

Electrostriction in Electrolyte Solutions

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1. INTRODUCTION

Electrostriction in general is the contraction of material under the influence of an electric field. This is manifested, for example, in condensers and piezoelectric devices. The restricted use of this term for the purpose of the present review is the effect that the electric field exerted by ions in solution has on the volume of the solution. The term has been coined by Drude and Nernst at the end of the 19th century¹ on the basis of their theoretical investigation

of the consequences of the presence of charged particles in dielectric media. It is now generally agreed that once the ion is in a condensed phase, the electric field has little, if any, effect on the volume of the ion itself and that the observed contraction in volume is to be assigned to compression of the solvent. For electrolytes in aqueous solutions, where the water has the characteristic hydrogen-bonded open structure, the compression is attributed to the breaking down of the hydrogen bond network and the diminution of the void spaces. This squeezing of void spaces apparently takes place also in other solvents.

The electrostriction in electrolyte solutions is not measurable directly but depends on accurate measurements of the densities of the solutions at constant temperature and pressure, see section 3. The derivation of the electrostriction from such data is the subject of this review, but the review does not deal directly with the (isobaric thermal) expansibilities and the (isothermal) compressibilities of the electrolyte solutions. The interpretation of the derived electrostriction values in terms of the properties of the ions and of the solvents and the interactions that take place between the ions and the solvent is a main feature of this review, dealing with publications mostly to the end of 2009.

2. HISTORICAL DEVELOPMENT

The comprehensive review by Millero^{2,3} of some 40 years ago "the molal volumes of electrolytes" summarized most of the previous publications dealing with electrostriction adequately. The subsequent book by Conway⁴ on "ionic hydration in chemistry and biophysics" also adds some insights. Hence, this section on the historical development of the concept and its manifestations is brief.

Drude and Nernst¹ derived the following expression for the change in volume, ΔV , occurring when a charged sphere of radius r_i (representing an ion) is placed in a dielectric medium of relative (dielectric) permittivity, ϵ_r , rewritten in modern terms:

$$\Delta V = (ze^2/(8\pi\epsilon_0)) \int_{r_i}^{\infty} \kappa_T \epsilon_r^{-2} (\partial \epsilon_r / \partial V)_T r^{-2} dr \quad (1)$$

Here ze is the charge on the sphere and κ_T is the compressibility of the medium. They then related to this electrostriction the observed small (even negative) volume that has to be ascribed to dissolved salts. Due to the enormous field strengths of the ions that have very small r_i values (but unknown at the time) and consequently the very large exerted pressures, appreciable volume contraction should result. Drude and Nernst made the assumptions (inevitable at the time due to lack of information) that κ_T , ϵ_r , and $(\partial \epsilon_r / \partial V)_T$ remain constant

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for the integration, the latter being a negative quantity. The result is

$$\Delta V = (\kappa_T z^2 e^2 / 8\pi\epsilon_0 \epsilon_r^2 r_i) (\partial \epsilon_r / \partial V)_T \quad (2)$$

They reported the general observation that the partial molar volume of electrolytes diminishes with increasing dilution and estimated for the molar electrostriction of 1:1 aqueous electrolytes an amount of $8\text{--}11 \text{ cm}^3 \cdot \text{mol}^{-1}$.

Originally developed for aqueous electrolytes, the concept of electrostriction was soon extended to nonaqueous solvents by Carrara and Levi.⁵ They, as well as Walden,^{6,7} noted that the molar volumes of electrolytes in organic solvents diminish as the dilution increases, whereas the degree of ionic dissociation increases. Campbell⁸ repeated the generalization that “the electrostriction should increase with dilution to a practically constant value”.

Baxter and Wallace⁹ reported the densities of the aqueous alkali metal halides at several concentrations and temperatures. They reported values of the volume change of a 1 M solution on deducting the sum of the volumes of a mole of fused salt and that of the pure water involved in the preparation of the solution. These volume changes were all negative, decreasing in absolute magnitude from chloride to iodide salts but increasing with the size of the alkali metal ion. They ascribed these volume changes to hydration of the ions and noted a parallelism with the magnitude of the compressibilities of the salts but did not refer at all to the theoretical considerations of Drude and Nernst.

Webb¹⁰ returned to the electrostatic effects of the ionic fields, pointing out that dielectric saturation occurs around the ions, but assumed the ion to be imbedded in a cavity, having a radius several times that of the ion, from which the water is excluded. He proceeded to calculate the electrical work involved in charging an ion in a dielectric medium, the consequent compression work (taking into account the pressure dependence of the compressibility of the solvent), and the resulting electrostriction. The volume contraction of the aqueous solvent per mole of singly charged ions of different sizes (radii of $0.0804\text{--}0.4165 \text{ nm}$) was reported ($15.69\text{--}1.40 \text{ cm}^3 \cdot \text{mol}^{-1}$), and the data were applied to actual ions but with radii differing considerably from what is now accepted.

Electrostatic considerations were abandoned for a while, and the electrostriction was estimated from measured apparent molar volumes, ${}^\phi V_2$ (section 3), and the volume of the ions themselves, their intrinsic volumes (section 3.2). Scott¹¹ suggested for this quantity the “critical disruptive volume” of the crystalline salt. The critical disruptive radius, R^* , was shown to be 0.047 nm larger, on average, than the interionic distance of the crystalline alkali metal halides, and the values of V^* (unspecified, but seemingly $4\pi N_A (R_+^{*3} + R_-^{*3})/3$) and an obscurely derived ϕ^* (on average $0.64V^*$, except for lithium salts, for which it is $0.77V^*$) were reported. The latter quantity represents the “volume domains of the salts as solutes”. Harned and Owen, in their book,¹² provided an explicit expression for ϕ^* , based on Masson’s empirical expression¹³ for the measured apparent molar volume:

$${}^\phi V = {}^\phi V^\infty + S_V^M c^{1/2} \quad (3)$$

where ${}^\phi V^\infty$ is the linearly extrapolated (versus $c^{1/2}$) value of the apparent molar volume to infinite dilution and S_V^M is a salt-specific coefficient. Then¹²

$$\phi^* = {}^\phi V^\infty + S_V^M (1000/V^*)^{1/2} \quad (4)$$

Since ϕ^* is independent of the concentration, the “contraction in the volume of the water molecules” (= electrostriction) according to Scott¹¹ is given, by ${}^\phi V - \phi^*$ at any concentration.

Frank¹⁴ in a very influential paper discussed the thermodynamics of a fluid substance (i.e., the solvent) in the electrostatic field (of an ion). He described a virtual instrument where the effects could be demonstrated and derived equations for the pressure arising by the field in the dielectric medium. The resulting differential equation was

$$dP = (8\pi)^{-1} \rho (\partial \epsilon_r / \partial \rho)_{T,E} dE^2 \quad (5)$$

where ρ is the density, but this was not integrated. The coefficient of electrostriction was given as

$$(\partial \ln V / \partial E^2)_{T,E} = -(8\pi)^{-1} [(\partial \epsilon_r / \partial P)_{T,E} - (\epsilon_r - 1) \kappa_T] \quad (6)$$

No numerical application of these theoretical expressions was supplied by Frank, however.

Hepler¹⁵ suggested that the standard partial molar volume of an ion is the sum of two terms, one due to its intrinsic volume, proportional to the cube of its radius, and the second due to the electrostriction, proportional to the square of its charge and inversely to its radius:

$$V_i^\infty = A r_i^3 - B z_i^2 / r_i \quad (7)$$

This view of the ionic partial molar volumes was taken up by many subsequent workers, see section 3.2.

Padova¹⁶ took up the derivations of Frank¹⁴ and included the field dependence of the relative permittivity (in addition to its pressure dependence) and arrived at a rather complicated integral expression for the electrostriction. The lower limit of the integral was an intrinsic radius $r_e = (3V_{i \text{ intr}}/4\pi N_A)^{1/3}$ assigned to each ion (see section 3.3 concerning the estimation of the ionic intrinsic volumes, $V_{i \text{ intr}}$), and the integrals were solved numerically and shown in graphs.

Further developments for the calculation of the electrostriction from the thermodynamic and electrostatic principles were later provided by Desnoyers et al.¹⁷ and by Marcus and Hefter¹⁸ as described in detail in section 4.

3. PARTIAL MOLAR VOLUMES

The densities, ρ , of solutions of electrolytes (subscript 2) in a solvent (subscript 1) are readily measurable with high accuracy (see ref 38, section 2.2) at concentrations, c_2 (down to $\sim 0.01 \text{ mol} \cdot \text{dm}^{-3}$), or molalities, m_2 (down to $\sim 0.01 \text{ mol} \cdot \text{kg}^{-1}$), up to the solubility limit and at temperatures, T , where the solvent exists as a liquid at ambient pressure. The densities of some electrolytes in water have been measured also at elevated temperatures along its saturation line, and for some salts the densities at high pressures were also determined. At ambient pressure, the apparent molar volumes, ${}^\phi V_2$, can be calculated from the densities $\rho(c_2, T)$ or $\rho(m_2, T)$:¹²

$${}^\phi V_2 = M_2 / \rho_1^* + 1000(\rho - \rho_1^*) / \rho_1^* c_2 \quad (8a)$$

$${}^\phi V_2 = M_2 / \rho + 1000(\rho - \rho_1^*) / \rho \rho_1^* m_2 \quad (8b)$$

The molality and the concentration are related to one another by

$$m_2 = c_2 / \rho_1^* (1 - c_2 {}^\phi V_2 / 1000) \quad (9)$$

Table 1. The Debye–Hückel Limiting Slope on the Molar Scale for the Partial Molar Volumes of 1:1 Electrolytes, S_V^{DH} , for Several Solvents^a at 25 °C¹⁸ and on the Molal Scale for Water at Several Temperatures along the Saturation Line, up to 100 °C⁵⁷ and beyond It²³

solvent, at 25 °C	$S_V^{\text{DH}}, \text{cm}^3 \cdot \text{dm}^{3/2} \cdot \text{mol}^{-3/2}$	water at t (°C)	$S_V^{\text{DH}}, \text{cm}^3 \cdot \text{kg}^{1/2} \cdot \text{mol}^{-3/2}$
water	1.85	0	1.57
methanol	18.57	25	1.89
ethanol	26.17	50	2.39
1,2-ethanediol	5.42	75	3.09
acetone	29.08	100	4.01
propylene carbonate	2.35	125	6.39
acetonitrile	13.40	150	9.21
nitromethane	12.24	175	13.54
formamide	1.12	200	20.33
N-methylformamide	0.66	250	51.06
N,N-dimethylformamide	8.13	300	170.3
dimethylsulfoxide	4.65	350	1451
hexamethyl phosphoric triamide	13.46		

^a Conversion of the entries to the molality scale requires their multiplication by $\rho^{3/2}$, where ρ is the density of the solvent in $\text{kg} \cdot \text{dm}^{-3}$.

The partial molar volumes, V_2 , are then obtained from

$$V_2 = {}^\phi V_2 + m_2(\partial {}^\phi V_2 / \partial m_2)_T \quad (10)$$

The factor 1000 in these expressions is needed when the molar mass of the solute, M_2 , is in $\text{g} \cdot \text{mol}^{-1}$, the densities of the pure solvent, ρ_1^* , and of the solution, ρ , are in $\text{g} \cdot \text{cm}^{-3}$, the concentrations, c_2 , are in $\text{mol} \cdot \text{dm}^{-3}$, and the molalities, m_2 , are in $\text{mol} \cdot (\text{kg solvent})^{-1}$, yielding the volumes in $\text{cm}^3 \cdot \text{mol}^{-1}$.

The apparent molar volume of an electrolyte, ${}^\phi V_2$, is related to its molar concentration, c , by Redlich's semitheoretical expression,¹⁹ which should replace calculations using the completely empirical Masson expression 3 (see below):

$${}^\phi V_2 = {}^\phi V_2^\infty + S_V^{\text{DH}} c_2^{1/2} + b_V c \quad (11)$$

Here ${}^\phi V_2^\infty$ is the limiting apparent molar volume at infinite dilution, where it equals the standard partial molar volume, $V_2^\infty = {}^\phi V_2^\infty$, S_V^{DH} is the Debye–Hückel limiting slope for volumes at the appropriate T , and b_V is an empirical coefficient characteristic for each electrolyte. A list of some S_V^{DH} values is shown in Table 1. Values of b_V for a large number of electrolytes in water and some nonaqueous solvents have been reported. This coefficient correlates well with the viscosity, B_η , coefficients of the electrolytes, unless crowding of the solvation shells at increasing concentrations occurs.²⁰

The standard partial molar volume, that is, that at infinite dilution, is obtainable from extrapolation of the apparent molar volumes at low concentrations according to¹⁹

$$V_2^\infty = \lim(c_2 \rightarrow 0)[{}^\phi V_2 - S_V^{\text{DH}} c_2^{1/2}] \quad (12)$$

The practice of plotting ${}^\phi V_2$ vs $c_2^{1/2}$ and extrapolation to $c_2 = 0$ (Masson plots, eq 3) with arbitrarily resulting slopes S_V^{M} may lead to serious errors in V_2^∞ as pointed out by several authors.^{2,21,22} Inaccurate values of V_2^∞ also result when insufficiently accurate density values are employed at low concentrations, the required

low limit of the latter being $\sim 0.01 \text{ mol} \cdot \text{dm}^{-3}$ or $\text{mol} \cdot (\text{kg solvent})^{-1}$ for accurate extrapolation.

The standard partial molar volume, that is, V_2^∞ , is additive for the constituent ions and is due to interactions of the ions with their surrounding solvent alone. This is not the case for V_2 at finite concentrations, where ion–ion interactions take place. However, the splitting of the V_2^∞ value into the contributions from the individual ions cannot be made on purely thermodynamic grounds. Conventional ionic values, $V_i^{\infty \text{conv}}$, in aqueous solutions are obtained on arbitrarily setting $V^{\infty \text{conv}}(\text{H}^+, \text{aq}) = 0$ at all temperatures. Estimates of the absolute ionic values, V_i^∞ , are obtained on application of the additivity principle and an appropriate extra-thermodynamic assumption. The absolute value for the hydrogen ion, $V^\infty(\text{H}^+, \text{aq})$, is generally employed for this purpose:

$$V_i^\infty = V_i^{\infty \text{conv}} + z \cdot V^\infty(\text{H}^+, \text{aq}) \quad (13)$$

where z is the algebraic charge number of the ion. For aqueous solutions, the expression

$$\begin{aligned} V^\infty(\text{H}^+, \text{aq}) / \text{cm}^3 \cdot \text{mol}^{-1} \\ = -5.1 - 0.008(t/^\circ\text{C}) - 1.7 \times 10^{-4}(t/^\circ\text{C})^2 \end{aligned} \quad (14)$$

was derived by Millero^{2,3} and is adopted here, yielding $V^\infty(\text{H}^+, \text{aq}) = -5.4 \text{ cm}^3 \cdot \text{mol}^{-1}$ at 25 °C. The values suggested by various authors have been reviewed by Millero² and by Conway²¹ among others. The extra-thermodynamic methods that have been suggested for the achievement of such splitting for nonaqueous solvents have been critically examined by Hefter and Marcus.²²

3.1. The V_i^∞ Database

Conventional values, $V_i^{\infty \text{conv}}$ of many aqueous ions, based on $V^{\infty \text{conv}}(\text{H}^+, \text{aq}) = 0$, have been critically compiled by Millero^{2,3} for 25 °C and for fewer ions also at 0 °C and at temperatures up to 200 °C. Revision of some of the values and supplementary data for additional ions that have been reported since then are listed in Table 2. These values may be converted to the absolute partial molar ionic volumes, V_i^∞ , required for the discussion of the electrostriction, by the application of eqs 13 and 14. The estimated uncertainty of the V_i^∞ values of the alkali metal and halide ions is as low as $\pm 0.2 \text{ cm}^3 \cdot \text{mol}^{-1}$ at 25 °C, due to the many excellently accurate determinations on which the compilation of Millero^{2,3} was based. The uncertainty for other ions is probably larger, since many values have been revised since this compilation. It is also larger at lower or higher temperatures and may reach $\pm 1.0 \text{ cm}^3 \cdot \text{mol}^{-1}$.

