

Ion-Solvent Interactions in Aqueous Solutions at Various Temperatures

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The temperature variation of the limiting partial molar volumes of a number of electrolytes in aqueous solution has been examined in terms of solvent electrostriction. The Desnoyers, Verrall, and Conway theory has been modified and extended to cover the temperature range 0–100°C. It has been shown that electrostriction effects alone cannot account for the observed maxima in the \bar{V}° - T plots for various electrolytes. It is concluded that solvent structural changes over this temperature range may well be important.

KEY WORDS: Aqueous; electrostriction; ion-solvent interactions; partial molar volumes.

At infinite dilution, where ion-ion interactions are absent, the partial molar volume of an electrolyte is of fundamental interest since its magnitude is determined solely by the intrinsic volumes of the ions in solution and by ion-solvent interactions. The limiting partial molar volumes^(1, 2, 3) of NaCl, KCl, KBr, KI, CaCl₂, and BaCl₂ in aqueous solution over the temperature range 0–70°C are plotted in Fig. 1. These data, combined with those of Ellis^(4, 5, 6) to 200°C, show clearly that a number of electrolytes in aqueous solution exhibit maxima in their \bar{V}° - T plots in the range 30–100°C. This may also be inferred from the data of Eucken⁽⁷⁾ and the recent extensive compilation of Millero.⁽⁸⁾

When one mole of electrolyte is dissolved in a very large volume of solvent under isothermal conditions, two major factors contribute to the partial molar volume of the electrolyte at infinite dilution: \bar{V}^{int} , the intrinsic volume of the electrolyte in solution, and V^{el} , the change in volume due to electrostriction of the solvent resulting from ion-solvent interactions. The limiting partial molar volume of an electrolyte, thermodynamically defined as the increase in volume

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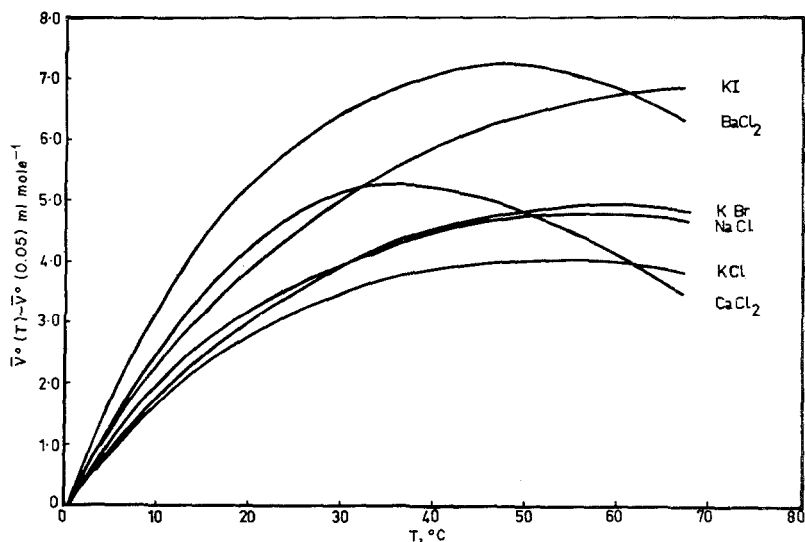


Fig. 1. Limiting partial molar volumes of NaCl, KCl, KBr, KI, CaCl₂, and BaCl₂ at various temperatures.

when one mole of electrolyte is dissolved in an infinitely large volume of solvent, may thus be expressed as

$$\bar{V}^o = V^{\text{int}} + V^{\text{el}} \quad (1)$$

Similar equations may be written for each ionic species in solution.

Various methods have been used to estimate the V^{int} and V^{el} terms of Eq. (1). Millero⁽⁸⁾ has reviewed the various methods employed to estimate the V^{int} contribution in terms of a crystal volume factor V^{cryst} , a void space factor V^{disord} , and a factor V^{caged} to allow for possible changes in the structure of the solvent. The Born equation,⁽⁹⁾ or some modification of it, has been the usual starting point of a number of methods for estimating V^{el} . Detailed calculations using this approach have been given by Laidler and Pegis,⁽¹⁰⁾ Benson and Copeland,⁽¹¹⁾ Padova,⁽¹²⁾ Hamann,⁽¹³⁾ and Whalley.⁽¹⁴⁾ Both Conway, Desnoyers, and Smith⁽¹⁵⁾ and Glueckauf⁽¹⁶⁾ have pointed to a serious restriction of this approach, namely, its inability to take into account the finite dimensions of the solvent molecules and the structural void space around the ions. Both of these factors are clearly related to the electrostriction effect.

