{-1}. The stock solution concentrations were determined to within ±0.03% by gravimetric analysis of chloride. The solution densities within the temperature range 15–55 °C were measured by a vibrating-tube densimeter (Mettler/Paar DMA 60 and DMA 602 remote glass cell). The densimeter constants were determined for each temperature by calibration with NaCl solutions of known concentrations using the density data of Millero et al. (*13*, *14*). The temperature was measured with a Leeds and Northrup platinium resistance thermometer (NBS calibrated) and a Müller bridge connected to a Leeds and Northrup dc null detector (Model 9828), yielding an accuracy of 0.001 °C. The experimental temperatures were controlled to ±0.005 °C with a Neslab EX-100 bath in conjunction with a Lauda K4/R thermostat. The relative densities were measured with a precision of ±5 ppm.

A vibrating-tube densimeter (DMA 512 remote stainless steel cell) was used to measure the densities at temperatures above 55 °C and at higher pressures. The 512 cell was operated in a flow mode. A HPLC injection valve (Rheodyne 7010) was used to introduce a 6-cm^3 sample solution into the inlet stream after which a water base line was reestablished. 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 temperature inside the cell was determined with a platinium resistance thermometer in the same way as in the low-temperature measurements. The cell temperature was maintained constant to ±0.005 °C in the temperature range 80–120 °C and to ±0.01 °C at 140 °C by a thermostating system which was designed and constructed by our Analytical Service Department. The design was based on the maximum minimization of heat losses. The heating system consists of two thermostats. One less precise (within ±0.05 °C) was used to bring the liquid in the main bath to the approximate temperature. Then, with the aid of 10 heaters of different powers placed on the surface of the main bath, the final temperature was tuned. The surface heaters were covered with a 4-in. layer of insulation and protected from the surroundings by a thermal barrier consisting of additional heaters and insulation. The control of all heaters was by Sargent-Welch temperature controllers.

The calibration procedure of the DMA 512 cell was similar to the procedure described for the DMA 602 cell. Water densities at experimental temperatures and pressures were calculated from the Haar et al. equation of state (*15*). The NaCl densities were calculated with Pitzer equations from his comprehensive review of NaCl solution properties at high temperatures and pressures (*16*).

Since the influence of pressure in the investigated pressure range on the calibration constants of the instrument was negligible (the random scatter was within ±0.2–0.5%), it was assumed that the values were a function of the temperature only. The relative densities at high temperatures and pressures were measured with lower precision than at low temperatures, in the range of 8–10 ppm.

Results and Discussion

Calculated densities were used to determine the apparent molal volumes, Φ_v, from

$$\Phi_v = (M_2/d) - 1000(d - d_0)/mdd_0 \qquad (1)$$

where M_2 is the solute molecular weight, d is the solution density, d_0 is the density of pure water, and m is the molality. The results are listed in Table I. The extrapolation of the apparent molal volumes to infinite dilution has been made with the Redlich–Meyer equation (*17*). It has been shown that the dilute apparent molal volume data for strong electrolytes can be accurately described by the Redlich–Meyer equation (*18–20*)

$$\Phi_v = \Phi^\circ_v + S_v m^{1/2} + b_v m \qquad (2)$$

where Φ°_v is the value of Φ_v at infinite dilution, S_v is the theoretical Debye–Hückel slope listed in Table II, and b_v is a solute-specific empirical parameter. The theoretical Debye–Hückel slopes have been calculated by Atkinson (*21*) for temperatures less than 100 °C and by Pitzer (*22*) for temperatures

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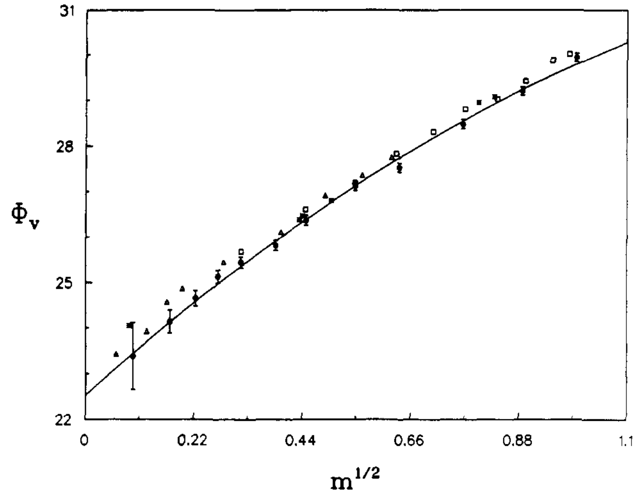

Figure 1. Apparent molal volumes of $BaCl_2$ in water solutions at 25 °C and at 0.987 bar: ●, present work; □, Millero (*11*); △, Perron (*10*); ✱, Dunn (*9*). The solid curve is the Redlich-Mayer equation fit.