Krumgalz et al.²⁴ reported V_2^∞ values for many salts, as well as the relevant Pitzer coefficients that permit the calculation of V_2 at finite molalities, in many cases up to very high values of the latter. Although the V_2^∞ values were reported to three decimals, ionic additivity is not adhered to for some of these values, so that they need not be more reliable than those in Millero's compilation.^{2,3}

The standard partial molar volumes, V_2^∞ , of electrolytes in many nonaqueous solvents at 25 °C have been critically compiled by Marcus and Hefter.³⁸ These data give rise to estimates of the ionic values V_i^∞ by means of the TPTB assumption, $V^\infty(\text{Ph}_4\text{P}^+) - V^\infty(\text{BPh}_4^-) = 2.0 \pm 2.0 \text{ cm}^3 \cdot \text{mol}^{-1}$, which has been suggested²² as providing the least objectionable estimates. Application of the additivity principle to salt data involving either Ph_4P^+

Table 2. Some Values of $V_i^{\infty\text{conv}}$ at 25 °C Supplementary to or Replacing Data in Millero's Compilations^{2,3a}

ion	$V_i^{\infty\text{conv}}, \text{cm}^3 \cdot \text{mol}^{-1}$	ref and comments
Ag ⁺	−1.61 (−0.7)	24
BuEt ₃ N ⁺	178.74	25
Bu ₂ Et ₂ N ⁺	199.76	25
Bu ₃ EtN ⁺	254.76	25
Be ²⁺	−10.30 (−12.0)	24
Sr ²⁺	−17.84 (−18.16)	26
Mn ²⁺	−17.45 (−17.75)	27, data also at 15, 35, 45 °C
Fe ²⁺	−22.63 (−24.7)	27, data also at 15, 35, 45 °C
Co ²⁺	−25.77 (−24.0)	26, data in ref 27 also at 15, 35, 45 °C
Ni ²⁺	−29.48 (−24.0)	26, data in ref 27 also at 15, 35, 45 °C
Cu ²⁺	−27.76 (−27.76)	26, data in ref 27 also at 15, 35, 45 °C
Zn ²⁺	−26.57 (−21.6)	26
Cd ²⁺	−13.03 (−20.0)	26
Hg ²⁺	−14.35 (−19.3)	28
Pb ²⁺	−17.99 (−15.3)	28
Al ³⁺	−45.04 (−42.2)	29
Cr ³⁺	−36.7 (−39.5)	30
Fe ³⁺	−36.5 (−43.7)	30
In ³⁺	−26	31
Y ³⁺	−40.58	32, values also at 15, 40, 55 °C and Pr ³⁺ , Gd ³⁺ , Ho ³⁺
Rh ³⁺	−43.5	30
Pr ³⁺	−42.8	33
Eu ³⁺	−41.66	33
Tm ³⁺	−43.18	34, values also at 15, 40, 55 °C and Pr ³⁺ , Gd ³⁺ , Ho ³⁺
Lu ³⁺	−45.85	33
SCN [−]	40.60 (35.7)	35, values also at 15, 20, 30, 35 °C
H ₂ PO ₄ [−]	31.7 (29.1)	36
CF ₃ SO ₃ [−]	74.7	37, values also at 10, 40, 55 °C
HPO ₄ ^{2−}	5.3 (7.7)	36
PO ₄ ^{3−}	−25.6	36

^a The replaced values are shown in parentheses.

or BPh₄[−] then leads to the individual ionic values, and these were reported.³⁸ In view of the inherent uncertainty in the TPTB assumption shown above, the uncertainty in the derived ionic V_i^{∞} values should be at least that large.

3.2. “Intrinsic” and “Electrostricted” Molar Volumes

The experimentally derived (eqs 10, 12, and 13) partial molar volumes of an ion in solution, V_i , describing the actual volume that is ascribable to it, are generally considered to reflect its intrinsic volume as modified by the compression of the solvent by its electric field, the electrostriction. This is expressed as follows:

$$V_i = V_{i \text{ intr}} + V_{i \text{ elec}} \quad (15)$$

where the second term on the rhs is negative. However, there is general agreement concerning neither the meaning of the “intrinsic volume” nor how the electrostriction is to be evaluated, and several models of the ions in solution have been invoked by various authors. If the restricted primitive model (hard sphere ions in a dielectric continuum as the solvent) is employed, then there is no place for solvent-structural considerations. Such a model is useful for the calculation of the

electrostriction from electrostatics. Then the intrinsic volume is calculated from the difference

$$V_{i \text{ intr}} = V_i - V_{i \text{ elec}} \quad (16)$$

but its meaning is rather obscure. Otherwise, if a molecular model for the solvent is employed, then its structural aspects, such as voids and hydrogen bonding, play a role in $V_{i \text{ intr}}$ in addition to the volume that the ion as a hard sphere occupies. In this case, the electrostriction is calculated from the difference

$$V_{i \text{ elec}} = V_i - V_{i \text{ intr}} \quad (17)$$

This procedure is what has been commonly followed, because of the difficulties of the electrostatic calculations that need to involve the dependence of the permittivity of the solvent on the electric field strength due to the ion and vice versa, in addition to its dependence on the temperature and the external pressure. In fact, the field involved is generally so large that dielectric saturation takes place in the immediate vicinity of an ion, but the spatial extent of this phenomenon is difficult to calculate.

3.2.1. The Intrinsic Volume of Ions and Electrolytes.

The intrinsic volumes of ions are closely related to their dimensions, and monatomic ions have been assigned radii, r_i , so that their molar volumes should be

$$V_{i \text{ bare}} = (4\pi N_A/3)r_i^3 \quad (18)$$

The subscript “bare” signifies that the volume of the non-solvated ion is considered, and the numerical coefficient is 2522 for volumes in $\text{cm}^3 \cdot \text{mol}^{-1}$ and radii in nm. The actual values of the ionic radii, however, are not as straightforward as they seem. It is generally agreed that the ions in condensed phases (crystals and solutions) are confined by similar forces as the respective lattice and solvation energies suggest, hence should have similar sizes. In fact, X-ray and neutron diffraction and EXAFS measurements of the distances d_{i-a} between the centers of ions and those of the nearest atoms of the solvents in solutions^{39,40} have confirmed the notion that the ionic radii in solutions are the same as in crystals.

However, the radii of ions in crystals depend on their coordination numbers, and so would the radii of ions in solution depend on the number of the solvent molecules in their solvation shells. It was shown³⁹ that the Pauling radii of monatomic ions as modified by Shannon and Prewitt,⁴¹ r_i^p , added to a fixed value of the radius of a water molecule, $r_w = 0.138$ nm, fit best to the experimental distances in aqueous solutions:

$$d_{i-\text{O of water}} = r_i^p + r_w \quad (19)$$

However, the use of a fixed r_w value was challenged by David and Fourest,⁴² who suggested that the polarizable water molecule is affected by the ionic electric field, so that r_w diminishes as the surface charge on the ion increases (from 0.143 nm for Na⁺ to 0.133 for Lu³⁺). It was also shown that the experimental distances d_{i-a} themselves are known only within an uncertainty of ± 0.002 nm for some of the ions. This could be due to different coordination numbers of the solvent molecules in the first solvation shell in the experimental determinations.

Polyatomic ions have been assigned thermochemical radii that express their sizes in crystals with respect to the lattice energies, and it is assumed that such radii are also valid for these ions in solution.⁴³ If the ions are compact and globular (tetrahedral or

octahedral), this assumption leads to reasonable values of $V_{i \text{ bare}}$. However, for other shapes, rod-like or oblate, ellipsoids of revolution need to be assigned with different major and minor axes. For the present purposes, such bodies can express the volume-occupying properties of these ions, $V_{i \text{ bare}}$, sufficiently well.

The simplest way to express the intrinsic volumes of ions in solutions is to equate them with the volumes of the bare ions, $V_{i \text{ bare}}$, using r_i^P for r_i in eq 18, as suggested by Benson and Copland.⁴⁴ When such values are introduced in eq 17 with experimental $V_{i \infty}^0$ data of aqueous solutions, the resulting values for the electrostriction are positive, signifying that such an estimate of the intrinsic volume is too small.

To counter this situation, modifications of the radii have been suggested on the basis that the intrinsic volume of an ion in solution needs to take into account the void spaces between the ion and the nearest solvent (water) molecules. This approach necessarily departs from the restricted primitive model of the solution (hard sphere ions in a dielectric continuum). The modification suggested by Mukerjee⁴⁵ is to multiply r_i of monatomic univalent ions by a constant coefficient k :

$$V_{i \text{ intr}}^M = (4\pi N_A/3)(kr_i)^3 \quad (20)$$

The value $k = 1.213$ was given by Mukerjee (for 25 °C) to account for the standard partial molar volumes of aqueous alkali metal and halide ions. This is near the value, 1.159, that is geometrically required for close-packed spheres of arbitrary but comparable sizes. Glueckauf⁴⁶ suggested that the void space between the water molecules surrounding an ion should be taken into account by the addition to the radii of monatomic ions of an addend, a , rather than using a factor as Mukerjee suggested:

$$V_{i \text{ intr}}^G = (4\pi N_A/3)(r_i + a)^3 \quad (21)$$

This addend is $a = (3V_W/(4\pi N_A))^{1/3} - r_W = 0.055$ nm at 25 °C. It is temperature-dependent (due to such dependence of the molar volume of water, V_W), increasing to 0.064 nm at 200 °C.⁴⁷ Somewhat different values were suggested for polyatomic ions, namely, tetrahedral oxy-anions and octahedral halide and cyanide complexes. For these, the factor $(r_i + a)^3$ in eq 21 is replaced by $(r_{M\text{-ligand}} + r_{\text{ligand}})^3$, where $r_{M\text{-ligand}}$ is the radial distance between the center of the anion and that of the donor atom of the ligand (O, halide, CN) and r_{ligand} is the radius of the latter, 0.138 nm for O, 0.181 nm for Cl[−], etc.⁴⁶

Hirata and Arakawa⁴⁸ took the idea of the cavity volume presented by Glueckauf⁴⁶ a step further and employed the scaled particle theory to obtain a cubic expression in the ionic radii:

$$V_{i \text{ intr}}^H = A_3 r_i^3 + A_2 r_i^2 + A_1 r_i + A_0 \quad (22)$$

where the A_j coefficients are functions of the compressibility and density, hence the packing fraction, of water at given temperatures. The A_j coefficients for $V_{i \text{ intr}}^H$ in $\text{cm}^3 \cdot \text{mol}^{-1}$ and r_i in nm are on the average $A_3 = 2522$, $A_2 = 475$, $A_1 = 24.3$, and $A_0 = 0.7$ over the temperature range 0 to 100 °C. However, for the alkali halides, this approach yields intrinsic volumes that are larger by some 14 (for the fluorides) to 22 (for the iodides) $\text{cm}^3 \cdot \text{mol}^{-1}$ than reasonable values of these quantities.

These and similar approaches, summarized by Millero,² depend on the values assigned to the effective radii of ions. Except for the approach of Mukerjee,⁴⁵ they yield values of the intrinsic volumes, $V_{i \text{ intr}}$, that are incompatible with the experimental V_i and reasonable estimates of the electrostriction, $V_{i \text{ elec}}$.

Other approaches do not involve the radii, r_i , of the ions for the estimation of their intrinsic volumes. Akitt³¹ presented some arguments that the electrostriction near an aqueous ion should be independent of its size and shape. Based on suggestions of Couture and Laidler,^{49,50} he derived the value $V_{i \text{ elec}} = -25.4|z_i|$, where z_i is its charge number. With eq 16, the intrinsic volume then is

$$V_{i \text{ intr}} = V_i + 25.4|z_i| \text{ cm}^3 \text{ mol}^{-1} \quad (23)$$

The resulting numbers are much larger than any reasonable estimates and cannot correspond to “intrinsic volumes” of the electrolytes.

Several approaches deal with entire electrolytes rather than with individual ions, so that eqs 15–17 need to be rewritten in terms of the sums $V_2 = V_{2 \text{ intr}} + \sum_i V_{i \text{ elec}}$, etc. Very long ago, Campbell⁸ suggested that the “true, incompressible volume” (i.e., V_{intr}) of the salts is given by the molar refraction, $M(n_\infty^2 - 1)/[\rho(n_\infty^2 + 2)]$, where M is the molar mass, n_∞ is the refractive index at infinite wavelength, and ρ is the density. He then calculated the electrostriction of three manganese salts from density and refractive index measurements at two wavelengths. However, his ideas were not taken up by others. Lundén⁵¹ summarized values of $V_{2 \text{ intr}}$ reported by others that were temperature-dependent but presumably solvent-independent and even split them into the individual ionic values. Padova⁵² listed the molar volumes of the crystalline salts, $V_{\text{cryst}} = M_{\text{salt}}/\rho_{\text{salt}}$, in a table of intrinsic volumes and compared them with values obtained by various methods but without specifying them. In a rarely mentioned paper, Pedersen⁵³ employed the molar volume of the molten alkali metal halides extrapolated with assumed constant values of the expansibilities down to ambient temperatures, $V_{\text{melt}} = M_{\text{salt}}/\rho_{\text{salt extrapol}}$, as a measure of their intrinsic volumes. He argued that the volume occupancy in crystals is constrained by the crystal structure and that the real intrinsic volume of ions in solution is more akin to that of the molten salt, albeit requiring a very long extrapolation down from the melting points.

Another method for the estimation of the intrinsic volumes of electrolytes, independent of values of the ionic radii and applicable to highly soluble salts, was proposed by Marcus.⁵⁴ Since the volumes considered (applied to aqueous solutions) are *intrinsic*, they should be independent of the concentration, c , and to a certain extent also of the temperature, T . Therefore, extrapolation of the partial molar volume of an electrolyte, $V_2(c, T)$, which describes the volume that is attributed to it in the solution, to such high concentrations $c_{2 \text{ max}}$ at which no more solvent that can be electrostricted exists (i.e., all of which is as closely packed as possible) is tantamount to considering the electrolyte as a molten salt but avoiding the long temperature extrapolation. For highly soluble salts, this extrapolation is not very long, and the resulting $V_{2 \text{ intr}}$ are not very sensitive to the choice of $c_{2 \text{ max}}$. The resulting values⁵⁴ of $V_{2 \text{ intr}}$ show that the surmise of Padova,⁵³ that V_{cryst} could serve for $V_{2 \text{ intr}}$, is an acceptable approximation if no better estimate can be made. Fair agreement of the calculated $V_{2 \text{ intr}}$ values with the V_{melt} values of Pedersen⁵³ and others and the $\sum_i V_{i \text{ intr}}^M$ of Mukerjee⁴⁵ is noted in Table 3.

In conclusion, the intrinsic volumes of ions (and electrolytes) are rather elusive quantities, there being many estimates of their values but no definite set. The situation that grieved McDevitt and Long⁵⁵ some 60 years ago, that $V_{2 \text{ intr}}$ “clearly cannot be determined directly from experiment”, hence it is preferable to circumvent its use, has not been definitely improved since then.

Table 3. Comparison of Various Measures of Intrinsic Volumes of Aqueous Electrolytes at 25 °C (in $\text{cm}^3 \cdot \text{mol}^{-1}$), Adapted from Marcus⁵⁴

salt	V_{intr}	$V_{\text{intr}}^{\text{M}}$	V_{cryst}	V_{melt}
LiCl	23.2	28.2	20.5	24.1
LiBr	32.9	35.4	25.1	30.3
LiI	41.1	49.4	33.0	38.1
LiNO ₃	34.1	37.5	29.3	35.9
LiClO ₃	40.6			41.2
NaOH	23.4		18.8	22.3
NaI	41.8	52.7	40.9	44.8
NaNO ₂	35.1		31.8	34.4
NaClO ₄	52.9	67.0	48.6	
NaCH ₃ CO ₂	49.4		53.7	
KOH	26.0		27.5	30.5
KF	27.5	22.4	23.4	23.7
KNO ₂	41.8		44.4	42.9
KSCN	59.8		51.7	57.7
KCH ₃ CO ₂	62.3		62.5	61.0
CsF	35.2	32.7	32.7	33.6
CsCl	46.5	48.8	42.3	48.8
NH ₄ SCN	61.2		58.6	
NH ₄ NO ₃	52.6	50.6	46.3	52.5
NH ₄ HCO ₂	54.1		49.7	
NH ₄ CH ₃ CO ₂	68.5		71.8	
AgF	18.7	17.4	21.8	
AgNO ₃	39.2	42.9	38.9	40.8
AgClO ₄	47.9	69.1	73.9	

3.2.2. The Electrostricted Volume of Ions and Electrolytes. There are two ways in which the electrostricted volume of ions and electrolytes can be estimated: either (a) from experimental partial molar volumes, V_i and V_2 , by eq 17, given the intrinsic volumes $V_{i \text{ intr}}$ or $\sum_i V_{i \text{ intr}}$, or (b) independently from electrostatic and mechanical considerations, as discussed in detail in section 4 for aqueous solutions, but it should be valid for nonaqueous solutions too. An early attempt to use electrostatic calculations, apart from that of Drude and Nernst¹ and those following their approach, was that of Helper,¹⁵ eq 7. This is not based on the Drude and Nernst derivation but rather on the pressure derivative of the Gibbs energy of hydration⁴⁴ according to the Born formulation.⁵⁶ At the time, the required values of $(\partial \ln \epsilon_r / \partial P)_T$ were available only for water and methanol, so the only effective use of this approach was the validation of the dependence of $V_{i \text{ elect}}$ on z_i^2/r_i , but this depended on valid values of $V_{i \text{ intr}}$. Such an approach, therefore, does not provide more insight into electrostriction.