Desnoyers, Verrall, and Conway⁽¹⁷⁾ have proposed an alternative approach to calculating V^{el} , based on an equation derived by Frank⁽¹⁸⁾ for the change in volume v of the solvent with field E during the process of charging an ion

isothermally in a solvent under conditions of constant chemical potential μ . They have solved this equation

$$(1/v)(\partial v/\partial E)_{\mu,T} = -(E/4\pi)(\partial \epsilon_d/\partial P)_{E,T} \quad (2)$$

at 25°C by calculating that effective pressure P which, in the absence of the field, would produce the same volume change that E would produce. This has been done by substitution of the compressibility expression

$$dv/v = -\beta dP \quad (3)$$

into Eq. (2) to give

$$dP/dE = (E/4\pi\beta)(\partial \epsilon_d/\partial P)_{E,T} \quad (4)$$

which then relates this effective pressure P to the field E . In order to integrate Eq. (4), β and ϵ_d must be expressed as functions of P . Desnoyers *et al.*⁽¹⁷⁾ have used the Tait—Gibson equation for the compressibility of water

$$\beta = D/(B + P) \quad (5)$$

which satisfactorily represents the experimental data of Adams⁽¹⁹⁾ at 25°C, and the empirical equation of Grahame⁽²⁰⁾

$$\epsilon_d = n^2 + (\epsilon - n^2)(1 + bE^2)^{-1} \quad (6)$$

to relate the differential permittivity ϵ_d to the field E . In order to relate ϵ_d to pressure, they have used the empirical expressions

$$(1/\epsilon)(\partial \epsilon/\partial P)_{E,T} = A/(B + P) \quad (7)$$

and

$$(1/n^2)(\partial n^2/\partial P)_{E,T} = C/(B + P) \quad (8)$$

to represent the pressure variation of the permittivity ϵ and the refractive index n . In Eqs. (5), (7), and (8), A , B , C , and D are constants. Hamann⁽¹³⁾ has shown that Eq. (7) satisfactorily represents the experimental data of Scaife⁽²¹⁾ at 20°C, while Harned and Owen,⁽²²⁾ using the more recent data of Owen *et al.*,⁽²³⁾ have argued that it is much less satisfactory for water than for other solvents. The experimental data of Rosen⁽²⁴⁾ for the refractive index of water at various pressures at 25°C are satisfactorily represented by Eq. (8). By substitut-

ing the integrated forms of Eqs. (7) and (8) into Eq. (6), Desnoyers *et al.*⁽¹⁷⁾ have expressed ϵ_d as a function of P and E , have thus found an expression for $(\partial\epsilon_d/\partial P)_{E,T}$ for use in Eq. (4), and have then integrated this equation by means of the Runge-Kutta numerical integration method. The calculated P values have then been substituted into the integrated form of Eq. (3),

$$\log (v_0/v) = D \log (1 + P/B) \quad (9)$$

where v_0 is the volume of one mole of water at zero field and v is the volume at field E and pressure P . The electrostriction volume per mole of water, Δv , given by the expression

$$\Delta v = v_0 - v \quad (10)$$

has then been calculated for a wide range of fields at 25°C.

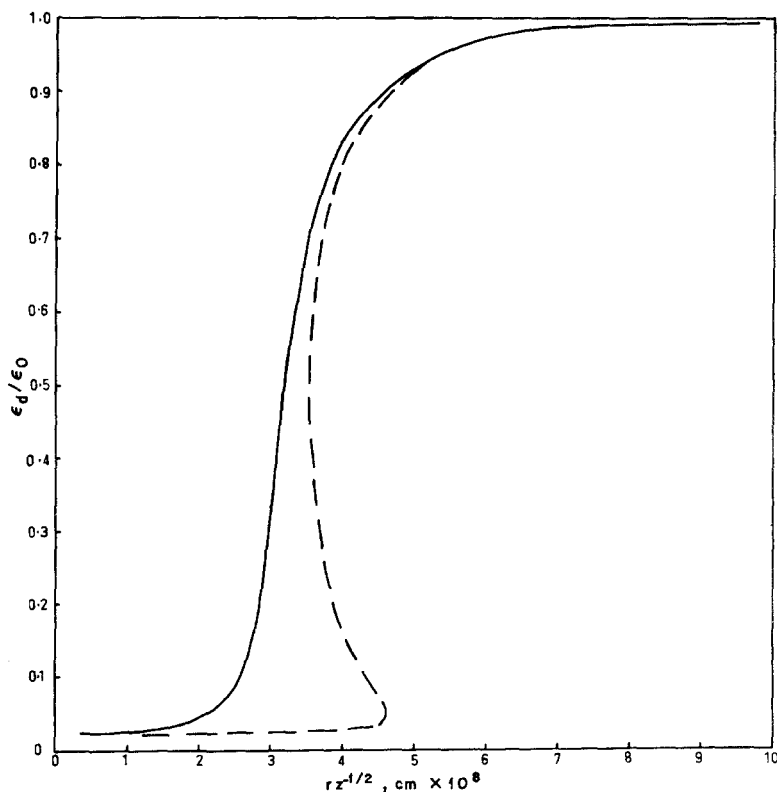


Fig. 2. Variation of the permittivity of water with distance from an ion at 25°C.

