Me_4Si. A very similar signal was observed by Shuppert and Angell (*5*) in the case of mixtures of hydrogen chloride and pyridinium chloride and was attributed to the HCl_2^- ions. The authors report that this sharp line disappears at high temperature (>338 K) because a rapid exchange occurs in this case between $N-H^+$ and HCl_2^- protons. In our case, the *N*-substitution of the pyridinium ion allows thus the observation of HCl_2^- ions at higher temperature.

Figures 1 and 2 show that some other process occurs for the dissolution of hydrogen chloride since a solubility of about 0.25 mol/L was measured for $X_{ZnCl_2} \geqslant 0.33$. Our experimental results do not allow any interpretation of this extra solubility. Assuming that this extra solubility remains constant in all the concentration range and particularly for the pure *N*-alkylpyridinium salt, it can be found that the solubility is somewhat lower than the analytical concentration of the *N*-alkylpyridinium halide. In the case of *N*-ethylpyridinium bromide, the solubility of HCl through HX_2^- formation is 6.25 mol/L when the analytical concentration of bromide ions is 7.34 mol/L. For *N*-methylpyridinium chloride, the solubility as HCl_2^- is 7.5 mol/L, the analytical concentration of chloride ions yielding 8.31 mol/L. The complexation reaction of hydrogen chloride by halide ions is thus not quite quantitative and a competition exists between *N*-alkylpyridinium cations and hydrogen chloride for the halide ions.

Registry No. EtPyBr, 1906-79-2; MePyCl, 7680-73-1; $ZnCl_2$, 7646-85-7; HCl, 7647-01-0.

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Received for review March 25, 1986. Accepted September 15, 1986.

Apparent Molar Heat Capacities and Volumes of Aqueous Solutions of $MgCl_2$, $CaCl_2$, and $SrCl_2$ at Elevated Temperatures[†]

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Heat capacity (C_p) and density (d) data at 0.6 MPa and in the temperature range 298.15–373.15 K are presented for aqueous $MgCl_2$, $CaCl_2$, and $SrCl_2$. Data were obtained over the concentration (m) ranges 0.1–0.53 mol·kg^{-1} for $MgCl_2$, 0.03–0.98 mol·kg^{-1} for $CaCl_2$, and 0.03–2.0 mol·kg^{-1} for $SrCl_2$. The values of C_p and d of a solution relative to that of water were measured with a precision of ±0.1 mJ·K^{-1}·g^{-1} and ±5 μg·cm^{-3}, respectively, at all temperatures. The C_p and d results were used to calculate the apparent molar heat capacities (${}^{\phi}C_p$) and volumes (${}^{\phi}V$), respectively. Our ${}^{\phi}C_p$ results at room temperature are in good agreement with available literature data; however, our ${}^{\phi}C_p$ values at 348.15 and 373.15 K differ considerably from the high-temperature literature data available only for $MgCl_2$, because of the much lower precision (±2 to ±13 mJ·K^{-1}·g^{-1}) of the C_p measurements reported in the literature.

Introduction

The present work is part of a continuing effort from this laboratory to obtain thermodynamic data for aqueous species at elevated temperatures. The importance of this work for modeling applications in the nuclear industry (e.g., waste management and safety) and in nonnuclear areas has been discussed in our earlier papers (*1–4*). We have recently reported apparent molar heat capacities, ${}^{\phi}C_p$, and volumes, ${}^{\phi}V$, up to 373 K for a number of 1:1 aqueous electrolytes (*3*). In this paper, we extend our studies to the 2:1 aqueous electrolytes, $MgCl_2$, $CaCl_2$, and $SrCl_2$.