4. ELECTROSTRICTION AROUND IONS IN AQUEOUS SOLUTIONS

The electrostriction around ions in aqueous solutions that has been estimated from fundamental considerations of the electrostatics and mechanics involved has been confined to the conditions of infinite dilution. Under these conditions an ion is surrounded by water in its hydration shells and by bulk water having the properties of pure water beyond these shells, but the region around a given ion is not affected by any other ions. Under “hydration shells” is to be understood the primary (in actual

contact with the ion) and possibly secondary hydration shell, but also a region beyond these, where the ionic field and the inner hydration shells still affect the structure of the water, causing it to differ from bulk water. The theoretical evaluation of the electrostriction around a given ion (characterized by its charge, size, hydration properties, and also its structure if polyatomic, and its hydrophobic properties) depends on the relevant properties of the water solvent, as described in section 4.1.

4.1. The Relevant Properties of Water

The main properties of water to be considered here are its dielectric permittivity and compressibility. These properties in regions near an ion depend, in turn, on the electric field exerted by the ion in an implicit manner, since the field at any point in the solvent near an ion depends on the permittivity there. Furthermore, the large pressure generated by the high field (section 4.2) affects the permittivity but also the compressibility of the water. In the following discussion, the restricted primitive model of an ion in water is employed, namely, the ion is regarded as a hard sphere with a radially symmetric electric field and the water as a compressible dielectric continuum.

The relative permittivity of water, ϵ_r , has been summarized as a function of the temperature and pressure in the absence of an electric field by Fernandez et al.⁵⁷ Also reported there are the first and second temperature and pressure derivatives, as well as the cross-derivative, $d^2\epsilon_r/(dTdP)$. The field dependence becomes of consequence only at $E \geq 100 \text{ MV} \cdot \text{m}^{-1}$, but such large fields are commonly obtained near ions. For a sodium ion, for instance, the field is $138.4 \text{ GV} \cdot \text{m}^{-1}$ right near its surface at 0.102 nm from its center. The field dependence of the permittivity of water at ambient pressure up to 100 °C was reported by Danielewicz-Ferchmin and Ferchmin⁵⁸ at room temperature and up to 600 MPa by Banachowicz and Danielewicz-Ferchmin,⁵⁹ and most recently along the saturation line above 100 °C by Danielewicz-Ferchmin and Ferchmin.⁶⁰ Some of these data are shown in Table 4. To be noted are the decrease of ϵ_r with increasing temperatures and its increase with increasing pressure. The field dependence is sigmoidal, and ϵ_r diminishes to very small values at high fields. At very high electric fields, the water molecules are immobilized and cannot any longer reorient their dipoles according to the direction of an external field, and only the electrons can respond to it. The high field limit of dielectric saturation is generally taken as the optical permittivity, that is, the square of the refractive index, approximated as $1.1n_D^2$ (for the value at the sodium D line) in lieu of n_∞^2 (the value at infinite frequency).

The mutual dependence of the electric field, E , and the relative permittivity, ϵ_r , is expressed by eq 24 defining the nonlinear dielectric effect, β :

$$\beta = [\epsilon_r(E) - \epsilon_r(0)]/E^2 \quad (24)$$

In water, $\beta = -1.080 \times 10^{-15} \text{ V}^{-2} \cdot \text{m}^2$ ¹⁸ and is practically temperature-independent at very high fields.⁵⁸ Liszi et al.⁶¹ and very recently Fulton⁶² compared various modes of calculation of the nonlinear dielectric effect of water and essentially confirmed this value. The field dependence of the relative permittivity in the vicinity of an ion has been studied by several authors and the most useful approximation seems to be the Booth–Grahame expression:^{63,64}

$$\epsilon_r(E) = n_\infty^2 + (\epsilon_r(0) - n_\infty^2)/(1 + bE^2) \quad (25)$$

neglecting the difference between the differential and integral permittivity. This expression is related to the nonlinear dielectric

Table 4. The Relative Permittivity of Water under Different Conditions

zero electric field at two external pressures as a function of the temperature ⁵⁷			0.1 MPa at two temperatures as a function of the logarithm of the electric field ⁵⁸		
$t, ^\circ\text{C}$	ϵ_r at 0.1 MPa	ϵ_r at 100 MPa	$\log(E, \text{V} \cdot \text{m}^{-1})$	ϵ_r at 25 $^\circ\text{C}$	ϵ_r at 100 $^\circ\text{C}$
0	87.81	91.68	7.6	79.7	
10	84.08	87.67	7.8	78.4	
20	80.45	83.83	8.0	77.1	
25	78.41	81.97	8.2	74.0	
30	76.94	80.15	8.4	67.7	53.4
40	73.53	76.63	8.6	57.8	50.3
50	70.23	73.27	8.8	44.6	45.1
60	67.03	70.06	9.0	30.7	37.4
70	63.95	66.99	9.2	19.5	28.1
75	62.44	56.50	9.4	12.1	19.2
80	60.96	64.06	9.6	7.91	11.8
90	58.09	61.26	9.8	5.72	7.71
100	55.33	58.60	10.0	4.65	5.48
125		52.47	10.2	3.57	4.44
150		47.06	10.4	2.89	3.40
175		42.28	10.6	2.51	2.47
200		38.06	10.8	2.29	2.26
250		30.97	11.0	2.12	2.00
300		25.21			
350		20.15			

effect β and the coefficient $b \approx -\beta/[\epsilon(0) - 1.1n_D^2]$ depends on the temperature and pressure through this dependence of $\epsilon(0)$ and to a minor extent that of n_D . At ambient pressures, the value of $b/(10^{-17} \text{ V}^{-2} \cdot \text{m}^2)$ varies practically linearly from -1.255 at 0°C via -1.443 at 25°C to -2.006 at 100°C . Dunn⁶⁵ derived values of b that depend on the inverse second power of the temperature but are valid only at relatively low field strengths, $\leq 30 \text{ MV} \cdot \text{m}^{-1}$.

The isothermal compressibility of water, κ_T , was reported by Fine and Millero⁶⁶ as a function of the temperature, $0 \leq t \leq 100^\circ\text{C}$, and pressure, $0 \leq P \leq 100 \text{ MPa}$. At ambient pressures, κ_T of water has a shallow minimum near 47°C that shifts to somewhat higher temperatures as the pressure is increased. At 25°C , $\kappa_T = 0.4525 \text{ GPa}^{-1}$ at ambient pressure and 0.3568 GPa^{-1} at 100 MPa external pressure. The isobaric expansibility of water, α_P , was also reported there⁶⁶ at the same ranges of temperature and pressure.

4.2. Electrostrictive Pressure

Frank¹⁴ in his fundamental paper on the thermodynamics of fluid substances in electrostatic fields reported the increment in pressure that is caused by the field, eq 5. From this expression, Desnoyers et al.¹⁷ derived the rearranged form:

$$dP = (8\pi\kappa_T)^{-1}(\partial\epsilon_r/\partial P)_{T,E} dE^2 \quad (26)$$

The dependence of the relative permittivity on the density ρ of the fluid is replaced by means of the compressibility, κ_T , with the dependence on the pressure P . This pressure tends to increase the relative permittivity (see Table 4 for the pressure effect at zero field), but this increase is more than counter-balanced by the direct effect of the field. This expression is implicit in the pressure and must be integrated in order to find the pressure at any point near an ion that is caused by the field prevailing there. This was done¹⁷ numerically for 25°C by invoking the Booth–Grahame

expression eq 25 as well as the Tait–Gibson equation for the density of water under pressure and analogous expressions for the relative permittivity and the refractive index. The tabulated results¹⁷ for high fields, $1.2 \leq E \leq 30 \text{ GV} \cdot \text{m}^{-1}$ are numerically fitted here by

$$P/\text{GPa} = 0.137 + 7.334 \times 10^{-3}(E/\text{GV} \cdot \text{m}^{-1}) + 4.599 \times 10^{-3}(E/\text{GV} \cdot \text{m}^{-1})^2 \quad (27)$$

The very large pressures that are due to high fields cause the water near the ion to be strongly compressed: the electrostriction. Some 40 years previously, Webb¹⁰ made a similar calculation of the pressure exerted by the field of an ion but treated only much lower fields, maximally $0.4 \text{ GV} \cdot \text{m}^{-1}$ (supposed to prevail at a distance of 0.08 nm from the center of a singly charged ion, a much too low estimate). However, the dependence of the relative permittivity on very high fields was not known at the time; hence the calculated pressures were much larger, maximally 50 GPa (compared with 0.14 GPa , from eq 27), leading to an impossibly large molar volume contraction of the water of $15.7 \text{ cm}^3 \cdot \text{mol}^{-1}$.

Bockris and Saluja,⁶⁷ somewhat later than the estimate of Desnoyers et al.,¹⁷ presented an expression for the effective pressure in (the middle of) the first hydration shell of ions, valid at 25°C due to the $\epsilon_r(P,T)$ dependence:

$$P_{\text{eff}}/\text{GPa} = 0.18305(r_i + r_w)^{-3} \quad (28)$$

with the radii in nanometers. Compared with the calculation by Desnoyers et al. for the field strength and pressure at a distance of 0.255 nm (presumed to be the middle of the first hydration shell of Na^+ or F^- ions), $P = 0.34 \text{ GPa}$, the result of Bockris and Saluja⁶⁷, $P_{\text{eff}} = 0.43 \text{ GPa}$, is somewhat higher. There are several assumptions involved in the derivation of eq 28 that may not be valid, but the order of magnitude of the pressures involved is realistic.

4.3. Dielectric Saturation

As seen in the right-hand side of Table 4, at very high fields the relative permittivity of water goes down to near the optical limit of n_{∞}^2 ($\sim 1.1n_D^2 = 1.953$ at 25 °C and 1.910 at 100 °C), signifying that the dipoles of the water molecules can no longer be oriented by external fields and only the electrons can respond to them. This situation represents dielectric saturation, which prevails at a short distance from the center of an ion, taken to be $\sim 0.08|z|^{1/2}$ nm, where z is the charge number of the ion.⁵⁸ Dielectric saturation in the near vicinity of ions was recognized qualitatively at an early stage of the discussion of electrostriction, for example, by Webb.¹⁰ Frank¹⁴ stated that “when it is desired to discuss ionic solutions it seems likely that neither saturation nor electrostriction can in fact be left out of account.” However, only when the actual values of the permittivity at very high fields could be evaluated quantitatively was it possible to take dielectric saturation into account in an appropriate manner. Still, in the 1970s the value of the b coefficient in eq 25 was not known definitely, Dunn⁶⁵ needing to choose between values suggested by Glueckauf⁶⁸ and an experimental value obtained at the maximal field, 25 MV·m⁻¹, which could be employed by Malsch.⁶⁹ Later, however, Liszi et al.⁵¹ calculated ϵ_r of water up to fields of 30 GV·m⁻¹ according to several expressions, resulting in values at the highest fields between 2.5 and 3.0, that is, practically dielectric saturation. Dielectric saturation was also invoked in the theoretical investigation of the nonlinear response in ion solvation by Hyun and Ichiye.⁷⁰

There could, however, be situations where the possibility of dielectric saturation might be ignored, namely, in the vicinity of very large ions with the charges buried deep inside them. Then the conclusion of Whalley⁷¹ that “if electric saturation does not occur, the compression of the *ion* appears to be a good deal greater than the electrostriction of the solvent in solvents of high dielectric constants like water” could be valid.

4.4. Electrostriction at infinite dilution

Early in the second half of the 20th century, Couture and Laidler^{49,50} derived semiempirical expressions for the ionic standard molar volumes in water at infinite dilution (differing for monatomic ions and oxyanions), in which the electrostriction was represented by $-26|z|$ cm³ mol⁻¹, irrespective of the sizes of the ions. This notion was taken up by Akitt,³¹ who modified the coefficient to -25.4 . Several authors estimated the electrostriction near aqueous ions at infinite dilution (mainly at ambient temperature and pressure) using the pressure derivative of the Born expression for the Gibbs energy of their hydration.^{44,56} According to this approach, the electrostriction should be proportional to $-z^2/r$, essentially also as suggested by Drude and Nernst.¹ Hepler¹⁵ obtained different coefficients of $-z^2/r$ for monatomic cations (4.7) and anions (19.0), but these would be adjusted to 9.9 and 13.6, respectively, if the more probable $V^{\infty}(\text{H}^+, \text{aq}) = -5.4$ cm³·mol⁻¹ would have been employed by him instead of -0.2 cm³·mol⁻¹. The problem of the proper value of the ionic radius r to be used was discussed in section 3.2. Mukerjee⁴⁵ obtained the coefficient 8.0 for $-z^2/kr$ for univalent ions, but for divalent and trivalent cations, the electrostriction did not depend on the ionic sizes, being respectively -32.5 and -58.5 cm³·mol⁻¹. Many other authors^{2,44,48,52,53} also employed eq 17 and various estimates of the intrinsic ionic molar volume (section 3.2) for obtaining the (negative) electrostriction volume.

More interesting, perhaps, are calculations of the electrostriction in a manner independent from experimental molar volume

data but rather based on electrostatic considerations. Desnoyers et al.¹⁷ abandoned the restricted primitive model of the infinitely dilute solution of an ion in a solvent in order to apply the field-induced pressure they calculated from Frank's general expressions (for 25 °C),¹⁴ section 4.2, to the electrostriction around aqueous ions. They chose aqueous Na⁺F⁻ as their example and calculated the electrostriction in the first hydration shell of the ions, taking the center of this shell to be at a distance of 0.255 nm from the centers of the ions (assuming them to have the same radii) to represent the site where the field and the pressure are operative. The resulting molar electrostriction (per mole of affected water) was -3.1 cm³·mol⁻¹, and it was necessary to use the hydration (coordination) numbers of the Na⁺ and F⁻ ions, 4, to obtain the total number of electrostricted water molecules, 8, and the total electrostriction volume, $V_{\text{elec}} = -24.8$ cm³ mol⁻¹. This value was in fair agreement with various estimates from standard molar volumes of aqueous NaF reported in the literature, using eq 17 and ranging from -17.9 to -21.1 cm³ mol⁻¹. Desnoyers et al.¹⁷ estimated that the electrostriction beyond the first hydration shell would not exceed 5% of the total effect. There are several weaknesses in this treatment, namely, the choice of the midpoint of the first hydration shell for the estimation of the relevant field strength and pressure and in particular the necessity to assume values for the hydration numbers of the ions.

Landau and Lifschitz,⁷² in their textbook “Electrodynamics of Continuous Media”, presented a problem, and the solution that they gave for it provided an expression of the electrostriction. This was calculated according to the restricted primitive model in terms of the electric field strength, the relative permittivity, the compressibility, and the pressure derivative of the permittivity. This expression was taken up by Kasprowicz and Kielch⁷³ and later by Marcus and Hefter,¹⁸ who provided an explicit equation for the shell-by-shell calculation of the cumulative electrostriction around an ion:

$$V_{\text{elec}} = -(8\pi^2 N_A \epsilon_0) \sum_j [r(j)^3 - r(j-1)^3] \{ \epsilon_r(j) [(\partial \ln \epsilon_r / \partial P)_T - \kappa_T] + \kappa_T \} E(j)^2 \quad (29)$$

In this expression, j is the ordinal number (starting at $j = 1$) of a solvent shell around the ion with a small constant thickness $\Delta r = r(j) - r(j-1)$ and $r(0) = r_i$, the (bare) radius of the ion. The summation is continued until $\epsilon_r(j)$ becomes practically equal to the bulk permittivity, $\epsilon_r(E = 0)$. The mutual dependence of $\epsilon_r(j)$ and $E(j)$ is taken into account according to the considerations in section 4.1. This expression was subsequently used by Marcus in a series of publications for the estimation of the electrostriction near ions at infinite dilution in water and nonaqueous and mixed solvents.^{20,74–77} The calculated field strengths, relative permittivities, and electrostriction volumes for several ions and solvents were reported in these papers in diagrams as functions of the distance r from the center of the ion. The diagrams for 25 °C pertain to Na⁺ in ethanol,¹⁸ K⁺ in dimethylsulfoxide, and Li⁺ in 1,2-ethanediol,^{74,75} whereas the data for F⁻ in water, also at 100 °C, are shown in Figure 1. Note that the sigmoid curves expressing $\epsilon_r(r)$ are similar to those shown by, for example, Laidler,⁷⁸ Padova,¹⁶ Abraham et al.,⁷⁹ and Danielewicz-Ferchmin and Ferchmin,⁵⁸ exhibiting essential dielectric saturation up to 0.2–0.3 nm from the periphery of an ion, a rather abrupt rise beyond this, and an asymptotic approach to the bulk value, $\epsilon_r(r \rightarrow \infty) = \epsilon_r(E = 0)$.