-----, Eq. (6); ———, Eq. (11).

In this approach to calculating V^{el} , the use of Eq. (6) is somewhat questionable, since it reproduces the experimental data of Malsch⁽²⁵⁾ and the more rigorous theoretical treatment of Booth⁽²⁶⁾ only up to fields of about 2×10^3 esu. The fields of interest in electrostriction calculations at a distance of one water molecule from the ions considered here lie in the range 7×10^3 to 4×10^5 esu, where the Grahame equation behaves rather irrationally. This is shown clearly in Fig. 2, where the relative permittivity ϵ_d/ϵ_0 , as calculated from Eqs. (6) and (11), is plotted as a function of distance from an ion at 25°C. Data at other temperatures show similar variation.

Thus, since accurate \bar{V}° data are available^(1-6, 8) for a number of electrolytes over a wide temperature range, it would seem desirable to estimate the V^{el} term of Eq. (1) over a wide temperature range by developing the Desnoyers *et al.*⁽¹⁷⁾ theory on the basis of the more rigorous Booth⁽²⁶⁾ equation. This equation

$$\epsilon_d = n^2 + \frac{28N_0\pi(n^2 + 2)\mu}{3\sqrt{73}E} L \left[\frac{\sqrt{73}\mu(n^2 + 2)}{6kT} E \right] \quad (11)$$

has been derived following an analysis and extension of the theories of Onsager⁽²⁷⁾ and Kirkwood⁽²⁸⁾ for the permittivities of polar liquids. Here, n is the optical refractive index, N_0 is the number of molecules per unit volume, μ is the solvent dipole moment, E is the field strength, T is the absolute temperature, L is the Langevin function defined by the expression

$$L(x) = \coth x - 1/x \quad (12)$$

and other symbols have their usual significance. It can be shown from Eq. (11) that in the zero-field limit, where $\epsilon_d = \epsilon$, we may write

$$(\epsilon - n^2) = 14N_0\pi\mu^2(n^2 + 2)^2/27kT \quad (13)$$

For water in the temperature range 0–100°C, the coefficient of E in the argument of the Langevin function in Eq. (11) has a value in the range 3.2 to 4.4×10^{-4} (see Table I). Hence, it can be shown that at low fields ($E < 1 \times 10^3$ esu) we may write

$$\epsilon_d = n^2 + (\epsilon - n^2)(1 - bE^2) \quad (14)$$

where

$$b = 73\mu^2(n^2 + 2)^2/540k^2T^2 \quad (15)$$

Table I. Numerical Values Used in the Estimation of Δv as a Function of Field at Various Temperatures

$T (^{\circ}\text{C})$	b	η	ϵ_0	n_0^2	A	B (bars)	C	D
0	1.29×10^{-8}	4.40×10^{-4}	87.73	1.7796	0.1213	2686.3	0.0704	0.1368
10	1.20	4.24	83.83	1.7795	0.1302	2840.5	0.0695	0.1368
20	1.12	4.10	80.11	1.7780	0.1378	2953.7	0.0688	0.1368
25	1.08	4.03	78.31	1.7769	0.1411	2996.0	0.0685	0.1368
30	1.04	3.96	76.55	1.7755	0.1441	3029.4	0.0683	0.1368
40	0.98	3.83	73.15	1.7722	0.1493	3071.3	0.0679	0.1368
50	0.92	3.71	69.91	1.7681	0.1535	3083.1	0.0676	0.1368
60	0.86	3.59	66.80	1.7634	0.1566	3068.3	0.0673	0.1368
70	0.81	3.48	63.84	1.7581	0.1589	3030.7	0.0670	0.1368
80	0.76	3.38	61.00	1.7523	0.1604	2973.8	0.0668	0.1368
90	0.72	3.28	58.29	1.7460	0.1612	2901.4	0.0666	0.1368
100	0.66	3.18	55.71	1.7393	0.1613	2817.1	0.0664	0.1368

Clearly, Eq. (14) is identical to Eq. (6) if terms in E greater than E^2 are neglected, and b is given by Eq. (15). Thus, Eq. (11) may be written

$$\epsilon_d = n^2 + [3(\epsilon - n^2)/\eta E] (\coth \eta E - 1/\eta E) \quad (16)$$

where

$$\eta^2 = 15b \quad (17)$$

Glueckauf^(29, 30) has pointed out that for water at room temperature the value of b according to Eq. (15) should be $0.4 \times 10^{-8} \text{ cm}^2 \text{ esu}^{-2}$, whereas the experimental value of Malsch⁽²⁵⁾ is $1.08 \times 10^{-8} \text{ cm}^2 \text{ esu}^{-2}$. Since there is no method at present for deciding between these two values, that of Malsch⁽²⁵⁾ is used in the following discussion. Values of b at other temperatures are readily calculated from Eq. (15).