While ${}^{\phi}C_p$ and ${}^{\phi}V$ data for aqueous 2:1 electrolytes are available at 298.15 K (*5–8*), very few values are available at higher temperatures (*9–12*). This is because both heat capacity, C_p, and density, d, were difficult to measure at elevated temperatures before the recent development of flow microcalorimeters (*1*, *13–15*) and flow densimeters (*1*, *16*, *17*) able to withstand higher operating temperatures and pressures. In this paper, we present measured values of C_p and d along with calculated ${}^{\phi}C_p$ and ${}^{\phi}V$ values for aqueous $MgCl_2$, $CaCl_2$, and $SrCl_2$ (a fission product electrolyte) from 298.15 to 373.15 K, at a constant pressure of 0.6 MPa. In an accompanying paper (*18*), we apply Pitzer's ion-interaction model (*1*, *4*) to our data, combined with some literature data of comparable precision (*5–12*), to obtain partial molar heat capacity, $\bar{C}^0_{p,2}(T)$, and volume, $\bar{V}^0_2(T)$, functions, and to generate temperature-dependent equations for calculating other thermodynamic properties (such as the enthalpy, Gibbs energy, and osmotic coefficient) of these electrolytes at higher temperatures.

Experimental Section

To apply the ion-interaction model (*4*), a large number of high-precision $C_p(T,m)$ and $d(T,m)$ measurements are required over a wide range of T and m. This approach yields reliable temperature-dependent $\bar{C}^0_{p,2}(T)$ and $\bar{V}^0_2(T)$ functions, along with ion-interaction parameters (*4*).

The flow C_p microcalorimeter and flow vibrating-tube densimeter system, and the operating procedure used for all the measurements, were similar to those described in detail elsewhere (*1*). The chemicals used for this study were obtained from Fisher ($MgCl_2$) and Alfa Products, Ventron Division ($CaCl_2$ and $SrCl_2$). Details of sample handling and solution preparation were similar to those described earlier (*1*). Simultaneous

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[†] Issued as AECL-9036.

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Table I. Apparent Molar Heat Capacities, $^{\phi}C_p$, and Heat Capacities, C_p, of $MgCl_2$, $CaCl_2$, and $SrCl_2$ in Aqueous Solutions as a Function of Temperature, at 0.6 MPa

molality, m/(mol·kg^{-1})	C_p/(J·K^{-1}·g^{-1})	$^{\phi}C_p$/(J·K^{-1}·mol^{-1})
	$MgCl_2$, 298.15 K	
water	(4.1779)[a]	(75.26)[a]
0.10844	4.1111	-224.6
0.19711	4.0590	-216.7
0.28186	4.0115	-208.4
0.38842	3.9533	-201.8
0.52775	3.8807	-193.6
	$MgCl_2$, 323.15 K	
water	(4.1790)[a]	(75.28)[a]
0.10844	4.1150	-198.4
0.19711	4.0654	-189.2
0.28186	4.0199	-181.7
0.38842	3.9644	-175.0
0.52775	3.8957	-165.9
	$MgCl_2$, 348.15 K	
water	(4.1911)[a]	(75.50)[a]
0.10844	4.1262	-205.6
0.19711	4.0766	-192.7
0.28186	4.0308	-184.9
0.38842	3.9751	-177.6
0.52775	3.9040	-172.3
	$MgCl_2$, 373.15 K	
water	(4.2143)[a]	(75.92)[a]
0.10844	4.1462	-233.2
0.19711	4.0946	-217.4
0.28186	4.0469	-208.6
0.38842	3.9894	-199.1
0.52775	3.9182	-188.0
	$CaCl_2$, 298.15 K	
water	(4.1779)[a]	(75.26)[a]
0.02976	4.1570	-240.9
0.09940	4.1097	-230.0
0.10213	4.1083	-225.5
0.19769	4.0467	-214.5
0.21251	4.0370_5	-214.7
0.42541	3.9089	-198.5
0.66613	3.7778	-181.3
0.88035	3.6708	-168.6
	$CaCl_2$, 323.15 K	
water	(4.1790)[a]	(75.28)[a]
0.02976	4.1592	-203.7
0.09940	4.1144	-193.2
0.10213	4.1129	-190.7
0.19769	4.0544	-180.3
0.21251	4.0455	-179.2
0.42541	3.9242	-163.4
0.66613	3.7982	-150.1
0.88035	3.6956	-138.9
	$CaCl_2$, 348.15 K	
water	(4.1911)[a]	(75.50)[a]
0.05108	4.1574	-198.3
0.10015	4.1267	-185.0
0.20271	4.0664	-163.8
0.49449	3.9032	-149.0
0.98452	3.6739	-117.6
	$CaCl_2$, 373.15 K	
water	(4.2143)[a]	(75.92)[a]
0.02976	4.1932	-243.6
0.09940	4.1470	-216.8
0.10213	4.1453	-215.5
0.19769	4.0859	-196.0
0.21060	4.0779	-195.1
0.21251	4.0768	-194.5
0.42541	3.9543	-172.3
0.46990	3.9269	-175.8
0.66613	3.8291	-153.3
0.88035	3.7284	-138.1
	$SrCl_2$, 298.15 K	
water	(4.1779)[a]	(75.26)[a]
0.02747	4.1527	-259.0
0.10044	4.0882	-245.0
0.20459	4.0028	-221.3
0.68309	3.6567	-183.3
1.00093	3.4709	-156.1
	$SrCl_2$, 323.15 K	
water	(4.1790)[a]	(75.28)[a]
0.02747	4.1549	-219.0
0.10044	4.0937	-200.3
0.20459	4.0126	-177.2
0.68309	3.6817	-144.4
1.00093	3.5017	-121.6
	$SrCl_2$, 348.15 K	
water	(4.1911)[a]	(75.50)[a]
0.02747	4.1670	-216.7
0.10044	4.1061	-195.3
0.20459	4.0257	-170.3
0.68309	3.6995	-133.2
1.00093	3.5227	-109.3
	$SrCl_2$, 373.15 K	
water	(4.2143)[a]	(75.92)[a]
0.0468	4.1737	-206.0
0.0998	4.1293	-197.0
0.2058	4.0456	-178.4
0.5013	3.8322	-154.7
1.0454	3.5096	-117.7

