Apparent molal expansibilities of some divalent chlorides in aqueous solution at 25°

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Apparent Molal Expansibilities of Some Divalent Chlorides

in Aqueous Solution at 25°

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(Received June 24, 1968)

The apparent molal volumes, ϕ_v, of dilute aqueous $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ solutions have been determined at 1° intervals from 20 to 30° from precision density measurements. The apparent molal expansibilities, ϕ_E, have been calculated from the apparent molal volumes at various temperatures and have been equated to the infinite-dilution partial molal expansibilities ($\phi_E^0 = \bar{E}^0$). The $\bar{E}^0$'s of the divalent chlorides increase in the order $MgCl_2 < CaCl_2 < SrCl_2 \approx BaCl_2$. The $\bar{E}^0$'s of these salts were divided into their ionic components, $\bar{E}^0(ion)$, by assigning a value for $\bar{E}^0(Cl^-) = 0.046$ ml/mol deg. The $\bar{E}^0$'s of the divalent cations can be represented by the equation $\bar{E}^0(ion) = -0.034(Z^2/r) + 0.092$ ml/mol deg. The $\bar{E}^0$'s of the divalent cations and other monovalent cations and anions are discussed by dividing $E^0(ion)$ into the following components: $\bar{E}^0(int)$, the intrinsic expansibility; $\bar{E}^0(elect)$, the electrostriction expansibility; and $\bar{E}^0(struct)$, the structural expansibility. The $\bar{V}^0$'s and $\bar{E}^0$'s of ions in solution are also qualitatively examined by describing the hydration of an ion by the Frank and Wen model.

Introduction

The partial molar volume of salts at infinite dilution, $\bar{V}_0$, in aqueous solutions have frequently been used to obtain a better understanding of solute–solvent interactions.[1–13] The $\bar{V}^0$'s of salts have been shown to be additive within experimental error;[14] however, the separation of the $\bar{V}^0$'s of salts into their ionic components, $\bar{V}^0(ion)$, cannot normally be made by direct experimental methods.[15] Once $\bar{V}^0$ of one ion is estimated by some correlation or curve-fitting method (by assuming some simple model for solute–solvent interactions), the $\bar{V}^0$'s of the other ions are fixed. Muker-

jee[16] has recently summarized the various estimates of $\bar{V}^0$ of a proton, and it is generally agreed that $\bar{V}^0(H^+)$ is about -4.5 ml/mol at 25° in aqueous solution.

(1) T. J. Webb, *J. Amer. Chem. Soc.*, **48**, 2589 (1926).

(2) H. M. Evjen and F. Zwicky, *Phys. Rev.*, **33**, 860 (1929).

(3) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

(4) O. Redlich and J. Bigeleisen, *Chem. Rev.*, **30**, 171 (1942).

(5) L. G. Hepler, *J. Phys. Chem.*, **61**, 1426 (1957).

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(7) S. W. Benson and C. S. Copeland, *ibid.*, **67**, 1194 (1963).

(8) J. Padova, *J. Chem. Phys.*, **39**, 1552 (1963).

(9) E. Whalley, *ibid.*, **38**, 1400 (1963).

Various workers[5-13] have attempted to divide $\bar{V}^0$(ion) into two components

$$\bar{V}^0(\text{ion}) = \bar{V}^0(\text{int}) + \bar{V}^0(\text{elect}) \qquad (1)$$

where $\bar{V}^0$(int) is the intrinsic volume of the ion including void space and $\bar{V}^0$(elect) is the decrease in volume due to electrostriction. It has been shown for some ions (Li$^+$, F$^-$, Be^{2+}, Mg^{2+}, and R$_4$N$^+$, for example) that another term may be necessary,[13,17-19] $\bar{V}^0$(struct), the volume change due to changes in the structure of water (i.e., changes in the ratio of "ice-like" to "non-icelike" forms of water). Thus $\bar{V}^0$(ion) can be expressed by the equation

$$\bar{V}^0(\text{ion}) = \bar{V}^0(\text{int}) + \bar{V}^0(\text{elect}) + \bar{V}^0(\text{struct}) \qquad (2)$$