Following the same procedure as Desnoyers, Verrall, and Conway,⁽¹⁷⁾ we can write

$$\epsilon_d = n_0^2 \left(1 + \frac{P}{B}\right)^C + \left[\epsilon_0 \left(1 + \frac{P}{B}\right)^A - n_0^2 \left(1 + \frac{P}{B}\right)^C \right] \left[\frac{3}{\eta E} \left(\coth \eta E - \frac{1}{\eta E} \right) \right] \quad (18)$$

and hence

$$\begin{aligned} \left(\frac{\partial \epsilon_d}{\partial P} \right)_{E,T} &= \frac{n_0^2 C}{B} \left(1 + \frac{P}{B}\right)^{C-1} + \left\{ \left[\epsilon_0 A \left(1 + \frac{P}{B}\right)^{A-1} - n_0^2 C \left(1 + \frac{P}{B}\right)^{C-1} \right] \right. \\ &\quad \times \left. \left[\frac{3}{\eta B E} \left(\coth \eta E - \frac{1}{\eta E} \right) \right] \right\} + \left[\epsilon_0 \left(1 + \frac{P}{B}\right)^A - n_0^2 \left(1 + \frac{P}{B}\right)^C \right] \frac{\partial f(E)}{\partial P} \quad (19) \end{aligned}$$

where $f(E) = (3/\eta E)(\coth \eta E - 1/\eta E)$. These two equations should be compared with Eqs. (11) and (12) of the Desnoyers *et al.*⁽¹⁷⁾ derivation. Since their derivation and that of Padova⁽¹²⁾ have shown that $(\partial b/\partial P)_{E,T}$ and hence $(\partial \eta/\partial P)_{E,T}$ are small, the last term in Eq. (19) may be considered negligible in comparison with the other terms, and we can write

$$\left(\frac{\partial \epsilon_d}{\partial P}\right)_{E,T} = \frac{n_0^2 C}{B} \left(1 + \frac{P}{B}\right)^{C-1} + \left\{ \left[\epsilon_0 A \left(1 + \frac{P}{B}\right)^{A-1} - n_0^2 C \left(1 + \frac{P}{B}\right)^{C-1} \right] \times \left[\frac{3}{\eta B E} \left(\coth \eta E - \frac{1}{\eta E} \right) \right] \right\} \quad (20)$$

Combination of Eqs. (4), (5), and (20) then leads to the expression

$$\frac{dP}{dE} = \frac{n_0^2 C E}{4\pi D} \left(1 + \frac{P}{B}\right)^C + \frac{3}{4\pi \eta D} \left[\coth \eta E - \frac{1}{\eta E} \right] \left[\epsilon_0 A \left(1 + \frac{P}{B}\right)^A - n_0^2 C \left(1 + \frac{P}{B}\right)^C \right] \quad (21)$$

Using Eq. (6), Desnoyers *et al.*⁽¹⁷⁾ derived the expression

$$\frac{dP}{dE} = \frac{n_0^2 C E}{4\pi D} \left(1 + \frac{P}{B}\right)^C + \frac{E}{4\pi D(1 + bE^2)} \left[\epsilon_0 A \left(1 + \frac{P}{B}\right)^A - n_0^2 C \left(1 + \frac{P}{B}\right)^C \right] \quad (22)$$

For comparison, Eqs. (21) and (22) have been integrated at various temperatures for several fields in the range 2.5×10^3 to 1.0×10^8 esu by the Kutta-Merson⁽³¹⁾ integration method, using an Elliott 503 computer. In order to perform the integrations at each temperature, values of the various constants in the equations must be known, as must initial values of P and E .

The b and η values given in Table I have been calculated from Eqs. (15) and (17), respectively, using the value⁽²⁵⁾ of 1.08×10^{-8} cm² esu⁻² for b at 25°C. The permittivities in Table I are averaged values of the data of Owen *et al.*,⁽²³⁾ Malmberg and Maryott,⁽³²⁾ and Dunn and Stokes.⁽³³⁾ It has been shown⁽²²⁾ that the D coefficient in Eq. (5) is independent of temperature and pressure, while the B coefficient, so chosen that P represents the pressure in excess of 1 bar, is given by

$$B = 2996.0 + 7.5554(t - 25) - 0.17814(t - 25)^2 + 6.08 \times 10^{-4}(t - 25)^3 \quad (23)$$

where B is in bars. Values of B and D at various temperatures are included in Table I. Estimates of the A coefficient of Eq. (7) have been obtained by using

the $(\partial \ln \epsilon / \partial P)_{E,T}$ data of Owen *et al.*⁽²³⁾ for water at various temperatures, values of B calculated from Eq. (23) at various temperatures, and Eq. (7) rearranged to

$$A = (1/\epsilon)(\partial \epsilon / \partial P)_{E,T}(B + P) \quad (24)$$

Since the values of A at higher pressures were found to be only slightly higher than the values at 1 bar, the values at 1 bar and various temperatures are given in Table I. To estimate the C coefficient of Eq. (8) for liquid water from the slope of the equation