[a] Values in parentheses are heat capacities ($C^0_{p,1}$) for pure solvent (water) taken from compilations of Kell et al. (*19*, *20*) and Raznjevic (*21*).

measurements of $d(T,m)$ and volumetric heat capacities at nearly the same temperature and pressure provided the $C_p(T,m)$ in J·K^{-1}·g^{-1}. Thus, both $^{\phi}C_p$ (J·K^{-1}·mol^{-1}) and $^{\phi}V$ (cm^3·mol^{-1}) were determined in a single experiment. The overall precisions in the C_p and d determinations were estimated to be ±0.1 mJ·K^{-1}·g^{-1} and ±5 μg·cm^{-3}, respectively (*3*).

Results and Discussion

Primary Results. The $C_p(T,m)$ and $d(T,m)$ values for aqueous $MgCl_2$, $CaCl_2$, and $SrCl_2$ were used to calculate the $^{\phi}C_p(T,m)$ and $^{\phi}V(T,m)$ values from the following equations:

$$^{\phi}C_p(T,m) = M_2C_p(T,m) + \frac{1000[C_p(T,m) - C^0{}_{p,1}(T)]}{m} \qquad (1)$$

$$^{\phi}V = \frac{M_2}{d(T,m)} - \frac{1000[d(T,m) - d^0{}_1(T)]}{md^0{}_1(T)\,d(T,m)} \qquad (2)$$

In the above equations, M_2 is the molecular weight of the dissolved solute. $C^0{}_{p,1}$ and $d^0{}_1$ are, respectively, the heat capacity and density of the pure solvent (water) at the operating temperature and pressure. The reference $C^0{}_{p,1}$ values for pure water, as a function of temperature, were obtained from the tables of Kell et al. (*19*, *20*). The $C^0{}_{p,1}$ values as a function of pressure were obtained from the *Handbook of Thermodynamic Tables and Charts* (*21*). The reference $d^0{}_1$ values for pure water were calculated by using the equations of Fine and Millero (*22*). The $C_p(T,m)$ and $^{\phi}C_p(T,m)$ values are given in Table I, and the $d(T,m)$ and $^{\phi}V(T,m)$ values are given in Table II.