Since the various components of eq 2 may be small when compared with the absolute size of the ion (excluding void effects), it is difficult to determine the individual components of $\bar{V}^0$(ion) or to separate them. By looking at the effect of temperature on $\bar{V}^0$(ion), it is possible to solve this problem. Upon differentiation of eq 2 with respect to temperature, $d\bar{V}^0(\text{ion})/dT = \bar{E}^0(\text{ion})$, one obtains the partial molal expansibility of an ion

$$\bar{E}^0(\text{ion}) = \bar{E}^0(\text{int}) + \bar{E}^0(\text{elect}) + \bar{E}^0(\text{struct}) \qquad (3)$$

where $\bar{E}^0$(int) is the expansibility due to void-space changes (assuming the intrinsic size of the ion does not change with temperature), $\bar{E}^0$(elect) is the expansibility due to electrostriction changes, and $\bar{E}^0$(struct) is the expansibility due to changes in the structure of water.

In recent papers[18-20] we have measured the apparent molal volume, ϕ_v, of a number of dilute aqueous salt solutions as a function of temperature. From these apparent molal volumes we have calculated the apparent molal expansibilities ($\phi_E = d\phi_v/dT$) and have equated them to the infinite-dilution apparent molal expansibility (the partial molal expansibility, $\phi_E{}^0 = \bar{E}^0$). The $\bar{E}^0$'s of the salts have been divided into their ionic components, $\bar{E}^0$(ion), by assuming that $\bar{E}^0$(H$^+$) = 0.000[18] and -0.012 ml/mol deg;[19] the results of this division have been discussed by comparing the terms of eq 3.

In this paper are reported the ϕ_E's of dilute aqueous MgCl$_2$, CaCl$_2$, SrCl$_2$, and BaCl$_2$ at 25°, calculated from precision density measurements made at 1° intervals from 20 to 30°. The results will be discussed by comparing $\bar{E}^0$(Mg^{2+}) $\bar{E}^0$(Ca^{2+}), $\bar{E}^0$(Ba^{2+}), and $\bar{E}^0$(Sr^{2+}) with the $\bar{E}^0$'s obtained for other ions.

Experimental Section

All the salts used were reagent grade Baker Analyzed chemicals and were used without further purification. The salts were dried in a vacuum desiccator at 70° for at least 1 week before use. The solutions were made by weight with doubly distilled water, degassed to

prevent the formation of bubbles on the magnetic float.

The magnetic float densitometer used to make the density measurements has been described elsewhere.[21] The densitometer was on the bottom of a constant-temperature bath that was controlled to better than $\pm 0.001°$ with a Hallikainen thermoregulator. The temperature of the bath was initially set and subsequently was read to within $\pm 0.002°$ with a Melabs platinum resistance thermometer.

Results

The densities of dilute MgCl$_2$, CaCl$_2$, SrCl$_2$, and BaCl$_2$ aqueous solutions have been measured at 1° intervals from 20 to 30° with a magnetic float densitometer. The apparent molal volumes, ϕ_v's, were calculated from the densities by using the equation

$$\phi_v = \frac{1000(d^0 - d)}{dd^0 m} + \frac{M}{d} \qquad (4)$$

where d^0 is the density of pure water,[22] d is the density of the solution, M is the molecular weight of the solute, and m is the molality of the solution (mol/1000 g of water). The apparent molal expansibilities, ϕ_E, for the various solutions were calculated from ϕ_v at various temperatures ($\phi_E = d\phi_v/dT$). The average apparent molal expansibilities and the average deviations from the mean are given in Table I. Although these ϕ_E values were not made as a function of concentration, we have equated these ϕ_E values to the infinite-dilution partial molal expansibilities, $\phi_E = \bar{E}^0$. Since ϕ_E does not vary considerably with concentration[23,24] and the measurements were made on dilute solutions, the differences between ϕ_E and $\bar{E}^0$ are well within the experi-

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(23) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," American Chemical Society Monograph No. 137, Reinhold Publishing Corp., New York, N. Y., 1958.