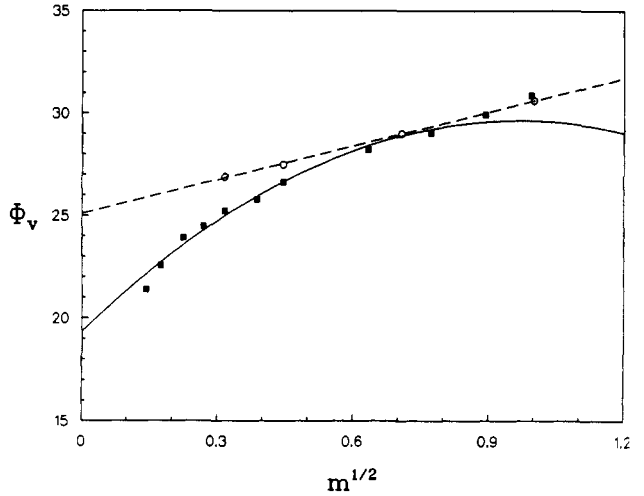

Figure 2. Apparent molal volumes of $BaCl_2$ in water solutions at 100 °C and 20 bar: ■, present work; ○, Ellis (*2*). The solid curve is the Redlich-Mayer equation fit.

exceeding 100 °C. The values of Φ°_v, b_v, and σ determined by a weighted fit of eq 2 are listed in Table III. Weighting was proportional to $1/\sigma$ where σ is the estimated error in Φ_v. Figure 1 shows a sample extrapolation curve at 25 °C with σ indicated by error bars.

Results of our data can be compared with the results of other investigators at 25 °C, the most extensively studied temperature. The agreement with the reliable literature values would at least serve as a check of the purity of our components and proper measuring procedure. The data of Dunn (*9*), Perron (*10*), and Millero (*11*) are marked in Figure 1. As is seen, the agreement is quite satisfactory at higher concentrations, but at high dilutions our data are somewhat lower, which is reflected in Φ°_v values equal to 22.53, 22.98, 23.21, and 23.24 $cm^3\ mol^{-1}$ obtained from our results, Perron, Millero, and Dunn, respectively.

It is difficult to compare our high-temperature, high-pressure results with those in the literature because the only existing results at high temperatures and a pressure of 20 bar are those of Ellis (*2*). At higher pressures, data are lacking. In Figure 2 the comparison of our results and those of Ellis at 100 °C and 20 bar is shown. There is a significant discrepancy in the dilute region that is reflected in Φ°_v values (19.3 and 23.9 $cm^3\ mol^{-1}$ from this work and Ellis's work, respectively). Ellis obtained his Φ°_v values, applying a straight-line extrapolation making use of only four data points, as is seen in Figure 2, which may explain the observed differences. The discrepancy between the Ellis and Dunn data at low temperature is also very significant. Dunn's Φ°_v values are 24.25 and 24.31 $cm^3\ mol^{-1}$ for the temperatures 45 and 55 °C, respectively. Ellis's Φ°_v value at 50 °C is 28.8 $cm^3\ mol^{-1}$.

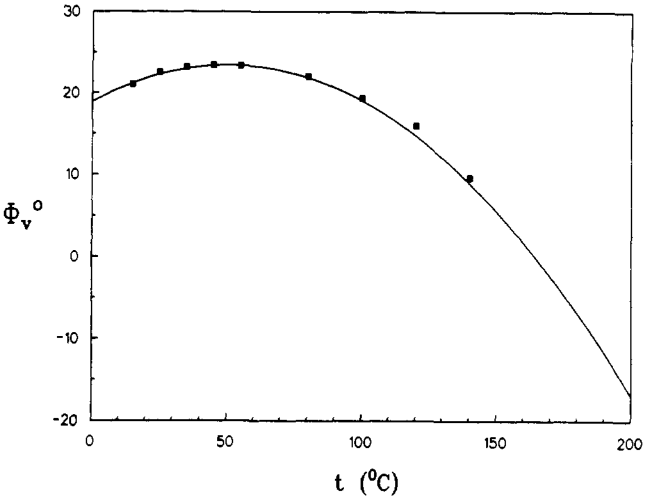

Figure 3. Temperature dependence of Φ°_v for $BaCl_2$ in water solution.