Comparison with Literature Heat Capacity Data

Room-Temperature $^{\phi}C_p(m)$ Values. Our $^{\phi}C_p(m)$ values at 298.15 K and 0.6 MPa for aqueous $MgCl_2$, $CaCl_2$, and $SrCl_2$ were compared with existing literature data (*5–8*). The room-

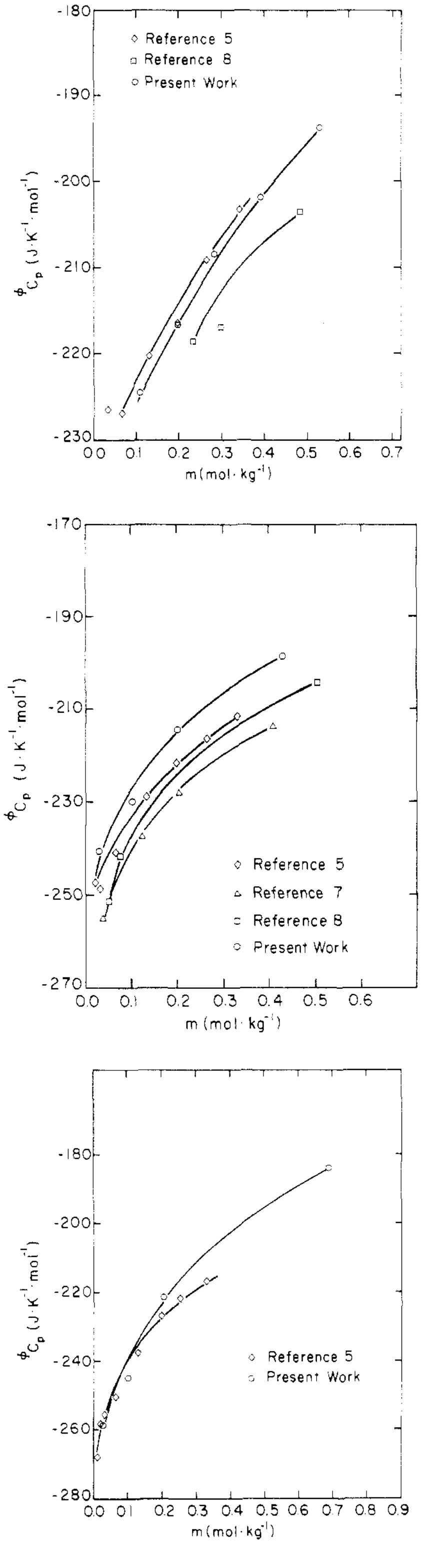

Figure 1. Apparent molar heat capacities, $^{\phi}C_p(m)$, as a function of molality, m, for aqueous solutions of (a, upper) $MgCl_2$, (b, middle) $CaCl_2$, and (c, lower) $SrCl_2$; a comparison with 298.15 K data of Perron et al. (*5*, *6*, *8*) and Spitzer et al. (*7*).