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Table I: Apparent Molal Expansibilities of $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ Aqueous Solutions at 25°

Salt	Concn, m	Apparent molal expansibility,[a] ml/mol deg
$MgCl_2$	0.06083	-0.013 ± 0.009
$CaCl_2$	0.06200	0.050 ± 0.017
$SrCl_2$	0.04243	0.082 ± 0.020
$BaCl_2$	0.07482	0.080 ± 0.029

[a] It should be kept in mind that an error of 1 ppm in the density at concentrations of ~0.05 m corresponds to an error of ± 0.02 ml/mol in ϕ_V or ± 0.04 ml/mol deg in ϕ_E. Since all the measurements were made with the same apparatus, the relative comparison of ϕ_E is probably more accurate than the average deviations indicate.

mental error (0.009–0.03 ml/mol deg). We know of few other expansibility data for the divalent salts or ions at 25° that can be used to compare with our results. Noyes[25] lists values for $\bar{E}^0(Mg^{2+})$, $\bar{E}^0(Sr^{2+})$, and $\bar{E}^0(Ba^{2+})$ (respectively, equal to 0.004, 0.12, and 0.18 ml/mol deg) where $\bar{E}^0(Cl^-) = 0$ and $\bar{E}^0(H^+) = 0$. These values were calculated from the tabulated and graphical information of Fajans and Johnson.[26] Since $\bar{E}^0(HCl) = 0.034$ ml/mol deg and not 0 at 25°, the results are not very reliable, but they do agree with our results within the combined experimental errors. Dunn[27] has recently measured $\bar{V}^0(CaCl_2)$ and $\bar{V}^0(BaCl_2)$ at 0.05, 5.0, 15°, and the $\bar{E}^0$'s extrapolated from these results (to 25°) agree within experimental error with our results for these salts ($\bar{E}^0(CaCl_2) \cong 0.08$ ml/mol deg and $\bar{E}^0(BaCl_2) \cong 0.11$ ml/mol deg). The $\bar{E}^0$'s of the divalent chlorides were divided into their ionic components, $\bar{E}^0$(ion), by assigning a value for $\bar{E}^0(Cl^-) = 0.046$ ml/mol deg.[19] Table II lists the $\bar{E}^0$(ion) for these divalent cations and other ions along with the literature references[18–20,23] and crystal radii.[28]

Discussion

The values of $\bar{E}^0$ of the divalent ions (given in Table II) vary with the crystal radius (or the radius of the ion in solution) unlike values of $\bar{V}^0$(elect) of these ions.[6] The apparently constant electrostriction for the divalent ions (and other polyvalent ions)[6] is due to the other terms of eq 3, $\bar{V}^0$(int) and $\bar{V}^0$(struct), masking the effects of $\bar{V}^0$(elect). The variation of the $\bar{E}^0$'s of the divalent cations (as a function of crystal radius) is in opposite order to the $\bar{E}^0$'s of the monovalent cations. Thus the effect of temperature on the hydration of divalent and monovalent cations is different. Also, $\bar{E}^0$(ion) appears to be a much more sensitive probe of ion–solvent interactions than $\bar{V}^0$(ion).