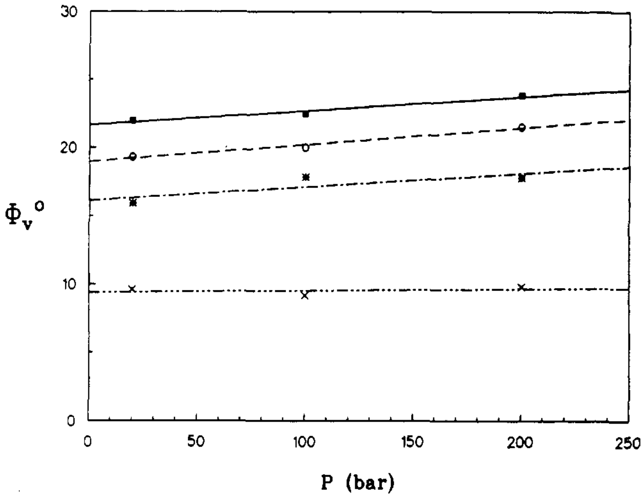

Figure 4. Effect of pressure on the Φ°_v values for $BaCl_2$ in water solutions: ■, 80 °C; ○, 100 °C; ✱, 120 °C; ×, 140 °C.

The hydration properties of the ions in $BaCl_2$ solutions can be estimated by examining the temperature and pressure dependence of the Φ°_v values. The dependence of the Φ°_v of $BaCl_2$ upon temperature follows the trend established in previous work for strong electrolytes (*19*, *20*, *23*). Figure 3 shows the plot of the volume-temperature curve. The Φ°_v values at the temperature range 80–140 °C were extrapolated to the pressure of 1 atm by using the straight-line dependencies of Φ°_v upon pressure for each measured temperature (Figure 4). The volume-temperature curve can be represent by the second-degree polynomial

$$\Phi^\circ_v = a + bt + ct^2 \tag{3}$$

where a, b, and c are empirical parameters and are 19.02 $cm^3\ mol^{-1}$, 0.174 $cm^3\ mol^{-1}\ {}^\circ C^{-1}$, and -0.0017 $cm^3\ mol^{-1}\ {}^\circ C^{-2}$, respectively. The temperature at which the maximum of the apparent molal volume occurs, t_{max}, was estimated to be 51.4 °C and was found by differentiating eq 3 with respect to t and setting the result equal to zero.

The ionic volume, Φ°_v consists of four contributions

$$\Phi^\circ_v = \Phi^\circ_{cryst} + \Phi^\circ_c + \Phi^\circ_{ele} + \Phi^\circ_r \tag{4}$$

where Φ°_{cryst} is crystallographic volume, Φ°_c is a cavity volume

Table I. Relative Densities and Apparent Molal Volumes of Aqueous $BaCl_2$ Solutions at Temperatures from 15 to 140 °C and Pressures from 1 to 200 bar