$$\log n^2 = \log n_0^2 + C \log (1 + P/B) \quad (25)$$

it has been assumed that Eq. (25) is linear in $\log (1 + P/B)$ to very high pressures, and that the constant K of the Lorentz–Lorenz equation,⁽³⁴⁾

$$K = (n^2 - 1)/(n^2 + 2)d \quad (26)$$

where n and d are the refractive index and density of water, respectively, is independent of temperature at fixed pressures.⁽³⁴⁾ Values of K for water at 25°C and pressures of 1, 500, 1000, and 1500 bars have been found by Rosen⁽²⁴⁾ to be 0.2063, 0.2059, 0.2053, and 0.2047, respectively. With the assumption that these K values are independent of temperature, values of n^2 have been calculated at corresponding pressures from Eq. (26) at various temperatures, using the specific-volume data of Kell and Whalley.⁽³⁵⁾ The calculated values of n_0^2 at 1 bar and various temperatures are included in Table I, where the C values have been obtained from plots of Eq. (25) at various temperatures, using the calculated values of n^2 at fixed pressures. The assumptions used in estimating C are probably questionable, and Desnoyers *et al.*⁽¹⁷⁾ have noted the need for accurate experimental refractive index data for water at high pressures over a range of temperatures. Perhaps a more realistic approach may be based on the work of Zel'dovich, Kormer, Sinitsyn, and Yushko.⁽³⁶⁾ With this in mind, the C values in Table I are considered at least qualitatively sufficient for the present discussion.

Since $\coth \eta E - 1/\eta E = \eta E/3$, and $bE^2 < 1$ for low fields ($E < 1 \times 10^3$ esu) at all temperatures, Eqs. (21) and (22) may be simplified to

$$dP/dE = (\epsilon_0 A E / 4\pi D)(1 + P/B)^A \quad (27)$$

which can then be integrated to give P for any $E < 1 \times 10^3$ esu. Several E values in the range $0.5 \times 10^2 < E < 1.5 \times 10^3$ esu with corresponding P values calculated from Eq. (27) have been used as the initial P and E values for the Kutta–

Table II. Electrostriction Data for Various Ions at Various Temperatures

$T(^{\circ}\text{C})$	ϵ	E (esu)	P (dyn-cm $^{-2}$)			$\Delta\nu$ (ml-mole $^{-1}$)		
			Eq. (22)	Eq. (21)	Eq. (30)	Eq. (22)	Eq. (21)	Eq. (30)
Na^+ ($r_i = 1.17 \times 10^{-8}$ cm, $rz^{-1/2} = 2.55 \times 10^{-8}$ cm)								
0	11.7	6.31×10^4	1.11×10^9	2.50×10^9	2.50×10^9	0.83	1.55	1.55
10	11.4	6.48	1.21	2.73	2.74	0.85	1.59	1.59
20	11.0	6.71	1.31	2.98	2.98	0.88	1.64	1.64
25	10.9	6.78	1.35	3.06	3.07	0.90	1.66	1.66
30	10.7	6.90	1.40	3.17	3.18	0.92	1.69	1.69
40	10.3	7.17	1.49	3.39	3.40	0.96	1.76	1.76
50	10.0	7.39	1.56	3.56	3.57	0.99	1.82	1.82
60	9.6	7.69	1.64	3.76	3.76	1.04	1.90	1.90
70	9.3	7.94	1.70	3.90	3.91	1.09	1.97	1.97
80	8.9	8.30	1.77	4.08	4.09	1.15	2.07	2.07
90	8.6	8.59	1.82	4.20	4.22	1.20	2.15	2.16
100	8.2	9.01	1.88	4.38	4.40	1.27	2.27	2.27
Cl^- ($r_i = 1.64 \times 10^{-8}$ cm, $rz^{-1/2} = 3.02 \times 10^{-8}$ cm)								
0	38.0	1.39×10^4	3.06×10^8	3.52×10^8	3.52×10^8	0.26	0.30	0.30
10	35.8	1.47	3.45	4.00	4.00	0.28	0.32	0.32
20	33.6	1.57	3.88	4.54	4.53	0.30	0.35	0.35
25	32.5	1.62	4.09	4.80	4.80	0.31	0.36	0.36
30	31.4	1.68	4.31	5.10	5.09	0.33	0.38	0.38
40	29.2	1.80	4.75	5.68	5.68	0.35	0.42	0.42
50	27.0	1.95	5.25	6.37	6.37	0.39	0.46	0.46
60	24.8	2.12	5.77	7.12	7.12	0.43	0.52	0.52
70	22.6	2.33	6.36	8.03	8.03	0.47	0.58	0.58
80	20.4	2.58	7.01	9.08	9.09	0.53	0.66	0.66
90	18.2	2.89	7.75	10.38	10.39	0.59	0.77	0.77
100	15.9	3.31	8.68	12.16	12.17	0.68	0.90	0.90
Ca^{++} ($r_i = 1.06 \times 10^{-8}$ cm, $rz^{-1/2} = 1.73 \times 10^{-8}$ cm)								
0	4.2	3.82×10^5	7.56×10^9	2.44×10^{10}	2.50×10^{10}	3.02	4.89	4.92
10	4.2	3.82	7.66	2.58	2.65	2.95	4.88	4.93
20	4.2	3.82	7.76	2.69	2.77	2.92	4.89	4.94
25	4.2	3.82	7.80	2.73	2.82	2.91	4.90	4.95
30	4.1	3.91	8.13	2.86	2.96	2.96	4.97	5.02
40	4.1	3.91	8.22	2.93	3.03	2.96	5.00	5.06
50	4.1	3.91	8.28	2.97	3.08	2.98	5.04	5.10
60	4.0	4.01	8.65	3.10	3.22	3.07	5.14	5.21
70	4.0	4.01	8.68	3.11	3.23	3.11	5.20	5.26
80	4.0	4.01	8.70	3.10	3.22	3.16	5.25	5.32
90	3.9	4.11	9.02	3.18	3.31	3.28	5.37	5.44
100	3.9	4.11	9.01	3.14	3.27	3.35	5.44	5.51