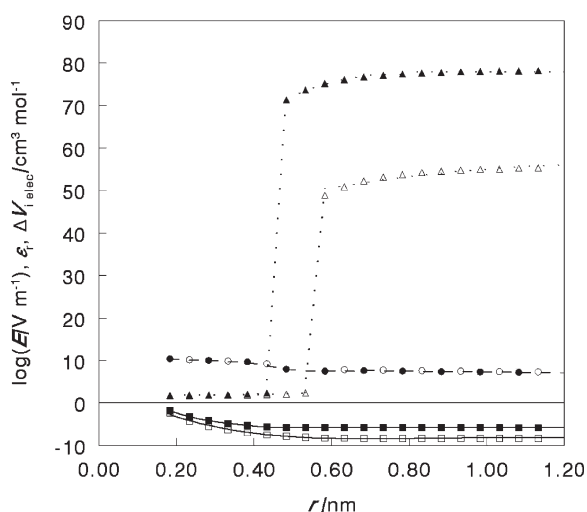


Figure 1. The electric field, $\log E$ ($\text{V} \cdot \text{m}^{-1}$) (\circ), the relative permittivity, ϵ_r (Δ), and the electrostriction, $\Delta V_{i \text{ elec}}$ ($\text{cm}^3 \cdot \text{mol}^{-1}$) (\square), near aqueous fluoride anions at 25 °C (filled symbols) and 100 °C (empty symbols), as functions of the distance from the center of the ion.

In view of the dielectric saturation occurring near the periphery of the ion, where its field is strongest and the pressure largest, it is to be expected that most of the compression of the water, that is, of the void spaces between the molecules, takes place in this region as is shown in Figure 1. Earlier views, such as those of Glueckauf^{46,47} and of Akitt³¹ that appreciable solvent compression takes place not in the immediate vicinity of the ion but “the bulk of the contraction arises in the water layers further out”,⁴⁷ cannot be supported.

Nonelectrostatic approaches to the estimation of the electrostriction in a manner independent of the use of eq 17 are based on the concentration dependence of compressibility of electrolyte solutions at high external pressures. Mukerjee⁸⁰ derived the expression

$$V_{\text{elec}} = 1000\kappa_T \lim(m \rightarrow 0) [d(B_T + P_{\text{eff}})/dm] \quad (30)$$

where B_T is the constant in the Tait expression for the compression of pure water and P_{eff} is an effective pressure obtained according to Gibson⁸¹ as $P_{\text{eff}} = L_{\text{salt}} c_{\text{salt}} c_{\text{water}}$. Values of L_{salt} for each salt must be obtained from the compressibility data of the aqueous salt solution. The resulting electrostriction values appeared to be lower than expected, partly because concentrations in the range $0.3\text{--}0.6 \text{ mol} \cdot \text{dm}^{-3}$ (rather than infinite dilution) were used to obtain the P_{eff} values. This approach was later taken up by Dack⁸² in terms of molar concentrations, c , not molal ones. An alternative way to obtain P_{eff} was suggested by him, equating it to the difference between the internal pressure, $P_i \approx T\alpha_p/\kappa_T$, of the electrolyte solution and a vaguely defined internal pressure of a noninteracting homomorph (NIH). Values of $P_i(\text{solution})$ and $P_i(\text{NIH})$ for $c = 1 \text{ mol} \cdot \text{dm}^{-3}$ were tabulated,⁸³ from which dP_{eff}/dc were obtained (without specification of how) leading to the electrostriction volume, V_{elec} , of several electrolytes. The derivative dP_{eff}/dc features also in the formulation by McDevitt and Long⁵⁵ of the electrostriction needed for the evaluation of the salting out (or in) of nonelectrolytes by electrolytes (section 7.1).

4.4.1. Temperature and Pressure Dependencies. For temperatures up to 100 °C, there are fairly abundant V_2^∞ data available^{2,3} for aqueous electrolytes, from which the individual

ionic partial molar volumes, V_i^∞ , can be calculated by means of eqs 13 and 14. On the assumption that the intrinsic molar volumes are not (or are negligibly) temperature dependent in this temperature range, eq 17 then yields the molar ionic electrostriction volume, $V_{i \text{ elec}}$. The standard partial molar volumes of electrolytes (or ions) exhibit mild maxima in this range of temperatures, generally around 50 °C. It follows from eq 17 that the electrostriction has the least negative value near 50 °C and becomes more and more negative at higher temperatures. Thus, values of $V_2^\infty < -300 \text{ cm}^3 \cdot \text{mol}^{-1}$ were obtained at $t > 300$ °C at saturation pressures. Helgeson et al.⁸⁴ proposed to separate the V_2^∞ values to contributions from the intrinsic, solvation, and solvent collapse volumes. This approach was essentially confirmed by Tanger and Helgeson,⁸⁵ validating the values calculated by Dunn.⁶⁵ The solvation contribution involves the temperature and pressure derivatives of the Born equation⁵⁶ of the Gibbs energy of hydration:

$$V_{\text{Born}} = -(N_A e^2 / 8\pi \epsilon_0) z^2 [\epsilon_r^{-2} (\partial \epsilon / \partial P)_T] - (1 - \epsilon_r^{-1}) r_i^{-2} (\partial r_i / \partial P)_T \quad (31)$$

The second term on the rhs is zero if the ionic radius is considered to be pressure-independent. The other contributions are expressed in terms of regressions fitting the data with a universal constant, $\theta = 228 \text{ K}$, and four electrolyte-specific coefficients:

$$V_{\text{intr} + \text{collapse}} = A_1 + A_2 P + (A_3 + A_4 P)(T - \theta)^{-1} \quad (32)$$

At temperatures up to 100 °C (and at $P = 0.1 \text{ MPa}$), eq 32 is simply $A_0 + A'/[(T/\text{K}) - 228]$ and this adds to $A''z^2[\epsilon_r^{-2}(\partial \epsilon / \partial P)_T]$ to describe empirically the temperature dependence of the electrostriction.

Shock et al.⁸⁶ developed these ideas further and presented expressions for the standard partial molar volumes and effective ionic radii valid up to 1000 °C and 500 MPa. These were based on experimental density data of aqueous NaCl.

Dunn⁶⁵ extended the calculations of Desnoyers et al.¹⁷ of the electric field-induced pressure in the hydration shell of ions, section 4.4, to temperatures from 0 to 100 °C. He then applied the resulting pressures to calculate the molar electrostriction of a water molecule in the hydration shells of Na^+ , Cl^- , and Ca^{2+} ions, but the total electrostriction around these ions depends as before on the hydration numbers assumed for these ions.

Akiniev⁸⁷ proposed to relate the ion charging effect to the pressure, leaning on the internal pressure concept of Gibson,⁸¹ as

$$V_{\text{Born}} = h\alpha_1(B_T(T) + P)^{-1}(1 - \alpha_2/T) \quad (33)$$

where $B_T(T)$ is the constant of the Tait expression for water, α_1 and α_2 are temperature- and pressure-independent constants, and h is the number of water molecules affected by the ionic charge, the hydration number. This expression is valid for $0 \leq t \leq 100$ °C and $0.1 \leq P \leq 200 \text{ MPa}$. At higher pressures, up to 500 MPa, a term in $B_2(T)P^2$ is also needed. The values $\alpha_1 = 4.056 \text{ kJ} \cdot \text{mol}^{-1}$ and $\alpha_2 = 490.2 \text{ K}$ were obtained from fitting data for NaCl by the sum of the contributions from eqs 31 and 33, representing the electrostriction, V_{elec} , and estimates of pressure- and temperature-independent values of V_{intr} and the hydration number h . The experimental NaCl data were then described well at the saturation vapor pressure up 300 °C and at pressures of 50, 100, 200, and 300 MPa to even higher temperatures. Experimental data for several electrolytes were then similarly described

with the same α_1 and α_2 values at 0–50 °C at 0.1 MPa and at 25 °C up to 100 MPa.

Marcus⁷⁷ in a recent paper calculated the electrostriction near the alkali metal and alkaline earth cations and the halide, perchlorate, and sulfate anions from eq 29 at five evenly spaced temperatures over the range 0–100 °C. It was pointed out there that the use of the values of $(\partial \ln \varepsilon / \partial P)_T$ and κ_T at the appropriate temperatures neglected their pressure dependence, which would have required an iterative calculation in view of the field-induced pressures, section 4.2. The latter, unfortunately, have not so far been evaluated for temperatures other than 25 °C. When the field-dependent permittivity of water at temperatures above 100 °C becomes available,⁶⁰ the electrostriction could be calculated also for the salts for which Ellis reported the standard partial molar volumes, V_2^∞ , up to 200 °C: alkali metal chlorides,⁸⁸ alkaline earth metal chlorides,⁸⁹ and some other halide and oxy-anion salts⁹⁰ (see also ref 2).

4.4.2. Isotope Effects. The relative permittivity of heavy water, D₂O, is similar to but not exactly the same as that of light water, H₂O, and so are also the compressibility and refractive index,⁹¹ of the properties that determine the electrostriction. Up to fields of 2.4 MV · m⁻¹, there appears to be no difference in the nonlinear dielectric effect between H₂O and D₂O.⁹² No information is available for higher fields that characterize the vicinities of ions in aqueous solution.

However, there exists definitely an isotope effect in the standard partial molar volumes of electrolyte solutions (the alkali metal halides) as summarized by Jákli,⁹³ reporting values at 15, 25, and 35 °C of his own and other authors (for 25 °C). The values of V_2^∞ are larger in H₂O than in D₂O by 0.2–1.7 cm³ · mol⁻¹, the isotope effect decreasing with the reciprocal radius of the ions, except for salts involving Li⁺. Since the intrinsic volumes are independent of the solvent, the (absolute) electrostriction in D₂O is larger than that in H₂O, cf. eq 17. This was ascribed to the D₂O having an inherently more open, collapsible H-bonded structure that is affected by the ionic electrical field.

4.5. Electrostriction at Finite Concentrations

Most of the attention concerning electrostriction in electrolyte solutions has been directed at infinitely dilute ones in water, where complete dissociation of strong electrolytes takes place, the ionic volumes are additive, and ion–ion interactions need not to be taken into account. Regarding finite concentrations, Mukerjee⁸⁰ stated that it “is well known that $[V_2] \dots$ increases with concentration because of a decrease in [electrostriction] caused by interionic interactions.” However, at finite concentrations, the ionic contributions to V_2 are no longer additive. It is then necessary to consider the electrostriction of entire electrolyte solutions rather than of the solvent near individual ions. In the application of, say, eq 17, the intrinsic volume of the electrolyte, $V_{2 \text{ intr}}$, should be used, and some manners of doing so that are independent of the individual ionic radii are discussed in section 3.2.1.

Discussions of the electrostriction at finite concentrations have in the past been related to Masson’s empirical expression:¹³

$${}^\phi V_2 = {}^\phi V_2^\infty + S_V^M c^{1/2} \quad (3)$$

instead of eq 11, using a salt-specific coefficient S_V^M instead of the theoretical Debye–Hückel one, S_V^{DH} . This expression is valid up to high concentrations and up to saturation in some cases. Rather than deal with the apparent molar volume, it is more appropriate

to deal with the partial molar volume, which is a measure of the actual volume occupancy of the solute salt. The partial molar volume, V_2 (cm³ · mol⁻¹), can be derived from eq 3 (if eq 10 is not used) as¹²

$$V_2 = V_2^\infty + (1000 - {}^\phi V_2)(2000 + S_V^M c_2^{3/2})^{-1} S_V^M c_2^{1/2} \quad (34)$$

Application of eq 17 then yields the electrostriction as a function of the concentration c . Such calculations have not been carried out so far, but were indicated long ago by Scott.¹¹

Pitzer’s semitheoretical formulation of the partial molar volume was employed by Krumgalz et al.²⁴ to present the parameters for 25 °C of the expression

$${}^\phi V_2 = V_2^\infty + |z_+ z_-| (A_V / (2b)) \ln(1 + bI^{1/2}) + 2RT\nu_+ \nu_- (Bm + C\nu_+ \nu_- m^2) \quad (35)$$

for the apparent molar volume. The values $A_V = 1.875 \text{ cm}^3 \cdot \text{kg}^{1/2} \cdot \text{mol}^{-3/2}$ at 25 °C and $b = 1.2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ are valid for all charge types, characterized by the charges z and stoichiometric coefficients ν of the cation and anion. The coefficients B and C are salt-specific. This expression is valid up to high molalities, in many cases up to saturation. The electrostriction may then be calculated by means of eqs 10 and 17, the latter applying to the entire salt.

Heyrovská⁹⁴ used eq 35 and her approach that involves incomplete ionic dissociation of salts (i.e., ion pairing) at appreciable concentrations to obtain the electrostriction in aqueous alkali metal halides at 25 °C. The intrinsic volumes employed were those of the solid salts, and the resulting electrostriction values were independent of the concentration. This conclusion is incompatible with the results of other workers (i.e., the electrostriction diminishes with increasing concentration). Also, the notion of partial dissociation (of aqueous alkali metal halides at room temperature) has not been confirmed by any other workers but on the contrary has been negated.¹¹¹

Values of V_2 for some highly soluble salts have been calculated by Marcus⁵⁴ using eqs 8–10 from the density data and expressions reported by Nowotny and Söhnel⁹⁵ and Krumgalz et al.,²⁴ and values for a few salts are shown in Figure 2. The former source, at several temperatures, is based on power series in $c^{1/2}$ and is empirical, whereas the latter source, at 25 °C, employs the semitheoretical Pitzer formulation, eq 35. It is seen that the V_2 values approach asymptotically constant ones as the concentration increases, namely, the value of $V_{2 \text{ intr}}$, as the essential independence from the temperature also indicates⁵⁴ (shown for NaOH but obtained also for many other salts). Therefore, the electrostriction manifested at low concentrations practically vanishes at higher ones, all the water still present being then maximally compressed (i.e., all the voids having been minimized).

Afanasiev et al.⁹⁶ studied the volumetric properties of aqueous NaCl at 0–100 °C and arrived at an empirical expression for the hydration number, $h = 24.43 \exp(-9.99x_2)$, where x_2 is the mole fraction of the salt, valid below an ill-defined “complete solvation limit” of 21.53 mass % (4.7 m, H₂O/NaCl = 11.8). The compression of the water in the hydration shells, per mole of water, is $\Delta V_{1h} = 0.432 - 8.23 \times 10^{-3}(t/^\circ\text{C}) + 8.21 \times 10^{-5}(t/^\circ\text{C})^2 \text{ cm}^3 \cdot \text{mol}^{-1}$, valid up to 50 °C. The electrostriction in the hydration shells of the ions of NaCl, $h\Delta V_{1h}$, can then be

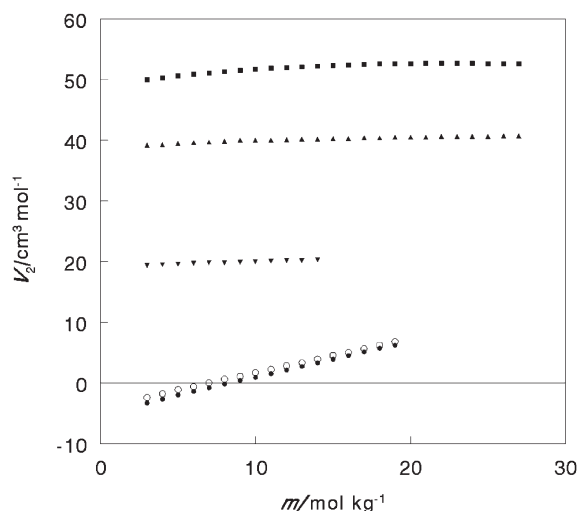


Figure 2. The partial molar volumes of some highly soluble salts: (●) NaOH at 25 °C, (○) NaOH at 50 °C, (▼) LiCl at 25 °C, (▲) LiClO₃ at 25 °C, and (■) NH₄NO₃ at 25 °C as functions of the salt molality.

calculated from these data over the relevant concentration range.