m/ (mol kg^{-1})	$10^3(d-d_0)$/ (g cm^{-3})	Φ_v/ (cm^3 mol^{-1})	$10^3(d-d_0)$/ (g cm^{-3})	Φ_v/ (cm^3 mol^{-1})
	15 °C and 0.987 bar		**25 °C and 0.987 bar**	
0.0093	1.742	21.59	1.722	23.39
0.0295	5.463	22.51	5.405	24.14
0.0501	9.257	23.11	9.149	24.65
0.0726	13.370	23.55	13.216	25.13
0.0998	18.354	23.79	18.154	25.44
0.1494	27.355	24.34	27.081	25.82
0.2000	36.503	24.71	36.100	26.37
0.3004	54.456	25.43	53.834	27.12
0.4064	73.250	25.96	72.453	27.52
0.5878	104.800	26.98	103.667	28.48
0.7877	–	–	137.521	29.20
0.9921	173.236	28.54	171.363	29.95
1.2243	211.135	29.44	209.035	30.67
1.5858	268.433	30.62	265.694	31.83
	35 °C and 0.987 bar		**45 °C and 0.987 bar**	
0.0093	1.712	24.00	–	–
0.0295	5.367	24.98	5.339	25.31
0.0501	9.089	25.46	9.037	26.09
0.0726	13.135	25.97	13.058	26.43
0.1494	26.862	26.81	26.319	27.32
0.2000	35.837	27.28	35.604	27.78
0.3004	53.427	27.99	52.989	28.85
0.4064	71.821	28.57	71.268	29.34
0.5878	102.903	29.28	101.939	30.30
0.7873	136.351	30.09	134.923	31.33
0.9921	170.068	30.74	168.410	31.76
1.2243	207.239	31.59	205.245	32.57
1.5858	263.758	32.53	260.943	33.62
	55 °C and 0.987 bar		**80 °C and 20 bar**	
0.0093	–	–	1.682	23.82
0.0201	3.636	25.33	–	–
0.0295	–	–	5.272	24.78
0.0501	–	–	8.948	25.07
0.0503	9.031	26.07	–	–
0.0727	13.033	26.48	12.899	25.86
0.1000	–	–	17.721	26.24
0.1494	–	–	26.356	26.90
0.1506	26.791	27.38	–	–
0.2000	35.392	28.15	35.127	27.48
0.3004	52.778	28.88	52.378	28.26
0.4064	71.024	29.28	70.308	29.12
0.5878	–	–	100.635	30.02
0.7877	134.598	31.14	133.206	31.08
0.9921	168.049	31.54	166.139	31.67
1.2243	204.651	32.48	–	–
1.5858	260.166	33.55	257.413	33.62
	80 °C and 100 bar		**80 °C and 200 bar**	
0.0093	1.681	24.39	1.678	25.58
0.0295	5.273	25.34	5.255	26.67
0.0501	8.950	25.63	8.914	27.06
0.0726	12.911	26.28	12.867	27.59
0.1000	17.714	26.88	17.690	27.81
0.1494	26.322	27.70	26.300	28.51
0.2000	35.094	28.20	35.066	29.01
0.3004	52.348	28.90	52.258	29.87
0.4064	70.328	29.59	70.243	30.42
0.5878	100.669	30.45	100.468	31.38
0.7877	133.330	31.40	133.137	32.20
0.9921	166.399	31.87	166.233	32.57
1.2243	202.617	32.83	202.421	33.49
1.5858	257.555	33.93	257.229	34.58
	100 °C and 20 bar		**100 °C and 100 bar**	
0.0201	–	–	3.616	22.52
0.0304	5.438	22.55	5.434	23.34
0.0503	8.923	23.92	8.943	24.12
0.0727	12.870	24.46	12.872	25.06
0.1000	17.606	25.22	17.609	25.81
0.1506	26.406	25.78	26.373	26.63
0.1994	34.758	26.64	34.792	27.06
0.2917	50.570	27.25	50.541	27.94
0.4015	69.013	28.23	68.958	28.93
0.5957	101.385	29.05	101.271	29.78
0.7962	134.038	29.94	134.106	30.37
0.9881	164.643	30.88	164.823	31.04
1.2467	205.286	31.41	205.190	31.95
	100 °C and 200 bar		**120 °C and 20 bar**	
0.0201	3.598	24.25	–	–
0.0204	–	–	3.617	19.52
0.0304	5.412	24.89	5.421	20.38
0.0503	8.908	25.63	8.900	21.69
0.0727	12.452	26.45	12.842	22.16
0.1000	17.586	26.80	17.554	23.12
0.1506	26.343	27.57	26.267	24.16
0.1994	34.783	27.83	34.696	24.70
0.2917	50.517	28.72	50.215	26.04
0.4015	69.036	29.41	–	–
0.5873	–	–	99.356	27.83
0.5957	101.105	30.69		
0.7912	–	–	132.391	28.79
0.7962	134.061	31.04	–	–
0.9881	164.519	31.92	163.477	29.77
1.2467	204.765	32.82	203.456	30.82
	120 °C and 100 bar		**120 °C and 200 bar**	
0.0201	3.590	21.24	–	–
0.0304	5.385	22.42	5.442	21.23
0.0503	8.883	22.77	8.914	22.97
0.0727	12.771	23.96	12.830	23.91
0.1000	17.493	24.49	–	–
0.1506	26.171	25.54	26.197	26.17
0.1994	34.399	26.69	34.521	26.83
0.2917	50.143	26.96	50.120	27.82
0.3961			67.609	28.50
0.5873	99.413	28.33	98.949	29.86
0.7912	132.343	29.42	131.805	30.79
0.9881	163.418	30.38	–	–
0.9962	–	–	163.997	31.74
1.2339	201.291	31.45	200.967	32.32
	140 °C and 20 bar		**140 °C and 100 bar**	
0.0295	–	–	5.345	14.332
0.0304	5.463	15.45	–	–
0.0501	8.946	16.68	–	–
0.0503			9.040	16.07
0.0727	12.898	18.03	12.993	17.40
0.1000	17.640	18.94	17.772	18.27
0.1494	26.218	19.88	–	–
0.1506	–	–	26.517	19.97
0.1994	34.736	21.10	–	–
0.2000	–	–	35.029	20.92
0.3004	51.967	22.10	52.043	22.59
0.4015	68.846	23.35	68.630	24.67
0.5878	99.849	24.35	99.826	25.10
0.7877	132.055	25.87	–	–
0.7962	–	–	132.924	27.22
0.9921	165.020	26.38	163.307	28.76
1.2243	200.225	28.23	199.669	29.28
1.5858	254.163	29.93		
	140 °C and 200 bar			
0.0304	5.585	12.81		
0.0501	9.106	15.60		
0.0727	13.006	18.21		
0.1000	17.750	19.53		
0.1506	26.470	21.29		
0.1994	34.773	22.63		
0.2917	50.284	24.49		
0.4015	68.561	25.73		
0.5957	100.188	27.62		
0.7962	132.459	28.61		
0.9881	162.490	29.69		
1.2243	199.462	30.16		