Merson⁽³¹⁾ integration of Eqs. (21) and (22). At all temperatures, the calculated P values from both equations for fields in the range $2.5 \times 10^3 < E < 1.0 \times 10^8$ esu were found to be independent of the initial values selected. As a check on the Kutta–Merson⁽³¹⁾ integration method, the Hamming⁽³⁷⁾ method was also used under similar conditions at several temperatures. Identical P values were obtained. It should also be noted here that at 25°C the P values calculated by the Kutta–Merson⁽³¹⁾ and Hamming⁽³⁷⁾ integrations of Eq. (22) are in excellent agreement with the P values calculated by the Runge–Kutta integration of Eq. (22), as reported by Desnoyers *et al.*⁽¹⁷⁾

The permittivity ϵ and field E values at a distance $rz^{-1/2}$ from each ion listed in Table II have been calculated from Eq. (11) and the expression

$$E = -ze/\epsilon r^2 \quad (28)$$

where

$$r = r_i + r_w \quad (29)$$

is the sum of the radii of the ion r_i and the water molecule r_w . Since Stokes⁽³⁸⁾ has shown that the crystal radii are appropriate to ions in solution, and because of the recommendation of Blandamer and Symons,⁽³⁹⁾ the crystal radii of Gourary and Adrian⁽⁴⁰⁾ and a value of 1.38×10^{-8} cm for r_w have been used to evaluate the r_i , $rz^{-1/2}$, ϵ , and E values given in Table II. Using the numerical data of Table I, P values at a distance of $rz^{-1/2}$ from several ions at various temperatures have been found by numerical integration of Eqs. (21) and (22); data for Na^+ , Cl^- , and Ca^{++} are listed in Table II. These P values have been substituted into Eq. (9), and Δv , the electrostriction volume per mole of water, has then been calculated using Eq. (10). These values are also listed in Table II.

It is of interest to note here that, if we divide Eq. (21) by $(1 + P/B)^A$ and make the assumption that $1 - A \approx 1 - C$ (see Table I), Eq. (21) can be integrated to give

$$\left(1 + \frac{P}{B}\right)^{1-A} = 1 + \frac{A(1-A)\epsilon_0 E^2}{8\pi BD} \left[\frac{n_0^2 C}{\epsilon_0 A} + 6(\eta E)^{-2} \left(1 - \frac{n_0^2 C}{\epsilon_0 A}\right) \ln \left(\frac{\sinh \eta E}{\eta E} \right) \right] \quad (30)$$

At low fields ($E < 1 \times 10^3$ esu), the $6(\eta E)^{-2} \ln (\sinh \eta E / \eta E)$ term is approximately unity at all temperatures, and the equation reduces to the integrated form of Eq. (27),

$$(1 + P/B)^{1-A} = 1 + A(1-A)\epsilon_0 E^2 / 8\pi BD \quad (31)$$

which is identical with the low-field equation of the Desnoyers *et al.*⁽¹⁷⁾ derivation. At high fields ($E > 1 \times 10^6$ esu), the $6(\eta E)^{-2} \ln (\sinh \eta E / \eta E)$ term can be neglected since it is very small ($\ll 1$) at all temperatures, and the equation reduces to

$$(1 + P/B)^{1-A} = 1 + C(1-A)n_0^2 E^2 / 8\pi BD \quad (32)$$

If we again use the approximation $1-A \approx 1-C$, this then takes the form

$$(1 + P/B)^{1-C} = 1 + C(1-C)n_0^2 E^2 / 8\pi BD \quad (33)$$

which is identical with the high-field equation of the Desnoyers *et al.*⁽¹⁷⁾ derivation. P and Δv values based on Eq. (30) have also been calculated for several ions, and data for Na^+ , Cl^- , and Ca^{++} are included in Table II.