If one assumes that the $\bar{E}^0$'s of the divalent cations (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) are mainly due to the electrostrictive expansibility, one would expect $\bar{E}^0$ of these ions to be proportional to Z^2/r (where r is the

Table II: Partial Molal Expansibility of Ions in Aqueous Solution at 25°

Ion	r (crystal radius),[a] Å	$\bar{E}^0$(ion), ml/mol deg	Ref
H^+	...	-0.012	b
Li^+	0.60	-0.014	c
Na^+	0.95	0.032	c
K^+	1.33	0.023	c
Rb^+	1.48	0.016	c
Cs^+	1.69	0.012	c
NH_4^+	1.48	-0.028	d
Me_4N^+	3.47	0.033	d
Et_4N^+	4.00	0.054	d
Pr_4N^+	4.52	0.095	d
Bu_4N^+	4.94	0.177	d
Mg^{2+}	0.65	-0.105	e
Ca^{2+}	0.99	-0.042	e
Sr^{2+}	1.13	-0.010	e
Ba^{2+}	1.35	-0.012	e
F^-	1.36	0.035	c
Cl^-	1.81	0.046	c
Br^-	1.95	0.050	f
I^-	2.16	0.069	c
NO_3^-	2.64	0.100	c
SO_4^{2-}	2.90	0.107	g

[a] The Pauling crystal radii as quoted in E. R. Nightingale, Jr., J. Phys. Chem., **63**, 1381 (1959). [b] Calculated from $\bar{E}^0(HCl)$ listed in ref 23 by assuming $\bar{E}^0(Cl^-) = 0.046$ ml/mol deg.[19] [c] Calculated from the $\bar{E}^0$'s of the salts listed in ref 18 by assuming $\bar{E}^0(Cl^-) = 0.046$ ml/mol deg.[19] [d] Calculated from the $\bar{E}^0$'s of the salts listed in ref 19. [e] Calculated from the $\bar{E}^0$'s of the salts listed in Table I by assuming $\bar{E}^0(Cl^-) = 0.046$ ml/mol deg. [f] Recalculated from $\bar{E}^0(KBr)$ given in ref 18 by using the data above 25° and comparing the nearly constant difference obtained between the values listed in ref 23 and ref 18. [g] Calculated from $\bar{E}^0(Na_2SO_4)$ given in ref 20.

crystal radius in ångströms). Figure 1 shows a plot of $\bar{E}^0$ for the divalent ions (listed in Table II) vs. Z^2/r. The slope of this line is found to be equal to 0.034 Å ml/mol deg and the intercept equal to 0.092 ml/mol deg. The value obtained for the slope agrees very well with the theoretical value (0.027 Å ml/mol deg) obtained by Noyes[25] by differentiating the Drude–Nernst[29] equation with respect to temperature

$$\bar{E}^0(\text{elect}) = \frac{d\bar{V}^0(\text{elect})}{dt} = \frac{-d}{dT}\left[\frac{1}{D}\left(\frac{d\ln D}{dP}\right)\right]\frac{e^2 Z^2}{2r} \quad (5)$$

The positive intercept indicates that there is a positive contribution to the $\bar{E}^0$ of the divalent ions similar to nonelectrolytes and other ions. At present it is not

(25) R. M. Noyes, J. Amer. Chem. Soc., **86**, 971 (1964).

(26) K. Fajans and O. Johnson, ibid., **64**, 668 (1942).

(27) L. A. Dunn, Trans. Faraday Soc., in press.

(28) The Pauling crystal radii as quoted by E. R. Nightingale, Jr., J. Phys. Chem., **63**, 1381 (1959).

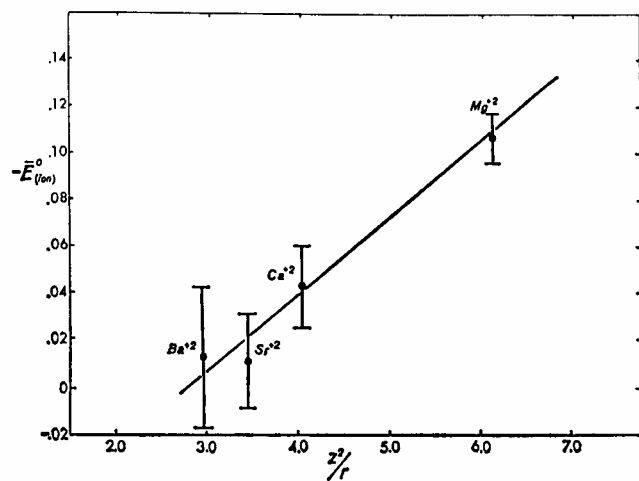(29) P. Drude and W. Nernst, Z. Phys. Chem. (Frankfurt am Main), **15**, 79 (1894).