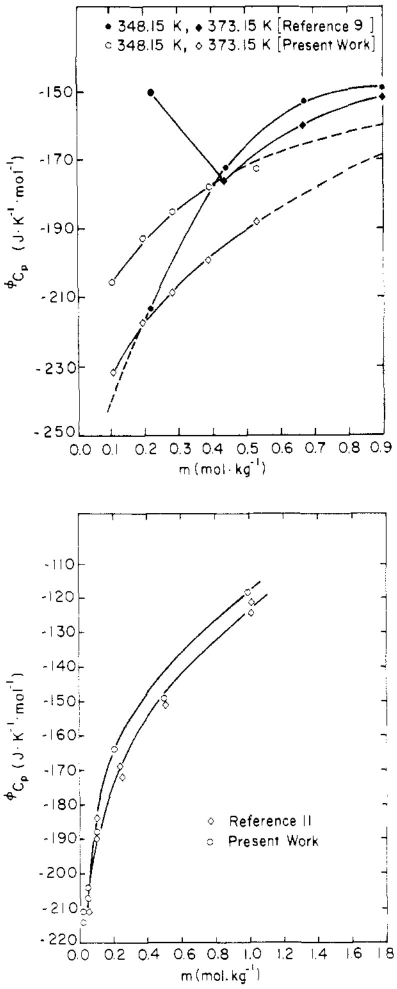

Figure 2. Apparent molar heat capacities, $^{\phi}C_p(m)$, as a function of molality, m, for aqueous solutions of (a, upper) $MgCl_2$ at 348.15 and 373.15 K, and (b, lower) $CaCl_2$ at 348.15 K and 0.6 MPa; a comparison with literature data of Likke and Bromley (*9*) for $MgCl_2$ at 348.15 and 373.15 K, and of Wood (*11*, *12*) for $CaCl_2$ at 349.86 K and 17.5 MPa.

temperature literature values for these electrolytes were obtained at atmospheric pressure (0.1 MPa), and thus should be extrapolated to 0.6 MPa. However, pressure corrections (<0.4 J·K^{-1}·mol^{-1}·MPa^{-1}) to convert literature data to 0.6 MPa are negligible (*4*) compared with the uncertainties in the experimentally determined $^{\phi}C_p(T,m)$ values, which can range from ±0.5 J·K^{-1}·mol^{-1} at higher concentrations (>1 mol·kg^{-1}) to >10 J·K^{-1}·mol^{-1} at lower concentrations (<0.2 mol·kg^{-1}). Thus, the literature data were used for comparison without correction. As shown in Figure 1a–c, our data at 0.6 MPa and the literature data (*5*–*8*) at 0.1 MPa agree very well for $MgCl_2$, $CaCl_2$, and $SrCl_2$, considering the estimated uncertainties discussed above.

High-Temperature $^{\phi}C_p(m)$ Values. Our $^{\phi}C_p$ results were first compared with the earliest high-temperature data for aqueous $MgCl_2$ reported in 1951 by Eigen and Wicke (*23*). These authors used an adiabatic calorimeter to measure $C_p(m)$ of aqueous $MgCl_2$ at only three, relatively high, concentrations (0.382, 0.714, and 0.949 M) in the temperature range 283.15–403.15 K. As discussed in our earlier papers (*3*, *4*), adiabatic calorimetry measurements require vapor-space corrections, because both liquid and vapor phases of the sample coexist during the course of C_p measurements. The large vapor-space corrections at high temperatures decrease the precision of the measured heat capacities and, consequently, of the $^{\phi}C_p(T,m)$ values. Eigen and Wicke (*23*) stated the precision of their C_p data as ±2 mJ·K^{-1}·g^{-1} (or 0.05%). This precision is about 20 times lower than the precision of ±0.1 mJ·K^{-1}·g^{-1} in the present work because the flow calorimetric method does not require such vapor-space corrections. Eigen and Wicke (*23*) also estimated that uncertainty of ±2 mJ·K^{-1}·g^{-1} in C_p measurements corresponds to the uncertainties of ±21 and ±5 J·K^{-1}·mol^{-1} in $^{\phi}C_p$ values for dilute (0.1 M) and concentrated (at and above 1 M) solutions, respectively. In any case, we have compared our $^{\phi}C_p$ values for 0.385 M (or 0.38842 mol·kg^{-1}) $MgCl_2$ with the $^{\phi}C_p$ values of Eigen and Wicke (*23*) at 0.382 M because the other concentrations (0.714 and

Table II. Apparent Molar Volumes, $^{\phi}V$, and Densities, d, of $MgCl_2$, $CaCl_2$, and $SrCl_2$ in Aqueous Solutions as a Function of Temperature, at 0.6 MPa