It is clear that the P and Δv values based on Eqs. (21) and (30) are in good agreement for all ions at all temperatures, while the P and Δv values based on

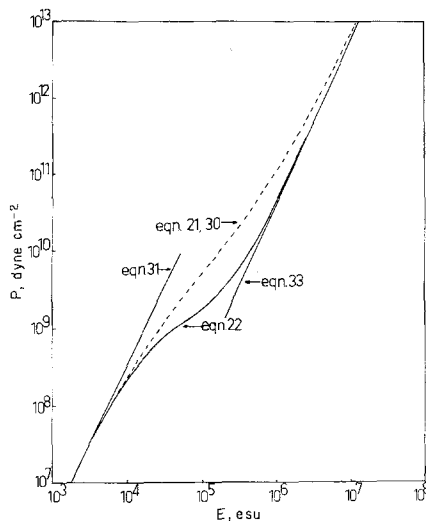


Fig. 3. Variation of pressure with field for aqueous solutions at 25°C.

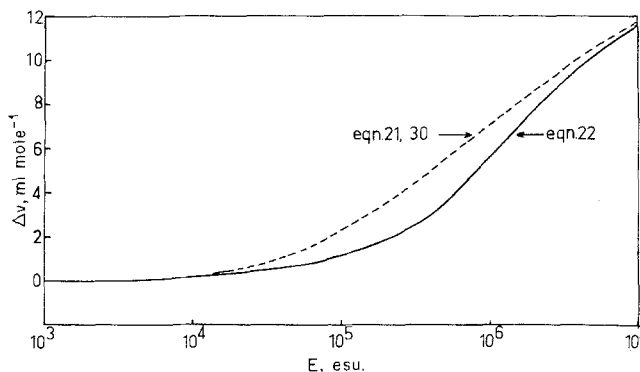


Fig. 4. Variation of electrostriction volume with field for aqueous solutions at 25°C.

Eq. (22) are seriously in error at all temperatures for fields in the range $1 \times 10^4 < E < 5 \times 10^7$ esu. As can be seen from Table II, the fields around the common ions fall into this range. This is shown more clearly in Figs. 3 and 4 where P and Δv values from Eqs. (21), (22), and (30) are plotted as functions of the field E at 25°C. Values of P from Eqs. (31) and (33) are also included in Fig. 3 for comparison. Similar trends are evident at other temperatures.

As noted above, since for any electrolyte we may write

$$\bar{V}^\circ = \sum_i \bar{V}_i^\circ \quad (34)$$

Eq. (1) can be written for each ionic species i as

$$\bar{V}_i^\circ = V_i^{\text{int}} + V_i^{\text{el}} \quad (35)$$

The Δv values of Table II are related to the V_i^{el} term of Eq. (35) by the expression

$$V_i^{\text{el}} = n_i \Delta v_i \quad (36)$$

and so we can write

$$\bar{V}_i^\circ = V_i^{\text{int}} + n_i \Delta v_i \quad (37)$$

where n_i is the appropriate solvation number of ion i . In view of the present confusion⁽⁸⁾ regarding the separation of \bar{V}° into ionic contributions according to Eq. (34) and regarding the correct method of estimating the V_i^{int} term of Eq. (37) at any temperature, it would be presumptuous here to calculate solvation numbers over a wide temperature range from Eq. (37) and the Δv data of Table II. Hopefully, this situation will be remedied at some future time. Perhaps the ionic vibration potential method of Zana and Yeager⁽⁴¹⁾ will be the source of absolute \bar{V}_i° data over a wide temperature range. However, this nonthermodynamic experimental method has been criticized by Panckhurst.⁽⁴²⁾ When and if this situation is clarified, the Δv data of Table II will be useful in estimating absolute solvation numbers.

Two qualitative conclusions can be drawn from the Δv data of Table II. Firstly, since they have relatively small Δv values, large ions are most likely unsolvated. This conclusion is largely unaffected by use of Pauling⁽⁴³⁾ radii in place of Gourary and Adrian⁽⁴⁰⁾ values, and is consistent with that of other workers.^(12, 44-47) Secondly, since the Δv values for each ion in Table II increase steadily with temperature, probably implying that the V_i^{el} term of Eq. (35) behaves similarly, the observed maxima in the $\bar{V}^\circ - T$ plots for most electro-

lytes cannot be explained solely by consideration of ion-solvent interactions and is most likely also associated with structural changes in the solvent over this temperature range.⁽⁴⁸⁾ Such structural changes are likely to affect the degree of solvation of the various ions in solution. This same problem exists⁽⁴⁹⁾ in the interpretation of the osmotic coefficients of NaCl in the range 0–100°C.