Figure 1. Partial molal expansibility of some divalent ions as a function of Z^2/r, where Z is the charge on the ion and r is the crystal radius in ångströms.

possible to separate this positive $\bar{E}^0$ effect (*i.e.*, $\bar{E}^0(\text{int})$ + $\bar{E}^0(\text{struct})$) or say that is is not a function of the size of the ion. The curve can be made to pass through zero by adjusting $\bar{E}^0(\text{Cl}^-)$ to a value of 0.092 ml/mol deg. This value for $\bar{E}^0(\text{Cl}^-)$, however, appears to be quite high compared with other estimates.[18,19,25] This division would also cause $\bar{E}^0$ of almost all the cations in Table II to be negative (except Et_4N^+, Pr_4N^+, and Bu_4N^+) and all the anions to be positive, which seems unreasonable.

The $\bar{E}^0$'s of the simple monovalent cations and anions vary with size or radius in an inverse order (Table I). Thus, although various workers have been successful in treating the ion–solvent interactions of these simple monovalent ions by a common relationship, the $\bar{E}^0$ results indicate that (1) the effect of ions on the structure of water (over and above the electrostrictive region) is very important and should not be neglected and (2) the effect of the ions on the structure of water is different for cations and anions of similar size and is not a smooth function of crystal radius or the charge on the ion.

Water is one of the few solvent systems where the $\bar{E}^0$'s of monovalent salts and ions have positive values at room temperatures. At temperatures above 50–70°, however, the $\bar{E}^0$'s of salts and ions are negative[30] in water, as predicted from the simple continuum model. The $\bar{V}^0$'s of salts are also in their predicted order at temperatures above 50° (*i.e.*, as a function of r^3). It appears as though the structure of water (that is thought to exist at room temperatures) accounts for the positive $\bar{E}^0$ and that at high temperatures the positive effect disappears. The exact form of the $\bar{E}^0$ due to the structure of water for various ions is quite complicated, and it is impossible at this time to predict the relationship of $\bar{E}^0$ to the intrinsic properties of the ions. Until more is known about the structure of water at

room temperatures, the division of $\bar{E}^0$'s or $\bar{V}^0$'s of ions into various components may be entirely arbitrary.

Another qualitative approach to the division of the $\bar{V}^0$'s and $\bar{E}^0$'s of ions into individual components can be developed by describing the hydration of an ion in solution by the Frank and Wen model.[31] From this model the $\bar{V}^0$ of an ion can be viewed as being due to the following four components: (1) the intrinsic volume of the ion, $\bar{V}^0(\text{int})$; (2) the electrostricted volume, $\bar{V}^0(\text{elect})$, due to the water firmly attached to the ion; (3) the disordered volume, $\bar{V}^0(\text{disord})$, due to the disordered region surrounding the electrostricted region of the ion; and (4) the caged volume due to the formation of structured or "caged" water around the ion (this region is important for ions that have a hydrocarbon portion or possibly for highly charged ions). The effect of temperature on these various regions can likewise be divided into four regions: (1) the intrinsic expansibility, $\bar{E}^0(\text{int})$, which is the volume change due to the expansion of the ion (this term is probably very small and can be neglected for normal ions); (2) the electrostriction expansibility, $\bar{E}^0(\text{elect})$, which is due to changes in the electrostricted region; (3) the disordered expansibility, $\bar{E}^0(\text{disord})$, which is due to changes in the disordered region; and (4) the "caged" expansibility, $\bar{E}^0(\text{caged})$, which is due to the changes in the "caged" or highly structured water around hydrocarbon portion of an ion (or possibly around highly electrostricted ions where the disordered region is very small).