4.6. Molar Solvent Electrostriction

Several approaches to the calculation of the electrostriction, for example, those of Desnoyers et al.,¹⁷ of Dunn,⁶⁵ and of Afanasiev et al.,⁹⁶ employed the concept of the mean molar electrostriction of the solvent (water). This means that the pressure exerted by the electric field of the ion, although changing continuously from the surface of the ion up to such large distances from where it becomes negligible, leads to an average compression of the solvent per mole of solvent that can be estimated. Once such an average value, $\Delta V_{1 \text{ elec}}$, has been estimated, the total electrostriction by the ion would be

$$V_{i \text{ elec}} = h_i \Delta V_{1 \text{ elec}} \quad (36)$$

where h_i is the solvation number, the total number of solvent molecules affected by the ionic field.

The solvation number, h_i , however, is an elusive quantity, best defined operationally, for example, by inversion of eq 36 if $\Delta V_{1 \text{ elec}}$ can be estimated independently. Such an estimate was provided by Marcus,⁹⁷ following an earlier derivation by Padova.⁵² This was done for complete electrolytes rather than for individual ions, based on the primitive model of the solution (spherical ions in a compressible dielectric medium) that allows for the molecular nature of the solvent only in terms of the solvation number but not in other respects. Letting the molar volume of solvent affected by electrostriction be $V_{1 \text{ elec}}$ then

$$V_{2 \text{ elec}} = {}^\phi V_2 - V_{2 \text{ intr}} = h_2(V_1^* - V_{1 \text{ elec}}) = h_2 \Delta V_{1 \text{ elec}} \quad (37)$$

Since all of the electrostricted solvent is accounted for by eq 37 only the bulk solvent can be compressed by an external pressure (generally much smaller than the electrostriction pressure, section 4.2), so that the fraction of a c_2 molar solution that is not compressible is

$$1 - \kappa_T / \kappa_T^* = (c_2 / 1000) [(V_{2 \text{ intr}} + h_2 V_{1 \text{ elec}}) / \text{cm}^3 \cdot \text{mol} - 1] \quad (38)$$

where $c_2[V_{2 \text{ intr}} + h_2 V_{1 \text{ elec}}]$ represents the volume of the solvated ions out of the 1000 cm³ volume of the solution. An apparent molar compressibility of the electrolyte can be defined, analogously to the apparent molar volume, section 3, as¹²

$${}^\phi K_2 = (1000 / c_2) (\kappa_T - \kappa_T^*) + \kappa_T^* {}^\phi V_2 \quad (39)$$

The limiting slope of the concentration dependence of the apparent molar compressibility of the electrolyte, ${}^\phi K_2 = {}^\phi K_2^\infty + S_K^{\text{DH}} c_2^{1/2}$, is analogous to that of the apparent molar volume, ${}^\phi V_2 = {}^\phi V_2^\infty + S_V^{\text{DH}} c_2^{1/2}$ (eq 10) according to the Debye–Hückel limiting law. Elimination of the solvation number at infinite dilution, h_2^∞ , and at finite concentrations, h_2 , from eqs 37 and 38, and application of the limiting slope expressions eventually yields the expression for the mean molar solvent electrostriction:

$$V_{1 \text{ elec}} = V_1^* [1 - (S_V^{\text{DH}} / S_K^{\text{DH}}) \kappa_T^*] \quad (40)$$

The Debye–Hückel theory provides explicit expressions for the limiting slopes S_V^{DH} and S_K^{DH} and on definition of the auxiliary function $X = 3(\partial \ln \epsilon_r / \partial P)_T - \kappa_T^*$ the final result is

$$\begin{aligned} \Delta V_{1 \text{ elec}} &= V^* - V_{1 \text{ elec}} \\ &= \kappa_T^* V_1^* [2X / \{X^2 - 2(\partial X / \partial P)_T\}] \end{aligned} \quad (41)$$

The required pressure derivatives in X and of X itself have been provided in the literature for several solvents,⁹⁷ permitting the calculation of $\Delta V_{1 \text{ elec}}$ shown in Table 5. The fraction $\Delta V_{1 \text{ elec}} / V^*$ at 25 °C ranges from 0.070 for dimethylsulfoxide to 0.345 for acetone, water having the intermediate value 0.161.

Ionic solvation numbers at infinite dilution, h_i^∞ , have been calculated from known ionic electrostriction volumes, $V_{i \text{ elec}}^\infty$, for many ions according to eq 36 for solutions in water, methanol, 1,2-ethanediol, propylene carbonate, acetonitrile, dimethylsulfoxide, and dichloromethane.⁹⁷ In aqueous solutions, h_i^∞ averages 2.2 for univalent cations, 1.2 for univalent anions, and 11.8 for divalent cations. The values for univalent ions do not differ much in nonaqueous solvents (except acetonitrile) but are only one-third to one-half as large as those for the divalent cations, where data are available.

5. ELECTROSTRICTION NEAR NONINDIVIDUAL CHARGED SPECIES

The foregoing discussion dealt with the electrostriction of the solvent around individual ions, assumed to be charged conducting spheres with radially symmetrical electric fields. When the shapes of individual polyatomic ions depart considerably from sphericity (i.e., when they are not globular, like regular tetrahedral or octahedral), the electrostatic calculation of the electrostriction (section 4.4) becomes extremely difficult and in fact has not been attempted. Still, electrostriction naturally does occur near rod-like ions such as SCN[−] or plate-like ions such as CO₃^{2−} or the polar part of an ion such as CH₃CO₂[−]. Some account of the electrostriction near such ions has been reported in the literature, for example, by Akitt,³¹ albeit with a molar ionic electrostriction volume independent of the ionic size and shape: $-25.4|z_i|$. This leads to unrealistic intrinsic volumes according to eq 17, based on the experimental standard partial molar ionic volume. However, if intrinsic molar volumes can be estimated for such nonglobular ions, using ellipsoids of revolution in lieu of spherical shapes, the molar ionic electrostriction volume could be

Table 5. The Mean Molar Electrostriction of Various Solvents at 25 °C or as Specified⁹⁷

solvent	$\Delta V_{1 \text{ elec}} \text{ cm}^3 \cdot \text{mol}^{-1}$
water, 0 °C ^a	3.57
water, 25 °C ^a	2.91
water, 50 °C ^a	2.55
water, 75 °C ^a	2.34
water, 100 °C ^a	2.20
methanol	5.99
1-propanol	14.41
2-propanol	26.67
1,2-ethanediol	9.46
diethyl ether, 30 °C	33.61
1,2-dimethoxyethane	10.60
acetone	25.50
propylene carbonate	7.12
4-butyrolactone	9.26
acetonitrile	4.93
formamide	16.29
N-methylpyrrolidinone	21.40
dimethyl sulfoxide	4.98
benzene	22.43
dichloromethane, 30 °C	19.76

^a From ref 77.

calculated. Else, for complete electrolytes, intrinsic molar volumes can be estimated from the molar volumes of molten salts or the partial molar volumes of highly concentrated solutions (where no compressible solvent exists anymore),⁵⁴ see Table 3, and the electrostriction volume can then be calculated, again from eq 17.

More complicated are the cases of particles in which both positive and negative charges exist simultaneously on different sites of the polyatomic species. Such cases comprise dipolar molecules with partial unlike charges separated spatially and also zwitterions that have integral charges on different parts of the species. Similar considerations pertain to ion pairs, whether of the contact or solvent-separated kinds, and polyelectrolytes, with fixed-ions bound to a polymeric backbone and counterions in the solvent surrounding them, as well as relevant biomolecules.

Another important class of nonindividual charged species that cause electrostriction of the solvent around them is those transition states of reactions in which partial charges reside at spatially separated sites. These and the consequences regarding reaction rates are briefly discussed in section 7.

5.1. Dipolar Molecules and Zwitterions

As early as 1929, Jung⁹⁸ took up the electrostriction theory of Drude and Nernst¹ and derived for a spherically shaped dipolar molecule of radius r_d with an imbedded dipole of moment μ_d the electrostriction volume expression

$$\Delta V = (15\mu_d^2\kappa_T/4\epsilon_r^2r_d^3)(\partial\epsilon_r/\partial V)_T \quad (42)$$

which is analogous to eq 2:

$$\Delta V = (\kappa_T e^2/2\epsilon_r^2r_i)(\partial\epsilon_r/\partial V)_T \quad (2)$$

dealing with spherical ions. The ratio e^2/r_i in eq 2 is of the same order of magnitude as the ratio μ_d^2/r_d^3 of eq 42. However, although

Jung mentioned the application of this result to zwitterions, it has been ignored since then.

Clarke and Tremaine¹⁷² calculated the pressure derivative of the Helmholtz energy of a dipole in a cavity in a dielectric medium, based on the Onsager reaction field, as reported by Beveridge and Schnuelle.¹⁷³ The resulting expression, yielding the volume change of electrostriction by the dipole, differs somewhat from that of Jung, eq 42, and is

$$\Delta V = -3(N_A/4\pi\epsilon_0)\mu^2a^{-3}(2\epsilon_r + 1)^{-2}(\partial\epsilon_r/\partial P)_T \quad (43)$$

Here a is the effective radius of the cavity, corresponding to r_d in eq 42, and $(\partial\epsilon_r/\partial P)_T = \kappa_T V(\partial\epsilon_r/\partial V)_T$ so that the difference is in the numerical constant and the term on the relative permittivity. Clarke and Tremaine¹⁷² applied eq 43 to represent the contribution to the standard partial molar volume of some amino acid zwitterions at elevated temperatures and pressures due to dipolar electrostriction.

Cohn et al.⁹⁹ appear to have been the first to consider quantitatively the electrostriction caused in water by zwitterionic amino acids. Noting the well-established volume increment per the $-\text{CH}_2-$ group of $16.3 \text{ cm}^3 \cdot \text{mol}^{-1}$, a comparison was made of the apparent molar volumes of 0.25 *m* aqueous hydantoic acid ($\text{H}_2\text{NCONHCH}_2\text{COOH}$), glycylglycine ($^+\text{H}_3\text{NCH}_2\text{CONHC}-\text{H}_2\text{CO}_2^-$), and asparagine ($^-\text{O}_2\text{CCH}(\text{NH}_3^+)\text{CH}_2\text{CONH}_2$), all being $77.6 \pm 0.6 \text{ cm}^3 \cdot \text{mol}^{-1}$ at 25 °C. The latter two are isomeric zwitterions but have one more $-\text{CH}_2-$ group than hydantoic acid, which has no charged group. It was concluded that the zwitterions cause electrostriction of the water by $16.3 \text{ cm}^3 \cdot \text{mol}^{-1}$, the volume increment per $-\text{CH}_2-$ group.

When the apparent molar volumes of 0.25 *m* aqueous α -amino acids at 25 °C (up to α -aminohexanoic acid) were compared with the volumes calculated from the group contributions, they were $13.3 \text{ cm}^3 \cdot \text{mol}^{-1}$ short on the average, indicating electrostriction by this amount. The same was true for β -amino acids, but when the distance between the $-\text{NH}_3^+$ and $-\text{CO}_2^-$ groups became larger, for example, in ϵ -aminohexanoic acid, the electrostriction increased to $17.3 \text{ cm}^3 \cdot \text{mol}^{-1}$, making the individual effects of the charged groups more apparent. The individual electrostriction volumes ascribable to the $-\text{NH}_3^+$ and $-\text{CO}_2^-$ groups of glycine are roughly one-half of this, in fact $9.3 \text{ cm}^3 \cdot \text{mol}^{-1}$ each at 0.25 *m* concentration (10.0 at infinite dilution), as obtained from its alkali metal or halide salts.

The maximal electrostriction, hence the maximal density at a given concentration, of amino acids appears to occur at the isoelectric point, at which the charge is maximal. It diminishes when either the ammonium or the carboxylate groups deprotonate or protonate, respectively.⁹⁹

Similar conclusions were reached by Gucker et al.¹⁰⁰ on comparison of the zwitterionic glycine, α -alanine, and β -alanine with their polar isomers glycolamide and lactamide that are devoid of charged groups. The differences in the standard partial molar volumes at 25 °C in $\text{cm}^3 \cdot \text{mol}^{-1}$ are 12.97 and 12.90 for glycine and α -alanine and 14.79 for β -alanine in favor of the nonzwitterionic isomers, increasing somewhat as the distance between the charges increases, indicating larger electrostriction. The electrostriction caused by the ammonium group of the amino acid zwitterions is considerably larger, $\sim 7.0 \text{ cm}^3 \cdot \text{mol}^{-1}$, than that caused by the carboxylate group, $\sim 3.5 \text{ cm}^3 \cdot \text{mol}^{-1}$.¹⁰¹

Shaidi and Farrell¹⁰² argued that the total electrostriction caused by the charged end groups of amino acids includes also contributions due to the hydrophobic hydration of the $-\text{CH}_2-$ groups in the

α position to them. In other words, the different orientations and hydrogen bonding of the water molecules in the border between the charged sites and the hydrocarbon parts should be taken into account. The electrostrictions caused by this effect are 2.5 and $3.5 \text{ cm}^3 \cdot \text{mol}^{-1}$ for $-\text{NH}_3^+$ and $-\text{CO}_2^-$, respectively, when the ionic groups are well separated as in α,ω -amino acids. Hence, the true electrostriction volumes due to these ionic groups are 9.8 ± 1.4 and $0.9 \pm 0.5 \text{ cm}^3 \cdot \text{mol}^{-1}$. Note the disagreement of these values with those reported previously for amino acids with more adjacent ionic groups. Addition of the cosolvent glycerol to aqueous solutions of glycine, α -alanine, and serine causes a diminution of the electrostriction,¹⁰³ but there is no convincing explanation for this effect, the preferential solvation of the ionic groups concerned in aqueous glycerol not having been studied.

The electrostriction caused by zwitterionic solutes is not confined to amino acids in aqueous solutions. Sulfamic acid ($^+\text{H}_3\text{NSO}_3^-$) on dissolution in several nonaqueous solvents (dimethyl sulfoxide, *N*, *N*-dimethylacetamide, *N,N*-dimethylpropanamide, *N*-methylpyrrolidin-2-one, hexamethyl phosphoric triamide, and tetramethylurea) shows considerable contraction, up to $\sim 7 \text{ cm}^3 \cdot \text{mol}^{-1}$.¹⁰⁴ In aqueous solutions, there appears to be no electrostriction,¹⁰⁵ contrary to expectation.

Very recent work on the neutron diffraction¹⁰⁶ and molecular dynamics simulation¹⁰⁷ of aqueous dipeptides (glycyl-L-alanine, glycyl-L-proline, and L-alanyl-L-proline) has shown that the water in the second hydration shell is compressed, that is, electrostricted, by the solute zwitterionic groups. This effect was not seen in solutions of L-proline alone.¹⁰⁶ No structural data on water molecules immediately adjacent to the ionic groups were presented for all these systems, however.

Gianni and Lepori¹⁰⁸ provided a group contribution scheme for the standard partial molar volumes of aqueous bifunctional ionic organic solutes, providing an extensive table in an appendix. As the distance between the charged groups diminishes, a cooperative effect becomes apparent, for example, in α,ω -oligomethylenediammonium cations and in α,ω -amino acid zwitterions. When the charged sites are far apart they show their individual electrostrictive behavior.

5.2. Ion Pairs

Despite the sweeping statement made by Marcus¹⁰⁹ long ago that “when symmetrical electrolytes associate in solution to ion pairs, the electrostriction caused by the ions disappears”, there is reason to believe that this is not the case. The charges residing on the ionic partners of the ion pair constitute an electric dipole and hence should cause some electrostriction as pointed out by Jung⁹⁸ (see section 5.1), although less than the free ions do.