molality, m/(mol·kg^{-1})	d/(g·cm^{-3})	$^{\phi}V$/(cm^3·mol^{-1})
	$MgCl_2$, 297.19 K	
water	(0.997 516)^a	(18.06)^a
0.10844	1.005 990	16.78
0.19711	1.012 824	17.14
0.28186	1.019 263	17.53
0.38842	1.027 274	17.94
0.52775	1.037 532	18.51
	$MgCl_2$, 321.9 K	
water	(0.988 817)^a	(18.22)^a
0.10844	0.997 266	16.47
0.19711	1.004 042	17.04
0.28186	1.010 422	17.52
0.38842	1.018 373	17.94
0.52775	1.028 562	18.53
	MCl_2, 346.92 K	
water	(0.975 797)^a	(18.46)^a
0.10844	0.984 371	14.42
0.19711	0.991 239	15.07
0.28186	0.997 705	15.60
0.38842	1.005 727	16.16
0.52775	1.016 023	16.84
	$MgCl_2$, 371.82 K	
water	(0.959 542)^a	(18.77)^a
0.10844	0.968 358	10.84
0.19711	0.975 379	11.78
0.28186	0.981 977	12.49
0.38842	0.990 268	12.91
0.52775	1.000 854	13.63
	$CaCl_2$, 297.19 K	
water	(0.997 516)^a	(18.06)^a
0.02976	1.000 203	20.47
0.09940	1.006 417	21.08
0.10213	1.006 601	21.67
0.19769	1.014 985	22.07
0.21251	1.016 264	22.19
0.42541	1.034 627	22.75
0.66613	1.054 641	23.72
0.88035	1.072 038	24.37
	$CaCl_2$, 321.90 K	
water	(0.988 817)^a	(18.22)^a
0.02976	0.991 453	21.60
0.09940	0.997 565	22.04
0.10213	0.997 752	22.56
0.19769	1.005 987	23.02
0.21251	1.007 253	23.09
0.42541	1.025 293	23.68
0.66613	1.044 979	24.62
0.88035	1.062 076	25.26
	$CaCl_2$, 348.15 K	
water	(0.975 066)^a	(18.48)^a
0.04975	0.979 451	21.03
0.05108	0.979 562	21.15
0.10015	0.983 770	22.22
0.20271	0.992 496	22.98
0.49449	1.016 907	23.81
0.98452	1.055 241	26.03
	$CaCl_2$, 371.82 K	
water	(0.959 542)^a	(18.77)^a
0.02976	0.962 271	16.03
0.09940	0.968 480	17.84
0.10213	0.968 692	18.19
0.19769	0.977 016	19.32
0.21251	0.978 289	19.48
0.42541	0.996 544	20.41
0.66613	1.016 391	21.69
0.88035	1.033 651	22.50
	$CaCl_2$, 371.96 K	
water	(0.959 443)^a	(18.78)^a
0.07520	0.966 150	18.60
0.2106	0.977 944	19.85
0.4699	1.000 449	20.02
	$SrCl_2$, 297.19 K	
water	(0.997 516)^a	(18.06)^a
0.02747	1.001 333	19.21
0.10044	1.011 335	20.37
0.20459	1.025 124	22.68
0.68309	1.087 538	24.29
1.00093	1.126 149	26.37
	$SrCl_2$, 321.90 K	
water	(0.988 817)^a	(18.22)^a
0.02747	0.992 566	20.66
0.10044	1.002 390	21.81
0.20459	1.015 897	24.28
0.68309	1.077 138	25.78
1.00093	1.115 043	27.80
	$SrCl_2$, 346.92 K	
water	(0.975 797)^a	(18.46)^a
0.02747	0.9799 524	19.90
0.10044	0.989 294	21.04
0.20459	1.002 735	23.53
0.68309	1.063 550	25.27
1.00093	1.101 154	27.41
	$SrCl_2$, 371.96 K	
water	(0.959 443)^a	(18.78)^a
0.0998	0.972 596	21.76
0.2058	0.986 422	22.20
0.5013	1.024 482	22.75
1.0454	1.091 347	24.76
1.9929	1.199 797	27.36

^{a} Values in parentheses are densities (d°_1) and volumes (V°_1) for pure water, calculated from equations of Fine and Millero (*22*).