The $\bar{V}^0(\text{int})$ of the ion is equal to the volume of the ion calculated from the crystal radius, and if it is assumed that the ion is hard sphere, $\bar{V}^0(\text{int}) = 2.52r^3$, where r is in ångströms. $\bar{E}^0(\text{int})$ is positive and very small for normal ions; however, it may be large for ions with hydrocarbon portions or simple hydrocarbon nonelectrolytes.

The $\bar{V}^0(\text{elect})$ and $\bar{E}^0(\text{elect})$ regions immediately surrounding an ion appear to be predictable in sign and order of magnitude from the simple continuum model or modifications to this model for dielectric saturation effects. $\bar{V}^0(\text{elect})$ and $\bar{E}^0(\text{elect})$ are both negative and proportional to Z^2/r.

The $\bar{V}^0(\text{disord})$ and $\bar{E}^0(\text{disord})$ region appears to be different for cations and anions of the same size, owing to the different orientation of the water molecules in the first electrostricted region. The size of the disordered region depends on the temperature and magnitude of the electrostriction region (*i.e.*, Z^2/r). For ions with a large electrostriction region (large Z^2/r) the disordered region is very small or nonexistent; however, for ions with a small electrostriction region (small Z^2/r like the large monovalent ions) this region is very

(30) A. J. Ellis, *J. Chem. Soc.*, 1579 (1966); 660 (1967).
(31) H. Frank and W. Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1967).

important. The disordered region appears to become less important at high temperatures, causing the maximum in $\bar{V}^0$ of the simple monovalent salts near 50°.[30] At low temperatures or near room temperature the $\bar{V}^0$ of the disordered region accounts for the $\bar{V}^0$'s of the large monovalent ions appearing to be larger in solutions than the crystal volume normally attributed to void-space effects. The $\bar{E}^0$ of the disordered region accounts for the large positive values for the monovalent ions at room temperatures and the differences between the cation and anion $\bar{E}^0$ dependence on size. The $\bar{V}^0$-(disord) and $\bar{E}^0$(disord) are both positive and become less important at high temperatures or as the structure of water is broken.

The $\bar{V}^0$ and $\bar{E}^0$ of the caged region which is important for ions with hydrocarbon tails (or possibly highly charged ions) has been discussed elsewhere.[19] The $\bar{V}^0$(caged) is negative and increases in magnitude with the size of the hydrocarbon portion of the molecule. This region may also exist for highly charged ions and may be the cause of the constant $\bar{V}^0$(elect) observed by Mukerjee.[6] The $\bar{E}^0$(caged) is positive and also increases in magnitude with size of the hydrocarbon portion of the ion. This positive contribution of $\bar{E}^0$(caged) may be the cause of the $\bar{E}^0$'s of the divalent cations appearing to be too large. Since $\bar{E}^0$(disord) can also cause the same positive effect, it cannot be stated with certainty which effect causes the positive contribution to the $\bar{E}^0$'s of the divalent ions.

In conclusion, the experimental results of the $\bar{V}^0$'s and the $\bar{E}^0$'s of ions indicate that solute–solvent interactions are very dependent upon the structure of water. After the structure of water is broken down (i.e., at high temperatures), the solute–solvent interactions appear to be normal (or predictable in magnitude and sign by a simple model). By saying that the structure of water is broken down it is not meant that water exists as only monomers but that one structured form responsible for the anomalous thermodynamic behavior[32] disappears at high temperatures. Accurate measurements of the $\bar{V}^0$'s of solutes (and other thermodynamic data) in water are needed at temperatures above 50°. From these data it may be possible to obtain a better understanding of the effects of the structure of water and the changes in structure caused by ions at lower temperatures.

(32) For example, the temperature coefficient of the isothermal compressibility of water: G. S. Kell and E. Whalley, *Phil. Trans. Roy Soc.* (London), **258**, 565 (1965).