The standard molar volume change on ion pairing, $\Delta_{\text{ip}}V^\infty$, has been reported by a large number of authors as summarized by Marcus.⁹⁷ These quantities have been obtained by two experimental and one theoretical method as follows. The pressure derivative of the ion pair association constant (K_m on the molal scale), generally obtained from conductivity measurements, yields the required quantity directly:

$$\Delta_{\text{ip}}V^\infty = -RT(\partial \ln K_m / \partial P)_T \quad (44)$$

Otherwise, from density measurements yielding the apparent molar volumes (section 3), the desired quantity is obtained from

$$\Delta_{\text{ip}}V^\infty = [\phi V(c^{-1} \rightarrow 0) - \phi V] / \alpha + S_V^{\text{DH}}(\alpha c)^{1/2} \quad (45)$$

where $(1 - \alpha)$ is the degree of ion pairing (again generally obtained from conductivity measurements) and $\phi V(c^{-1} \rightarrow 0)$ is the apparent molar volume of the ion pair, assuming complete ion pairing as the concentration is increased indefinitely. Both experimental methods have drawbacks leading to inaccuracies, some being due to the obtaining of the association constant and the degree of association from inadequate conductivity expressions. Other inaccuracies arise from difficulties of measurements at the high pressures required to obtain significant results (~ 100 MPa), the needed derivatization for using eq 44, and the estimation of the molar volume of the ion pair needed for using eq 45. The theoretical estimation of $\Delta_{\text{ip}}V^\infty$ was reported by Hemmes¹¹⁰ and by Marcus¹⁰⁹ among others. Hemmes¹¹⁰ derived the following expression on the basis of the Bjerrum approach to ion pairing:¹¹¹

$$\Delta_{\text{ip}}V^\infty = RT\{[3 + \exp(b)/Q(b)^3](\partial \ln \epsilon_r / \partial P)_T - \kappa_T\} \quad (46)$$

In this expression $b = |z_+z_-|(e^2/4\pi\epsilon_0k_B)/T\epsilon_r a$ is the Bjerrum parameter, the ratio of the cutoff distance above which ions of opposite charge are free (and below which they are paired) to the distance of closest approach $a \approx r_+ + r_-$, and $Q(b)$ is a numerically solved integral that is approximated by $\exp(b)/b^4$ at sufficiently large b values.

A comparison of the electrostriction volume of ion-pairing electrolytes with the volume change (increase) on ion pairing should indicate whether the ion pairs still exert electrostriction of the solvent. Such a comparison is shown in Table 6, for the purpose of which the molar electrostriction, $V_{2 \text{ elec}}^\infty = V_2^\infty - V_{2 \text{ intr}}^\infty$, of the electrolyte (cf. eq 17) is obtained from $\sum V_i^\infty$ of the aqueous cation and anion² (as amended in Table 2) or V_2^∞ in nonaqueous solvents³⁸ and $V_{2 \text{ intr}}^\infty$ as the molar volumes of the crystalline salts in default of better values (section 3.2). In the cases of the aqueous Rb^+NO_3^- and Ti^+NO_3^- ion pairs, these appear not to cause electrostriction, as inferred by Masterton et al.,¹¹² but the aqueous alkali metal fluoride and in particular the aqueous sulfate ion pairs still cause appreciable electrostriction, an effect that is even stronger in nonaqueous solvents.

It is obvious from Table 6 that the volume increase on ion pairing, $\Delta_{\text{ip}}V^\infty$, for symmetrical electrolytes (1:1, 2:2, etc.) does not remove the electrostriction. Still, this is smaller than the electrostriction caused by the ions, considerably so for multivalent ions. Application of eq 36 to the $\Delta_{\text{ip}}V^\infty$ yields the number of solvent molecules per ion pair that are released from the electrostriction. Such numbers were found to agree with similar numbers obtained from the entropy change on ion pairing.⁹⁷ Of course, the residual charges on ion-paired nonsymmetrical electrolytes are expected to cause electrostriction of the solvent. The volume change on ion pairing of $\text{La}^{3+} + \text{SO}_4^{2-}$, $24.0 \text{ cm}^3 \cdot \text{mol}^{-1}$,¹¹³ is 2–3 times larger than that for symmetrical sulfate ion pairs (Table 6), but then the electrostriction around the La^{3+} cation is expected to be much larger than that around M^{2+} cations.

If the ideas of Heyrovská^{94,114} that strong electrolytes such as alkali halides are only partly dissociated in aqueous solutions were accepted, though not endorsed by any other authors, then the fraction dissociated, α , could be estimated from the osmotic coefficients, ignoring the ion atmosphere effects. The molar volume of the electrolyte is given by:

$$V_2 = V_{2 \text{ intr}}(1 - \alpha) + (V_+ + V_- + V_{2 \text{ elec}}) \quad (47)$$

at any molality up to the point of minimal dissociation (minimal α). Here $V_{2 \text{ intr}}$ is taken as the crystal molar volume, $V_{2 \text{ intr}} = V_{2 \text{ cryst}}$

Table 6. Electrostriction Volumes of Ion Pairs at 25 °C (^a)

cation	anion	solvent	V_2^∞	$V_{2\text{ cryst}}^b$	$V_{2\text{ elec}}^\infty$	$\Delta_{\text{ip}}V^\infty$	ref	$V_{\text{ip elec}}$
Li ⁺	F [−]	water	−2.1	9.8	−11.9	7.9	97	−4.0
Na ⁺	F [−]	water	−2.4	15.1	−17.5	4.6	97	−12.9
K ⁺	F [−]	water	7.8	23.4	−15.6	3.4	97	−12.2
Rb ⁺	F [−]	water	12.9	32.6	−19.7	4.0	97	−15.7
Cs ⁺	F [−]	water	20.1	32.7	−12.3	4.2	97	−8.4
Rb ⁺	NO ₃ [−]	water	43.1	47.4	−4.3	5	112	
Tl ⁺	NO ₃ [−]	water	39.6	48.0	−8.4	12	112	
Mg ²⁺	SO ₄ ^{2−}	water	−7.2	45.3	−52.5	7.4	97	−45.1
Ca ²⁺	SO ₄ ^{2−}	water	−3.9	46.0	−49.9	11.7	97	−38.2
Mn ²⁺	SO ₄ ^{2−}	water	−3.7	46.5	−50.2	7.4	97	−42.8
Co ²⁺	SO ₄ ^{2−}	water	−11.6	41.8	−53.4	10.9	97	−42.5
Ni ²⁺	SO ₄ ^{2−}	water	−15.5	38.6	−54.1	11.4	97	−42.7
Cu ²⁺	SO ₄ ^{2−}	water	−13.8	44.3	−58.1	11.3	97	−46.8
Zn ²⁺	SO ₄ ^{2−}	water	−12.6	42.5	−55.1	10.0	97	−45.1
Cd ²⁺	SO ₄ ^{2−}	water	−6.0	44.5	−50.5	9.3	97	−41.2
La ³⁺	Fe(CN) ₆ ^{3−}	water	81.7	217.8	−136.1	8.0	97	−128.1
Li ⁺	Cl [−]	MeOH	−4.5	20.5	−25.0	18	97	−7
Li ⁺	Br [−]	MeOH	3.1	25.1	−22.0	17	97	−5
K ⁺	Cl [−]	MeOH	7.0	37.5	−30.5	29	97	−1.5
Li ⁺	I [−]	acetone	−31	33.0	−61	21	134	−40
Na ⁺	I [−]	acetone	−19	35.0	−54	25	134	−29

^a All volumes are in cm³·mol^{−1}. ^b From handbook densities.¹³³

and is equated with the molar volume of the ion pair, and $V_+ + V_- + V_{2\text{ elec}} = V_2^\infty$ is the infinite dilution partial molar volume (where $\alpha = 1$). The sum of the ionic volumes, $V_+ + V_-$, is calculated from the radii of the bare ions, eq 18; therefore both positive and negative values of the electrostriction volume, $V_{2\text{ elec}}$, result.⁹⁴ It is difficult to accept this interpretation of the volumetric data.

Volume changes on ion pairing have been used to distinguish contact from solvent-shared (or solvent-separated) ion pairs.¹¹¹ This subject is outside the scope of this review.

5.3. Polyions

The first paper that dealt specifically with the electrostriction at aqueous polyions and provided data on the magnitude of this effect was that of Ise and Okubo.¹¹⁵ They mentioned two previous reports, that of Inagaki and Teramoto¹¹⁶ and that of Conway et al.¹¹⁷ The first of these mentioned that in proteins there occurs an electrostriction of 18 cm³·mol^{−1} per amino acid residue, without providing details. Conway et al. calculated the dielectric saturation near charged rods and reported the salting-out of solutes by polyelectrolytes, just mentioning electrostriction as a cause. Ise and Okubo described the standard molar volumes of polyelectrolytes (noting independence of the apparent molar volumes from the concentration) as

$$V_2^\infty = 2522(kr_{\text{ic}})^3 - 9.7/kr_{\text{ic}} + V_{2\text{P int}} + P_{2\text{P}} + E_{2\text{P}} \quad (48)$$

The first two terms in eq 47 pertain to the counterion of the polyelectrolyte (subscript c) and express it in terms of Hepler's eq 7, with the radius modified according to Mukerjee's suggestion, eq 20. The other terms, $V_{2\text{P}}^\infty = V_{2\text{P int}} + P_{2\text{P}} + E_{2\text{P}}$, pertain to the polyion (subscript p) and include its intrinsic volume, the hydrophobic effect of the backbone of the polyion, and its electrostrictive effect. In the cases of weak polyelectrolytes, the

sum $V_{2\text{P int}} + P_{2\text{P}}$ is obtained from V_2^∞ values at zero dissociation ($\alpha = 0$, where $E_{2\text{P}} = 0$ and no electrostriction occurs). This sum, taken to be independent of α , then yields the electrostrictive volume $E_{2\text{P}}$. The intrinsic volume of the polyion is calculated from its geometrical dimensions:¹¹⁷

$$V_{\text{int } 2\text{P}} = N_A \pi \lambda a^2 [1 + (4/\pi - 1)(r_w/a)] \quad (49)$$

where λ is the monomeric segment length between charged sites and a is one-half of the diameter of the polymeric backbone. This mode of calculation permitted the estimation of the electrostriction at sodium polyacrylate and potassium polymethacrylate at various degrees of neutralization and also at nearly neutralized ($\alpha = 0.8$) polyethyleneimine hydrochloride. Such a calculation could not be made for strong polyelectrolytes, such as sodium polystyrenesulfonate and polyethylenesulfonate that are completely ionized. For these, the values of $P_{2\text{P}}$ were estimated from analogous hydrocarbons, and in the case of sodium polyphosphate, $P_{2\text{P}}$ was assumed to be zero. The resulting values are shown in Table 7. The number of water molecules hydrating the fixed ions and undergoing electrostriction, h_p (see section 4.6), are obtained from the calculated $E_{2\text{P}}$ values by eq 36. The resulting values are shown in Table 7. No explanation was given by Ise and Okubo¹¹⁵ for the negative values of the hydrophobic term $P_{2\text{P}}$, nor were comments on the hydration numbers provided.

A fundamental problem with the approach of these authors is the assumption, inherent in eq 48, that the counterions and the polyions interact only with the surrounding water at infinite dilution of the polyion and hence that their volumes are additive, disregarding the site binding of counterions characteristic of polyelectrolytes even at high dilution.¹¹⁸ In fact, the partial molar volume of the polyion, $V_{2\text{P}}^\infty$, depends on the nature of the counterions used, indicating its site binding, except when the counterion is very large, such as tetramethylammonium. Only then can $V_2^\infty = V_{2\text{P}}^\infty + V_{\text{Me}_4\text{N}^+}^\infty$ be assumed and $V_{2\text{P}}^\infty$ be obtained, as argued by Tondre and Zana.¹¹⁸ The revised values of $E_{2\text{P}}$ for polyacrylate and polymethacrylate are −17.6 and −22.1 cm³·(monomeric mol)^{−1}, on the basis of the volume changes on association with hydrogen ions. For the strong polyelectrolytes, the revised value of the electrostriction caused per monomeric unit of the polyion is obtained from the difference between $V_{2\text{P}}^\infty$ and V_1^∞ of the monomer itself, vinylsulfonate and styrenesulfonate; it is −25.9 and −19.8 cm³·mol^{−1} for polyethylenesulfonate and polystyrenesulfonate.¹¹⁸ Another way to estimate the cooperative electrostriction exerted by the charges on a polyion according to Zana¹¹⁹ is to compare the experimental $V_{2\text{P}}^\infty$ values with results from group contributions. Only lower bounds of the values are obtained in this manner, being −9.8, −5.7, and −7.3 cm³·mol^{−1} for polyacrylate, polystyrenesulfonate, and polyethylenesulfonate. Considerations of counterion association with cationic polyions were also made by Kumar et al.¹²⁰ in solutions in the aprotic dipolar solvents propylene carbonate and sulfolane (see also section 6). A qualitative balance between solvophobic and electrostrictive effects for such systems was presented.

Conway⁴ presented a theoretical expression for the field strength near a model of a polyion as a rod with evenly spaced discrete charges along it in a dielectric continuum. The resulting electrostriction is presented as an integral expression that has not been solved. Based on the considerations of Conway et al.,¹¹⁷ dielectric saturation results from the electric field, as for an individual spherical ion, so that ion association is the probable result of this treatment.

Table 7. Volume Contributions Per Monomer of the Polyion Terms in eq 47 in $\text{cm}^3 \cdot \text{mol}^{-1}$ for High Degrees of Neutralization α at 25 °C¹¹⁵

polyelectrolyte	α	V_{2P}^∞	$V_{\text{int } 2P}$	P_{2P}	E_{2P}	h_P
sodium polyacrylate	0.8	40.6	65.3	−17.5	−7.2	2.5
potassium polymethacrylate	0.8	45.2	81.6	−9.1	−27.3	9.4
polyethyleneimine hydrochloride	0.8	20.1	54.7	−21.5	−4.1	1.4
sodium polystyrenesulfonate	1.0	116.0	125.0	−6.0	−3.0	1.0
sodium polyethylenesulfonate	1.0	−4.9	61.5	−20.0	−46.4	15.9
sodium polyphosphate (2800) ^a	1.0	27.5	55.0	0	−27.5	9.5

^a Degree of polymerization.

Gianni and Lepori¹⁰⁸ provided a group contribution scheme for the standard partial molar volumes of aqueous ionic organic solutes with some emphasis on polyelectrolytes, V_{2P}^∞ . They provided an extensive table in an appendix, showing, however, serious discrepancies between reports of diverse authors. In all cases, the cooperative electrostrictive effect of neighboring charges causes V_{2P}^∞ to be smaller than calculated from the group contributions by an amount called Δ per repeating unit. Because of site binding of the counterions, Δ is less negative the larger the site binding is, and in the case of weak polyelectrolytes, Δ is more negative the larger the degree of neutralization (ionic dissociation) α is. For sufficiently large polyions, the values of Δ become independent of the degree of polymerization, since then the effects of the end groups become inappreciable. A more recent review of group contributions to the molar volumes of organic compounds, among other thermodynamic functions was presented by Sedlbaur and Jakubu.¹⁷⁴

5.4. Biomolecules

Electrostriction plays a role also for biological polyelectrolytes, such as proteins and nucleic acids. Cohn and Edsall¹²¹ already long ago concluded that electrostriction would reduce the specific volume of ovalbumin by 2.43% relative to the value calculated from its amino acid content due to the charged groups it contains.¹²² A comparison of the specific volume of three muscle proteins (rabbit myosin, rabbit tropomyosin, and Pinna tropomyosin) in xylene and in water by Kay¹²³ indicated volume reduction in water by 0.028, 0.040, and 0.030 $\text{cm}^3 \cdot \text{g}^{-1}$, respectively, ascribed to electrostriction. These volume reductions were proportional to the number of charged groups in the proteins: 270, 376, and 315 per 10^5 g.

More recently, Mauzerall et al.¹²⁴ used pulsed photoacoustic measurements on the proteins involved in bacterial photosynthesis and applied the Drude–Nernst eq 2 but used the compressibility of the protein rather than that of water. The calculated electrostriction of $-0.030 \text{ nm}^3/\text{pair of ions}$ (formed by charge separation on the absorption of light) is compatible with an assumed compressibility of 170 MPa^{-1} and a relative permittivity in the protein of 4 ± 1 .