0.949 M) are outside the range of our C_p measurements. The literature $^{\phi}C_p$ values for 0.382 M $MgCl_2$ in the temperature range 298.15–373.15 K were obtained by graphical interpolation of the curve I of Figure 2c from the paper of Eigen and Wicke (*23*). Our $^{\phi}C_p$ values at 298.15, 323.15, 348.15, and 373.15 K are −202, −175, −178, and −199 J·K^{-1}·mol^{-1} as compared to the literature $^{\phi}C_p$ values (*23*) of −204, −175, −170, and −179 J·K^{-1}·mol^{-1}, respectively. Our $^{\phi}C_p$ values at 348.15 and 373.15 K are 8 and 20 J·K^{-1}·mol^{-1} more negative than $^{\phi}C_p$ values of Eigen and Wicke (*23*). Thus, the two sets of data for 0.382 M $MgCl_2$ can be considered in agreement only within the large uncertainties (about ±21 J·K^{-1}·mol^{-1}) in the high-temperature literature $^{\phi}C_p$ data for such concentrations.

Our $^{\phi}C_p(m)$ results for $MgCl_2$ at 348.15 and 373.15 K and 0.6 MPa can be compared with the high-temperature data published by Likke and Bromley for $MgCl_2$ (*9*). Likke and Bromley (*9*) determined their C_p data for $MgCl_2$ in 1973 at relatively high concentrations (0.22, 0.44, 0.67, and 0.90 mol·kg^{-1}) and in the temperature range 353.15 to 453.15 K, using bomb calorimetry. The $^{\phi}C_p(m)$ values at 353.15 and 373.15 K and 0.1 MPa were calculated from corresponding $C_p(m)$ data (*9*) at four concentrations. The $^{\phi}C_p(m)$ values at 348.15 K were obtained by linear extrapolation of $^{\phi}C_p(T,m)$ data from ref *9* at 353.15 and 373.15 K. Our values at 0.67 and 0.90 mol·kg^{-1} were obtained by graphical extrapolation of our $^{\phi}C_p(m)$ data. As shown in Figure 2a, the two sets of $^{\phi}C_p(T,m)$ data differ considerably. The $^{\phi}C_p(m)$ values from ref *9* are about 15 J·K^{-1}·mol^{-1} less negative than our values at both temperatures, 348.15 and 373.15 K, except at the lowest concentration (0.22 mol·kg^{-1}), where the $^{\phi}C_p$ values of ref *9* are about 25 J·K^{-1}·mol^{-1} more negative at 348.15 K, and about 60 J·K^{-1}·mol^{-1} less negative at 373.15 K, compared with our $^{\phi}C_p$ values. We believe that the reason for such gross discrepancy at the lower concentration is the poor precision in the C_p measurements (e.g., ±12.6 mJ·K^{-1}·g^{-1}, as stated in ref *9*, or ±60 J·K^{-1}·mol^{-1} in $^{\phi}C_p$ value at 0.22 mol·kg^{-1}) attainable by nondifferential bomb calorimetric measurements (*9*). Thus, the greater precision of the present C_p measurements (±0.1 mJ·K^{-1}·g^{-1}), using differential C_p calorimetry in the flow mode, is evident at lower concentrations (≤0.22 mol·kg^{-1}). As expected, $^{\phi}C_p(m)$ values at high concentrations (0.44, 0.67, and 0.90 mol·kg^{-1}) become increasingly less sensitive to uncertainties in C_p measurements and, hence, differ from ours by only about 15 J·K^{-1}·mol^{-1}. Thus, the two sets of $^{\phi}C_p(T,m)$ data at 348.15 and 373.15 K can be considered in agreement only within the stated large uncertainties in the literature $^{\phi}C_p(T,m)$ data.

We also compared our $^{\phi}C_p(m)$ results for $CaCl_2$ at 348.15 K with the C_p measurements by Wood (*12*), which were recently quoted by Ananthaswamy and Atkinson (*11*). It should be noted that Wood's data (*12*) at 349.86 K were obtained at 30 times higher pressure (17.5 MPa) than the 0.6 MPa in the present work. It has been pointed out (*13*, *14*) that the pressure dependence of $^{\phi}C_p(m)$ values can be significant at higher temperatures for such a large pressure range (0.1–20 MPa). Thus, a comparison at two very different pressures, as shown in Figure 2b, has limited validity until appropriate pressure corrections can be estimated and applied to convert Wood's data at 17.5 MPa to data near atmospheric pressure (0.1 or 0.6 MPa). Nevertheless, a reasonable agreement between our $^{\phi}C_p(m)$ values at 348.15 K and 0.6 MPa and the uncorrected $^{\phi}C_p(m)$ values of Wood (*11*) at 349.86 K and 17.5 MPa suggests that pressure corrections to $^{\phi}C_p(T,m)$ values may become significant only beyond the temperature range

298.15–348.15 K.