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REFERENCES

1. L. A. Dunn, *Trans. Faraday Soc.* **62**, 2348 (1966).
2. L. A. Dunn, *Trans. Faraday Soc.* **64**, 1898 (1968).
3. L. A. Dunn, *Trans. Faraday Soc.* **64**, 2951 (1968).
4. A. J. Ellis, *J. Chem. Soc. (A)*, 1579 (1966).
5. A. J. Ellis, *J. Chem. Soc. (A)*, 660 (1967).
6. A. J. Ellis, *J. Chem. Soc. (A)*, 1138 (1968).
7. A. Eucken, *Z. Electrochem.* **51**, 6 (1948).
8. F. J. Millero, in *Water and Aqueous Solutions—Structure, Thermodynamics, and Transport Processes*, R. A. Horne, ed. (Wiley-Interscience, New York, 1972), p. 519.
9. M. Born, *Z. Physik.* **1**, 45 (1920).
10. K. J. Laidler and C. Pegis, *Proc. Roy. Soc. (A)* **241**, 80 (1957).
11. S. W. Benson and C. S. Copeland, *J. Phys. Chem.* **67**, 1194 (1963).
12. J. Padova, *J. Chem. Phys.* **39**, 1552 (1963).
13. S. D. Hamann, *Physico-chemical Effects of Pressure* (Butterworths Scientific Publications, London, 1957).
14. E. Whalley, *J. Chem. Phys.* **38**, 1400 (1963).
15. B. E. Conway, J. E. Desnoyers, and A. C. Smith, *Phil. Trans. (A)* **256**, 389 (1964).
16. E. Glueckauf, *Trans. Faraday Soc.* **61**, 914 (1965).
17. J. E. Desnoyers, R. E. Verrall, and B. E. Conway, *J. Chem. Phys.* **43**, 243 (1965).
18. H. S. Frank, *J. Chem. Phys.* **23**, 2023 (1955).
19. L. H. Adams, *J. Am. Chem. Soc.* **53**, 3769 (1931).
20. D. C. Grahame, *J. Chem. Phys.* **21**, 1054 (1953).
21. B. K. P. Scaife, *Proc. Phys. Soc. (B)* **68**, 790 (1955).
22. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* (Reinhold, New York, 1963), 3rd ed.
23. B. B. Owen, R. C. Miller, C. E. Milner, and H. L. Cogan, *J. Phys. Chem.* **65**, 2065 (1961).
24. J. S. Rosen, *J. Opt. Soc. Am.* **37**, 932 (1947).
25. J. Malsch, *Z. Physik.* **29**, 770 (1928).
26. F. Booth, *J. Chem. Phys.* **19**, 391, 1327, 1615 (1951).
27. L. Onsager, *J. Am. Chem. Soc.* **58**, 1486 (1936).
28. J. Kirkwood, *J. Chem. Phys.* **7**, 911 (1939).
29. E. Glueckauf, *Trans. Faraday Soc.* **60**, 1637 (1964).

30. E. Glueckauf, *Trans. Faraday Soc.*, **60**, 776 (1964).
31. P. M. Lukehart, *Comm. Assoc. Comp. Mach.*, **6**, 737 (1963).
32. C. G. Malmberg and A. A. Maryott, *J. Res. Nat. Bur. Std.*, **56**, 1 (1956).
33. L. A. Dunn and R. H. Stokes, *Trans. Faraday Soc.*, **65**, 2906 (1969).
34. R. J. W. LeFevre, *Dipole Moments* (John Wiley, New York, 1953).
35. G. S. Kell and E. Whalley, *Phil. Trans. (A)*, **258**, 565 (1965).
36. Y. B. Zel'dovich, S. B. Kormer, M. V. Sinitsyn, and K. B. Yushko, *Dokl. Akad. Nauk SSSR*, **138**, 1333 (1961).
37. R. W. Hamming, *J. Assoc. Comp. Mach.*, **6**, 37 (1959).
38. R. H. Stokes, *J. Am. Chem. Soc.*, **86**, 979 (1964).
39. M. J. Blandamer and M. C. R. Symons, *J. Phys. Chem.*, **67**, 1304 (1963).
40. B. S. Gourary and F. J. Adrian, *Solid State Phys.*, **10**, 127 (1960).
41. R. Zana and E. Yeager, *J. Phys. Chem.*, **70**, 954 (1966); **71**, 521 (1967); **71**, 4241 (1967).
42. M. H. Panckhurst, *Rev. Pure Appl. Chem.*, **19**, 45 (1969).
43. L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1960), 3rd ed.
44. K. Fajans and O. Johnson, *J. Am. Chem. Soc.*, **64**, 668 (1942).
45. L. G. Hepler, *J. Phys. Chem.*, **61**, 1426 (1957).
46. R. H. Stokes and R. A. Robinson, *Trans. Faraday Soc.*, **53**, 301 (1957).
47. J. Padova, *J. Chem. Phys.*, **40**, 691 (1964).
48. R. H. Stokes, *Australian J. Chem.*, **20**, 2087 (1967).
49. E. Glueckauf, *Proc. Roy. Soc. (A)*, **301**, 449 (1969).