Several reports from X-ray and neutron scattering concluded that the water in the hydration shell of a protein is electrostricted, being 5–25% denser than bulk water. The surface charge density of proteins is¹²⁵ $\sigma = 0.08\text{--}0.48 \text{ C} \cdot \text{m}^{-2}$ and the related field strength is $E = \sigma/(\epsilon_0 \epsilon_r)$. As shown in sections 4.2 and 4.3, the permittivity of water is drastically reduced by high electric fields ($\sim 1 \text{ GV} \cdot \text{m}^{-1}$), ϵ_r being reduced (at 20 °C) from 82 at zero charge density to 79 at $\sigma = 0.1 \text{ C} \cdot \text{m}^{-2}$, to 63 at $0.2 \text{ C} \cdot \text{m}^{-2}$, to 11 at $0.3 \text{ C} \cdot \text{m}^{-2}$, and to 4 at $0.4 \text{ C} \cdot \text{m}^{-2}$.¹²⁶ The chemical potential

of the water near the protein surface would be reduced by the lower dipole orientation work (lower ϵ_r) compared with pure water; hence water flows into this region compressing it for thermodynamic equilibrium to be established. The density of the water at the surface layer of the protein stays at $1 \text{ g} \cdot \text{cm}^{-3}$ up to $0.24 \text{ C} \cdot \text{m}^{-2}$ charge density but increases to $1.087 \text{ g} \cdot \text{cm}^{-3}$ at $\sigma = 0.3 \text{ C} \cdot \text{m}^{-2}$, to $1.417 \text{ g} \cdot \text{cm}^{-3}$ at $\sigma = 0.4 \text{ C} \cdot \text{m}^{-2}$, to $1.704 \text{ g} \cdot \text{cm}^{-3}$ at $\sigma = 0.5 \text{ C} \cdot \text{m}^{-2}$, and to $1.846 \text{ g} \cdot \text{cm}^{-3}$ at $\sigma = 0.6 \text{ C} \cdot \text{m}^{-2}$ (The resulting molar volumes at 0.5 and $0.6 \text{ C} \cdot \text{m}^{-2}$ are 10.6 and $9.7 \text{ cm}^3 \cdot \text{mol}^{-1}$, smaller than the van der Waals volume of $12.4 \text{ cm}^3 \cdot \text{mol}^{-1}$, an unlikely result.) The density values reported for the surface layer of water of several proteins, such as chicken ovalbumin lysozyme (ranging from 1.08 to $1.22 \text{ g} \cdot \text{cm}^{-3}$) agreed with the values calculated from the surface charge densities and the corresponding electric fields (ranging from 2.34 to $5.69 \text{ GV} \cdot \text{m}^{-1}$) and permittivities.¹²⁶ This compacting of the water in the layer near a protein molecule also accounts for the nonfreezing of this water when the temperature is reduced below 0 °C, ascribable to the electrostriction pressures generated by the charges (section 4.2), ranging from 0.1 to 0.6 GPa .¹²⁷

The effect of electrostriction caused by the charges on the walls of ion channels and by the ions passing through them has been discussed by several authors.^{127–130} The formation of duplex structures from single-strand nucleic acids is also accompanied by volume changes accompanied by the release of sodium ions to the solution. In the presence of $0.1 \text{ mol} \cdot \text{dm}^{-3}$ NaCl and for the B conformation of the duplex, appreciable electrostrictive volume diminution was observed.^{131,132} Detailed evaluation of these reports is outside the scope of this review.

6. ELECTROSTRICTION IN NONAQUEOUS AND MIXED SOLVENT SOLUTIONS

As mentioned earlier (section 2), already more than 100 years ago Carrara and Levi⁵ considered the electrostriction of electrolyte solutions in nonaqueous solvents. Since then several authors have taken up this subject at various levels of sophistication, from the phenomenological to the theoretical. In order to deal with this subject properly and be able to apply insights that were gained regarding aqueous solutions and that are described in the previous sections, a comparison of the relevant properties of nonaqueous solvents with those of water is useful. Subsequently, the reported information concerning electrostriction caused by electrolytes in neat nonaqueous solvents and in mixed solvents is reviewed.

6.1. The Relevant Properties of Solvents for Electrolytes

Common solvents for electrolytes are those that permit their ionic dissociation to a large extent, though some ion pairing may still occur in them. They thus have relative permittivities of at least ~ 10 and exclude hydrocarbons and most halogenated hydrocarbons and ethers, among other classes of solvents. Compilations of the properties of solvents have been published by Riddick et al.¹³⁵ and by Marcus¹³⁶ among others. As mentioned above (section 4.1) for water, the solvent properties that are relevant for the electrostriction are the relative permittivity, its pressure derivative, and the isothermal compressibility, if discussion is limited to ambient temperatures and pressures. These properties are shown in Table 8 for a representative list of solvents, selected mainly on the basis of the existence of data on the standard partial molar volumes of electrolytes, V_2^∞ , in them.³⁸ The Debye–Hückel limiting slopes, S_V^{DH} , required for obtaining these

Table 8. Some Properties of Nonaqueous Solvents at 25 °C That Are Relevant to the Electrostriction of Electrolytes Dissolved in Them

solvent	ϵ_r	$(\partial \ln \epsilon_r / \partial P)_T$, GPa ⁻¹	κ_T , GPa ⁻¹	$-\beta$, 10 ⁻¹⁸ m ² V ⁻²
water	78.36	0.476	0.457	1080
methanol	32.66	1.220	1.248	590
ethanol	24.55	1.18	1.153	400
1,2-ethanediol	40.61	0.541	0.392	723
acetone	20.56	1.115	1.324	
propylene carbonate	64.92	0.500	0.590	517
acetonitrile	35.94	1.163	1.093	355
nitromethane	35.87	0.89 ^a	0.790	389
formamide	109.50	0.447	0.399	814
N-methylformamide	182.40	0.58 ^b	0.560	739
N,N-dimethylformamide	36.71	0.300	0.642	294
dimethylsulfoxide	46.45	0.53 ^b	0.524	444
hexamethyl phosphoric triamide	29.30	0.80 ^b	0.790	

^a At 30 °C. ^b Estimated as $1.039\kappa_T - 0.920\kappa_T/\epsilon_r$.¹⁸

standard partial molar volumes from extrapolation to infinite dilution of the experimental apparent molar volumes, ${}^\phi V_2$, (section 3) have already been listed in Table 1. The molar electrostrictions, ΔV_{elec} , of some solvents (section 4.6) have been listed in Table 5.

The calculation of the electrostriction from electrostatic principles requires knowledge of the dependence of the relative permittivity of the solvent on the electric field exerted by the ions. This dependence is expressed by means of eq 25

$$\epsilon_r(E) = n_\infty^2 + (\epsilon_r(0) - n_\infty^2)/(1 + bE^2) \quad (25)$$

which, in turn, requires the values of the infinite frequency refractive index, n_∞ , and of the nonlinear effect parameter $b \approx -\beta/(\epsilon_r - n_\infty^2)$. The values of n_∞^2 , approximated by $(1.1n_D)^2$, range for the solvents listed in Table 8 from 2.13 to 2.64. Therefore the mean value, 2.3, which is small relative to ϵ_r , can be used in these expressions. Unfortunately, the values of β (or of b) are known for only a few of the solvents of interest. Values of β may, however, be estimated from solvatochromic parameters of the solvents as described by Dutkiewicz and Dutkiewicz¹³⁷ and by Marcus and Hefter.¹⁸ Mikhailov¹³⁸ attempted to calculate values of b of the Grahame–Booth expression, eq 25, for some nonaqueous solvents from electrostatic considerations involving the dipole moments and the polarizability of the solvent molecules but found poor agreement with experimental values obtained from the measured nonlinear dielectric effect.

6.2. Electrostriction in Neat Nonaqueous Solvents

A large body of standard partial molar volumes, V_2^∞ , of electrolytes in neat nonaqueous solvents was critically compiled by Marcus and Hefter,³⁸ and only a few more values that need consideration have been published since then. Whenever it was possible, the ionic V_i^∞ values were derived in that review, based on the TPTB assumption (section 3.1). The molar intrinsic volumes of the ions, $V_{i,\text{intr}}$, are independent of the solvent, hence if these are known, the electrostriction volume, $V_{i,\text{elec}}$, can be evaluated by means of eq 17. In general, the values to be considered pertain to such solvents (Table 8) that have sufficiently high relative permittivities to permit a large degree of ionic dissociation in dilute solutions, at which measurements are made, leading to complete dissociation at infinite dilution, for which V_2^∞ and V_i^∞ have been compiled.³⁸

The observation that electrostriction increases with increasing dilution of an electrolyte in an organic solvent, being parallel with the increasing ionic dissociation when this is relevant, was made more than 100 years ago by Carrara and Levi⁵ and by Walden.^{6,7} This was ascribed to the electrostatic effect of the ions according to the Debye–Hückel theory.¹ At these early times, the data had not been extrapolated to infinite dilution, where ionic dissociation should be complete, and the extents of dissociation at finite concentrations have been calculated from inadequate conductivity expressions. Therefore the quantitative conclusions are not valid.

Once infinite dilution values, that is, standard partial molar volumes, are considered, even if derived by the Masson expression, eq 3, which may be inaccurate, more reliance can be placed on the conclusions. This is the case with the report by Vosburgh et al.¹³⁹ concerning some alkali metal halides in the lower aliphatic alcohols. These authors attempted to develop an electrostatic theory for the electrostriction, analogous to that presented by Webb,¹⁰ but were hampered by inadequate knowledge of some of the required parameters. Furthermore, they could not deal with the ionic partial molar volumes but only with those of the entire salts. Still, they could conclude that the electrostriction is larger in the alcohols than in water, the difference being of the right order of magnitude. The theoretical calculations lead to negative V_2^∞ values for salts for which the mean ionic radius, r_{mean} (the mean of those of the cation and anion), is ≤ 0.2 nm. The derived values of r_{mean} for a given salt depended slightly on the alcoholic solvent, a fact ascribed to inadequate knowledge of some of the required parameters of the theory.

In papers bearing the title “electrostriction in polar solvents”, Fuoss and co-workers^{140,141} discussed the difference between the partial molar volume and the viscosity effect of some spherical ions and nonelectrolytes in acetonitrile. Tuan and Fuoss¹⁴⁰ ascribed such differences qualitatively to the fact that “the small ions in acetonitrile pull solvent dipoles to themselves (electrostriction) and thereby ...[cause] the holes in the vicinity of the ions [to be] squeezed shut.” The *small* ions in this case are bromide and iodide, compared with tetraalkylammonium, picrate, and tetraphenylborate ones. No more detailed and sophisticated conclusions were drawn by these authors from their data, however, despite the suggestive titles of the papers.

Definite values of the ionic electrostriction volume, $V_{i,\text{elec}}$, in methanol and N-methyl-propanamide (NMP) were presented by

Millero,¹⁴² based on eq 17 with several models for the ionic intrinsic volume, $V_{i \text{ intr}}$. The B parameter of eq 7 expressing the electrostriction was $\sim 60\%$ larger in methanol than in water and about a quarter as large in NMP as in water. For methanol, this trend is in approximate accord with the expectation from the Drude–Nernst theory (section 2), but lack of $(\partial \ln \epsilon_r / \partial P)_T$ data for NMP precluded such a comparison for this solvent. Dunn¹⁴³ ascribed the smaller electrostriction he found for KCl in formamide than that for this salt in water (on the basis of eq 17) to the larger relative permittivity of formamide than that of water (Table 8).

Padova¹⁴⁴ was practically the only author at the time who calculated the electrostriction in a nonaqueous solvent, namely, methanol, from electrostatic principles (according to his earlier expressions¹⁶ based on Frank's approach¹⁴). Ionic volumes of transfer from water to methanol were calculated and found to be negative for all ions examined (only univalent ones were considered), due to the considerably larger electrostriction in methanol. Thus, even Cl^- has a negative $V_{i \infty}$ value in methanol. The mean molar electrostriction (section 4.6) of methanol itself, $V_{1 \text{ elec}}$, was given as $7.54 \text{ cm}^3 \cdot \text{mol}^{-1}$ (somewhat larger than the value calculated from more recent data, see Table 5) so that solvation numbers could be calculated by means of eq 36.

Zana and co-workers dealt with the partial molar volumes of electrolytes and ions in methanol,¹⁴⁵ ethanol, and N,N -dimethylformamide (DMF),¹⁴⁶ dimethylsulfoxide (DMSO),¹⁴⁷ acetonitrile,¹⁴⁸ 1,2-ethanediol (EG),¹⁴⁹ and propylene carbonate (PC).¹⁵⁰ The $V_{i \infty}$ values obtained by means of ultrasonic vibration potentials are on the whole compatible with those estimated by the TPTP assumption.³⁸ The electrostriction was calculated from eq 17 using Hepler's expression 7 to specify values of its coefficient B .

$$V_i^\infty = Ar_i^3 - Bz_i^2/r_i \quad (7)$$

The B values derived from the experimental data (Table 9) depend strongly on the intrinsic volumes assumed in eqs 7 and 17 and hence may be questioned. They were the same for cations (alkali metal) and anions (halide) in some solvents (water, methanol, ethanol, acetonitrile, and PC) but differed (being near zero for the halide ions) in others (DMF, DMSO, and EG). The difference was explained by the different steric accessibility of the positive and negative poles of the solvent dipole to anions and cations. The "experimental" B values were compared with values calculated from the Drude–Nernst theory and the Born model (section 4.4), that is, values depending on $(\partial \ln \epsilon_r / \partial P)_T$ data. These were not available to the authors except for water and methanol and for the other solvents were estimated as being equal to the isothermal compressibility, κ_T (see Table 8). Poor agreement was noted, but this could be due to improper choice of the intrinsic volumes in eq 7 from which the "experimental" values were derived.

An interesting result from the work of Zana et al. is that the apparent B values of the tetraalkylammonium ions (R_4N^+) in the nonaqueous solvents is many times larger ($\sim 10 \text{ cm}^3 \cdot \text{nm} \cdot \text{mol}^{-1}$) than those for the alkali metal and halide ions ($0\text{--}2 \text{ cm}^3 \cdot \text{nm} \cdot \text{mol}^{-1}$). This was explained by noting that the electrostriction takes place in the near environment of the ions, and in the cases of the R_4N^+ , this environment consists of the alkyl groups of these solvents, rather than the polar groups. The κ_T and $(\partial \ln \epsilon_r / \partial P)_T$ values for hydrocarbons are larger than those for water; hence the dielectric saturation should be more effective in the solvent alkyl groups adjoining the alkyl groups of the R_4N^+ ions.

Sen also reported standard partial molar volumes of alkali metal and halide ions in EG, formamide, and formic acid¹⁵¹ and

Table 9. Values of the B Coefficient of the Electrostriction Volume (in $\text{cm}^3 \cdot \text{nm} \cdot \text{mol}^{-1}$, Probable Error 0.2 Units) for Alkali Metal and Halide Ions

solvent	Zana et al. ^{149,150}		Sen ^{151,152}	
	cations	anions	cations	anions
water	1.0	1.0	1.0	1.0
methanol	1.7	1.7	1.6	1.6
ethanol	1.2	1.2	1.8	1.8
1,2-ethanediol	0.8	−0.1	0.9	0.9
formic acid			0.9	0.9
formamide			0.7	0.7
<i>N</i> -methylacetamide			0.5	0.5
<i>N</i> -methylpropanamide			0.2	0.2
<i>N,N</i> -dimethylformamide	1.8	0.2	1.7	2.5
HMPT ^a			0.2	8.6
acetonitrile	2.4	2.4	2.1	5.7
dimethylsulfoxide	1.2	0	0.1	4.4
propylene carbonate	1.0	1.0	0.4	0.4

in DMSO, hexamethyl phosphoric triamide (HMPT), PC, acetonitrile, and DMF,¹⁵² in general agreement with those of Zana et al. dealt with above.^{149,150} He also used eq 17 to obtain the electrostriction, but contrary to Zana et al. did not apply eq 7 as given but modified its first term to take into account voids in the solvents. The resulting B values differ, therefore, from those of Zana et al., and diverse sets were reported, depending on how the intrinsic volumes were calculated. These B values are shown in Table 9. The general conclusion from these data is that the cation and anion values tend to be the same for protic solvents and tend to differ for bulky aprotic ones, but details differ due to different choices of the intrinsic volume term.

The most recent contribution on this subject is the one by Marcus,⁷⁶ who calculated the molar electrostriction volume, $V_{i \text{ elec}}$, independently of the experimental $V_{i \infty}$ and the intrinsic volumes, that is, by not using eq 17 but instead from electrostatic considerations and a shell-by-shell computation according to eq 29. He applied this to univalent cations and anions in both protic solvents (water, methanol, ethanol, formamide, *N*-methylacetamide, and *N*-methylpropanamide) and dipolar aprotic ones (acetonitrile, nitromethane, PC, DMSO, and DMF). The intrinsic volumes, $V_{i \text{ intr}}$, of the ions were taken from Marcus et al.,¹⁵³ based on the volumes of ion crystals in which voids are also manifested, which differ from the volumes of the bare ions, eq 18. The sums $V_{i \text{ elec}} + V_{i \text{ intr}}$ were then compared with the experimental $V_{i \infty}$ (based on the TPTB assumption) in plots that yielded $V_{i \text{ elec}} + V_{i \text{ intr}} = (1.004 \pm 0.012)V_{i \infty}$ with a correlation coefficient of 0.9885 for protic solvents and $= (0.960 \pm 0.018)V_{i \infty}$ for the dipolar aprotic ones. The standard deviations of the fits were, respectively, 3.0 and 2.3 $\text{cm}^3 \cdot \text{mol}^{-1}$, commensurate with the probable error of the TPTB assumption, $\pm 2.0 \text{ cm}^3 \cdot \text{mol}^{-1}$. Thus, this approach appears to provide a valid estimate of the electrostriction in these nonaqueous solvents (although it was admitted that in the cases of the anions the electrostriction was small relative to the intrinsic volume, so the agreement with the experimental $V_{i \infty}$ is not a very strict test.)