In the case of $SrCl_2$, no literature ${}^{\phi}C_p(T,m)$ data at higher temperatures are available for comparison.

Conclusions

We have obtained the heat capacities (C_p and ${}^{\phi}C_p$), densities (d) and volumes (${}^{\phi}V$) of $MgCl_2$, $CaCl_2$, and $SrCl_2$ in water as a function of temperature and concentration. Our ${}^{\phi}C_p(T,m)$ data for all three electrolytes are in good agreement with 298.15 K data available in the literature (*5–8*). Our ${}^{\phi}C_p(T,m)$ data at 348.15 and 373.15 K differ considerably from the sparse data (*9*, *23*) for $MgCl_2$ at relatively higher concentrations. This large discrepancy in the two sets of data is attributed to the much lower precision (±60 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ in the ${}^{\phi}C_p$ value at 0.22 $mol{\cdot}kg^{-1}$) attainable by bomb calorimetry C_p measurements in the literature (*9*). The present data are used in an accompanying paper (*18*) to determine reliable $\bar{C}^0_{p,2}(T)$ functions, which can then be used to calculate the thermodynamic properties of ions in water over an extended temperature range.

Registry No. $MgCl_2$, 7786-30-3; $CaCl_2$, 10043-52-4; $SrCl_2$, 10476-85-4.

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Received for review March 25, 1986. Accepted July 23, 1986.

Thermodynamics of Aqueous Magnesium Chloride, Calcium Chloride, and Strontium Chloride at Elevated Temperatures[†]

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Heat capacities and densities of aqueous $MgCl_2$, $CaCl_2$, and $SrCl_2$ from the accompanying paper are combined with literature data up to 473 K to yield temperature-dependent equations by using the ion-interaction model of Pitzer. These heat capacity equations have been integrated to yield the enthalpy and the Gibbs energy. The enthalpy parameters for 298 K are evaluated in separate calculations using published high-temperature osmotic data as well as heats of dilution, while the Gibbs energy parameters for 298 K are taken from the literature. The range of validity of the final equations is described.

Introduction

We (*1*) have recently completed a study where thermodynamic data on a number of 1:1 aqueous electrolytes have been analyzed using the ion-interaction model. Apparent molar heat capacities and volumes up to 373 K were fitted to the Pitzer equations and the resulting heat capacity equations were integrated to obtain the enthalpy and Gibbs energy functions. In the present paper, we extend the study to the 2:1 electrolytes $MgCl_2$, $CaCl_2$, and $SrCl_2$. In each case the heat capacity and density have been measured to 373 K by Saluja and LeBlanc (*2*), and are reported in the accompanying paper. We have fitted these data, together with some values from literature, to the appropriate equations.

There is special interest in these results for $MgCl_2$ because they can be combined with similar values for Na_2SO_4 (*3*, *4*) and NaCl (*5*, *6*) to yield indirectly the properties of infinitely dilute $MgSO_4$. Phutela and Pitzer (*4*, *7*) have completed measurements of the heat capacity and density of aqueous $MgSO_4$ to 473 K and used these indirect results for the infinitely dilute standard state of $MgSO_4$ in their general treatment of the thermodynamic properties of aqueous $MgSO_4$. In the case of $MgCl_2$, we have heat capacity data to 453 K from Likke and Bromley (*8*); thus, our treatment for $MgCl_2$ is valid over this extended temperature range.

Our data bases for the apparent molar volumes of all three salts include the measurements of Ellis (*9*) which extend to 473 K and 1.0 $mol{\cdot}kg^{-1}$; thus, our volumetric equations are valid over that range.

[†] Issued as LBL-21304 and as AECL-9042.

0021-9568/87/1732-0076$01.50/0