within a solvent which can partially accommodate an ion. Its contribution to the overall ionic volume is negative. Φ°_{ele} is the electrostriction volume, resulting from electrostatic compression of the solvent, and its negative contribution depends upon the ionic charge density. Φ°_r is the solvent response term closely related to the secondary hydration effect.

The shape of the volume–temperature curve and t_{max} are dependent upon whether the electrostriction or positive volume

Table II. Debye–Hückel Slopes, S_v (cm^3 kg$^{1/2}$ mol$^{-3/2}$), for 2:1 Electrolytes at Various Pressures (bar) and Temperatures (°C)

T/°C	S_v 0.987 bar	20 bar	100 bar	200 bar
15	8.818			
25	9.706			
35	10.631			
45	11.608			
55	12.653			
80		16.967	16.509	15.653
100		21.347	20.694	19.917
120		27.114	26.204	25.123
140		35.025	33.706	32.110

Table III. Parameters for Equation 2 at Temperatures from 15 to 140 °C and Pressures from 1 to 200 bar

P/bar	t/°C	Φ°_v/ (cm^3 mol^{-1})	b_v/ (cm^3 kg mol^{-1})	σ/ (cm^3 mol^{-1})
0.987	15	21.06	-1.37	0.06
0.987	25	22.53	-2.42	0.05
0.987	35	23.16	-3.18	0.05
0.987	45	23.43	-3.26	0.07
0.987	55	23.37	-4.54	0.09
20	80	21.97	-9.64	0.11
20	100	19.33	-11.04	0.13
20	120	15.94	-14.70	0.12
20	140	9.60	-19.88	0.25
100	80	22.47	-7.74	0.11
100	100	19.93	-9.92	0.10
100	120	17.84	-15.47	0.16
100	140	9.16	-15.64	0.18
200	80	23.82	-7.51	0.13
200	100	21.53	-10.74	0.14
200	120	17.81	-12.04	0.17
200	140	9.80	-11.54	0.49

contribution dominates. The curved section before t_{max} is dominated by the positive volume contribution and beyond t_{max} by the electrostriction. In the series of alkaline-earth cations, barium is the largest and, hence, has the smallest charge density, resulting in the lowest electrostriction volume contribution in comparison with the other alkaline-earth cations. The values of t_{max} for $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ were calculated from Ellis's results over the temperature range from 25 to 200 °C and pressures to 20 bar and are equal to 44.6, 46.8, 56.5, and 58.7 °C for magnesium, calcium, strontium, and barium chlorides, respectively. The observed temperature trend is in good agreement with the ionic hydration concept. The discrepancy between our and Ellis's t_{max} values for $BaCl_2$ might be explained in terms of the different extrapolation procedures applied for the evaluation of Φ°_v values.

The effect of pressure on Φ°_v in the temperature range 80–140 °C is shown in Figure 4. The Φ°_v values at 80 and 100 °C increase with pressure in a nearly linear way. At higher temperatures the pressure has little effect on the Φ°_v values. At 120 °C there is a small increase up to 100 bar, and at 140 °C the values of Φ°_v are independent of pressure.

It is well-known that pressure and temperature act as opposing forces on the cavity volume contribution. The solvent structure becomes more open with increasing temperature, making the cavity volume more negative. In contrast, increasing the pressure reduces the void space in the solvent, reducing the cavity volume. The small change of the Φ°_v values with pressure at higher temperatures can be explained in terms of the near equality of the opposing effects of temperature and pressure.

The electrostriction volume is considered to be only a function of temperature, and its negative contribution should be taken into account when the effect of pressure at elevated temperatures is considered.

We could not compare our high-pressure, high-temperature $BaCl_2$ results with other alkaline-earth-metal chlorides because of lack of literature data. There are either high-temperature data at constant low pressure (*2*, *7*, *4*) or high-pressure data at low temperature up to 50 °C (*3*, *8*).

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Registry No. $BaCl_2$, 10361-37-2.

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