6.3. Electrostriction in Mixed Solvents

Few authors dealt specifically with the electrostriction that takes place near ions in mixed solvents, one deterrent being the

possibility of preferential solvation of the ions, so that it becomes unclear to which of the solvents in the mixture the electrostriction applies. A further complication would be partial ion association to ion pairs if the relative permittivity of the mixed solvent falls sufficiently low. Another point to be considered is the determination of the theoretical slope, S_V^{DH} , of eq 11 for the mixed solvent, requiring knowledge of $(\partial \ln \epsilon_r / \partial P)_T$ and of κ_T , for proper extrapolation of the apparent molar volumes calculated from the densities to infinite dilution. This was demonstrated for mixtures of acetonitrile and water by Schwitzgebel, et al.,¹⁵⁴ where S_V^{DH} is approximately linear with the mole fraction of the acetonitrile.

In the case of cadmium sulfate in aqueous acetonitrile, Schwitzgebel et al.¹⁵⁴ used independently obtained association constants (from conductivity) to calculate the fraction associated with neutral ion pairs that presumably do not cause major electrostriction. The dissociated ions, however, cause large electrostriction, $\sum V_i^\infty$ being $-64 \pm 9 \text{ cm}^3 \cdot \text{mol}^{-1}$ at a mole fraction of acetonitrile of 0.2132 (but at an only slightly lower mole fraction, 0.2092, $\sum V_i^\infty$ is much less negative, $-36 \pm 4 \text{ cm}^3 \cdot \text{mol}^{-1}$, a fact that was not explained).

Kawaizumi et al.¹⁵⁵ presented a theoretical evaluation of the electrostriction in aqueous methanol solutions along the lines developed by Desnoyers et al.¹⁷ and discussed in sections 4.2 and 4.4. They applied their calculations to measured data for LiCl, KCl, and CsCl in these mixed solvents, ignoring knowingly the possibility of preferential solvation in their systems. The non-linear dielectric effect parameter b of eq 25 was assumed to vary linearly with the solvent composition. It was also necessary to estimate the pressure dependences of the relative permittivity, the refractive index, and the compressibility of the mixtures, and appropriate values were presented in a table. The electrostriction volume, $V_{2 \text{ elec}}$, and the disordered partial molar volumes, V_{2d} , of the three electrolytes were presented in another table for mole fractions of 0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1 of methanol. However, the authors caution that “one should retain prudence in discussing V_{2d} and V_{2e} separately, as they are essentially interrelated in the present treatment”.

Wang et al.¹⁵⁶ discussed the electrostriction ensuing in solutions of LiBr and LiClO₄ in mixtures of propylene carbonate (PC) with dimethylformamide (DMF), acetonitrile, tetrahydrofuran (THF), and methylformate (MF). The electrostriction (called interaction volume) was obtained from the oV_2 values extrapolated to infinite dilution by means of Masson's eq 3, which does not prevent any dependence on ion pairing that should take place in mixtures rich in the low-permittivity cosolvents THF and MF ($\epsilon_r < 10$). Equation 17 was then invoked, the intrinsic volumes (called cavity volumes) being calculated according to Glueckauf⁴⁷ from eq 21, but with an addend a (called Δ) depending on the cosolvent in a linear manner between the values for the neat solvents. The interaction volumes decrease (to more negative values) slowly and monotonously for both salts for mixtures of PC with DMF and acetonitrile (except for LiBr in PC + acetonitrile, having a maximum) but show a steep decrease for the low-permittivity cosolvents THF and MF, until a minimum is reached near a mole fraction of the latter of 0.8. The differences in the electrostriction were ascribed to a combination of effects: steric ones, permittivities that extend the effects of the ionic electric field, and solvation abilities of the solvent molecules. Preferential solvation of Li⁺ (by DMF with regard to PC and by PC with regard to acetonitrile) is invoked in order to rationalize qualitatively some of the observed effects.

Marcus took the consideration of the preferential solvation in solvent mixtures a step further, by devoting one paper⁷⁴ to

mixtures where no preferential solvation is expected and another¹⁵⁷ to systems where it is practically complete, that is, where selective solvation prevails. Thus, mixed solvents where some preferential solvation occurs were knowingly left out of consideration, due to the author's inability to deal with the very complicated relationships that ensue in such systems. The electrostriction was calculated by the shell-by-shell model, eq 29, given that the ionic intrinsic volume is independent of the solvent. The key quantity, the pressure derivative of the permittivity $(\partial \ln \epsilon_r / \partial P)_T$, is not known for the mixtures, so it was assumed that its ratio to the isothermal compressibility κ_T was linear with the composition.

For the case of no preferential solvation,⁷⁴ the hypothesis that solvents that do not differ too much in their polarity or hydrogen bonding ability would be represented in the solvation shells of ions in similar ratios as in the bulk, was examined. This proposition was tested for five cations and eight anions (all univalent) in mixtures of PC/acetonitrile and water/methanol and was found to be valid on the whole. The decrease in V_i^∞ with increasing contents of acetonitrile and of methanol is directly ascribable to their $(\partial \ln \epsilon_r / \partial P)_T$ being more than 2 times larger than those of PC and of water (Table 8).

For the case of selective solvation,¹⁵⁸ the same calculation was carried out, but then the relevant properties, ϵ_r , $(\partial \ln \epsilon_r / \partial P)_T$, and κ_T of the preferred solvent (which may differ for cations and anions), were used for the calculations. In water/ethanol, both K⁺ and Cl[−] were taken to be solvated by the water, in water/dimethylsulfoxide (DMSO), halide anions are solvated by the water and alkali metal ions and Ag⁺ by the DMSO, and in water/acetonitrile, Ag⁺ and Cu⁺ are solvated by the acetonitrile, whereas Na⁺, Cl[−], and I[−] are solvated by the water. The values for the cation and anion (intrinsic and electrostricted volumes) were added to yield calculated V_2^∞ ones compared with the experimental standard partial molar volumes. It was concluded that the use of the properties of the neat selectively solvating solvents in the calculated values produces reasonable agreement with the experimental data but the use of prorated properties (with respect to the bulk composition, as in the previous case) does not.

Wang et al.¹⁷⁴ presented a model for the excess Gibbs energy of electrolytes in mixed solvents that includes a long-range electrostatic interaction, a middle range second-virial-coefficient-type term, and a short-range interaction term expressed by the UNIQUAC model. Standard state properties were calculated for aqueous solutions according to the Helgeson, Kirkham, and Flowers approach,⁸⁴ constraining the model to reproduce the standard molar Gibbs energy of transfer to the mixed solvent. This model was used mainly for the calculation of activity coefficient, but was demonstrated for one example of an electrolyte in a mixed solvent, namely, for NaCl in water/methanol mixtures.

7. SOME CONSEQUENCES OF ELECTROSTRICTION

Electrostriction around ions in solution produces a pressure as described in section 4.2. This pressure that compresses the solvent can be termed an effective pressure, P_e , on the solution as shown, among others, by Leyendekkers.¹⁵⁹ In dilute solutions, as derived from the Tamman–Tait–Gibson approach, this effective pressure can be written as

$$P_e = [\ln(10) \exp(\alpha_0 m) - 1](B_T + P^o) \quad (50)$$

Here m is the salt molality, B_T is the Tait coefficient (300.5 MPa in water at 25 °C), P° is the standard pressure of 0.1 MPa, and

$$\alpha_0 = (V_{2\text{ intr}} - V_2^\infty)/315\nu_1 \quad (51)$$

where ν_1 is the specific volume of pure water. These two expressions connect the electrostriction, $V_{2\text{ elec}} = -(V_{2\text{ intr}} - V_2^\infty)$, with the effective pressure, P_e . The limiting partial molal effective pressure is

$$(\partial P_e^\infty / \partial m_2)_T = \ln(10)(B_T + P^\circ)\alpha_0 \quad (52)$$

and is, thus, directly proportional to the electrostriction volume.

McDevitt and Long⁵⁵ derived from the Gibson approach⁸¹ the equivalent expression:

$$(\partial P_e^\infty / \partial c_2)_T = (V_2 - V_2^\infty)/\kappa_T \quad (53)$$

In terms of the partial molar effective pressure and the isothermal compressibility of the solvent, κ_T (which is equivalent to $315\nu_1$ in the denominator of eq 51¹⁵⁹). In eq 53, V_2 was called the “liquid volume of the pure salt”, that is, its intrinsic volume (section 3.2).

It must be realized, however, that the effective pressure and its partial molar (or molal) derivative are *not* the same as the internal pressure of the solution and its concentration dependence. The thermodynamic internal pressure is $P_i = T\alpha_p/\kappa_T - p_1 \approx T\alpha_p/\kappa_T$ (the vapor pressure, p_1 , is negligible relative to the first term and α_p is the isobaric expansibility). Leyendekkers¹⁵⁹ showed that the internal pressure, P_i , consists of several terms, some are positive and others can be negative, of which the effective pressure, P_e , is only one.

The electrostriction caused by the ions of an electrolyte may be negligible (for large ions) but always causes an increased pressure (diminution of the solvent volume). However, whereas some salts do increase the internal pressure of the solution, others diminish it (Table 10). Therefore, phenomena that can be explained in terms of changes in internal pressure induced by salts need not be rationalized also in terms of the electrostriction, as is seen below.

7.1. Electrostrictive Effects on Solubilities

Long and McDevitt¹⁶⁰ reviewed the salting-out (and -in) of nonelectrolyte solutes (subscript 3) by aqueous salt (subscript 2) solutions. This phenomenon can be described by the Setchenow coefficient k_s that relates the solubility s_3 of the nonelectrolyte solute in a salt solution of concentration c_2 to that in the salt-free solvent (water), s_3° , as

$$\log(s_3^\circ/s_3) = k_s c_2 \quad (54)$$

For most solutes and salts, $k_s > 0$, so the solubility of the solute is lowered in the presence of the salt and salting-out occurs. For some combinations of solute and salt, $k_s < 0$ and salting-in takes place. Several theories have been proposed to account for this effect as reviewed,¹⁶⁰ including the effective removal of water solvent by the hydration shell of the ions and electrostatic effects related to the permittivity decrement caused by the solute. The theory preferred by the authors is that developed by them,⁵⁵ based on the effective pressure concept of Gibson,⁸¹ that is seen to be equivalent to that based on the electrostriction caused by the ions of the salt, eq 53. This theory is best suited for nonpolar solutes, exemplified by benzene, but does not preclude the operation of additional forces, such as direct interactions of the solute with either the solvent (water) or the ions or both by dispersion, donor–acceptor, and hydrogen-bonding interactions. These interactions may turn salting-out expected from the electrostriction to salting-in.

Table 10. The Internal Pressures, P_i (MPa), at 25 °C of Some Aqueous Salt Solutions^a

salt, 1 M	P_i , MPa	salt, 2 M	P_i , MPa	salt, 1.4 M in acetone	P_i , MPa
none	167.8			none	326.5
LiCl	186.6	LiClO ₄ ^b	146.8	LiClO ₄ ^f	651.8
LiI	200.8	NaCl ^c	380.5	NaClO ₄ ^f	507.4
Li ₂ SO ₄	241.8	NaBr ^c	374.0	Mg(ClO ₄) ₂ ^f	951.5
NaOH	247.7	NaBF ₄ ^c	228.0	Ba(ClO ₄) ₂ ^f	826.6
NaCl	233.9	NaClO ₄ ^c	155.0		
NaBr	239.3	NaClO ₄ ^e	149.8		
Na ₂ CO ₃	310.9	NaPF ₆ ^c	146.0		
Na ₂ SO ₄	305.9	NaAsF ₆ ^c	139.1		
KCl	229.3	NaCF ₃ CO ₂ ^e	154.2		
(C ₂ H ₅) ₄ NBr	245.6	KSCN ^e	156.7		
MgSO ₄	247.7	GnCl ^{b,d}	144.5		
BaCl ₂	281.2	GnBr ^{b,d}	142.0		
CuSO ₄	266.1	GnBF ₄ ^{b,d}	124.6		
		GnClO ₄ ^{b,d}	116.1		
		CaCl ₂ ^b	323.6		

^a from ref 82 and other sources as marked and in acetone solutions.

^b From ref 166. ^c From ref 165. ^d Gn = guanidinium, C(NH₂)₃⁺. ^e Read from a figure in ref 167. ^f Private communication from Kumar.¹⁶⁸

McDevitt and Long⁵⁵ derived for cases when such additional interactions are absent the expression:

$$k_s = V_3(V_2 - V_2^\infty)/RT\kappa_T \ln(10) \quad (55)$$

V_3 being the molar volume of the solute and V_2 the intrinsic volume of the salt. The value in parentheses in the numerator is, thus, the negative of the electrostriction, $V_{2\text{ elec}}$, cf. eq 17. This expression was verified qualitatively (to a factor of 3) for benzene¹⁵⁷ and for some other solutes but depends strongly on the assumed values of the intrinsic volumes, V_2 . Although salting-in was observed for benzene in aqueous HClO₄ and (CH₃)₄NBr, their assumed intrinsic volumes, V_2 , that yield this effect with eq 55 are highly questionable. The fact remains that some salts (tetraalkylammonium halides, alkali metal benzoates¹⁶¹) do cause salting-in, and this would be due to other effects that counterbalance the electrostriction.

Salting out of solutes by polyions was ascribed to electrostriction by Conway et al.¹¹⁷ but without giving details. The salting out due to electrostriction should pertain also to other solvents besides water, but this has not been tested in detail (but see ref 162).

7.2. Electrostrictive Effects on Reaction Rates

The rates of reactions depend on the activation volume when pressure is applied and hence are affected by electrostriction. Cases where charged (or dipolar) species are formed from neutral ones in the transition state (ionogenic reactions) were recently reviewed by Jenner.¹⁶³ The electrostriction of such species was briefly discussed in section 5.1. Electrostrictive effects on reaction rates occur also in the presence of electrolytes that do not necessarily partake in the reaction, as cursorily reviewed here.

It is to be expected that reactions involving a negative activation volume, $\Delta V^\ddagger < 0$, would be accelerated in the presence of salts that exhibit strong electrostriction, that is, large negative values of $V_{2\text{ elec}}$. However, cases of reactions that are retarded by certain salts exist, but these cannot be explained in terms of

electrostriction. As mentioned in section 7.1 for the explanation of the salting-in by such salts, other interactions should be invoked for their rate retardation effects.

The rates of Diels–Alders reactions, having negative activation volumes, have been studied in this connection.¹⁶⁴ For example, the reaction between anthracene-9-carbinol and *N*-ethylmaleimide carried out in 2 M aqueous NaCl, NaBr, and NaBF₄ was enhanced relative to the rate in water in decreasing order, but in 2 M NaClO₄, NaPF₆, and NaAsF₆ it was retarded. This was interpreted by Kumar¹⁶⁵ indirectly in terms of the electrostriction, but rather in terms of the internal pressure P_i of these solutions, see Table 10. The rates in the corresponding aqueous 2 M guanidinium (Gn) salts were retarded with respect to that in water, again in agreement with the lower internal pressures they have compared with water.

Not only reaction rates but also steric selectivity are affected by salt electrostriction, as demonstrated by the reaction of cyclopentadiene with methyl acrylate (involving an activation volume $\Delta V^\ddagger = -30 \text{ cm}^3 \cdot \text{mol}^{-1}$) in aqueous solutions of LiCl, NaCl, NaBr, CaCl₂, LiClO₄, and GnCl.¹⁶⁶ The faster the reaction proceeds, the higher becomes the relative yield of the *endo* form of the product. One of the reactants, methyl acrylate, was shown to be salted-out by the first four salts, which also increase the *endo/exo* ratios of the reaction products, but it is salted-in by the other two that decrease these ratios. Again, the results are consistent with an explanation in terms of the internal pressure changes, but only partly by their being caused by the salt electrostriction.

Not only Diels–Alders-type reactions, such as the above, of which the rates are affected by aqueous salts, can be discussed in terms of the electrostriction concept. The thermal stability of the DNA duplex is an example.¹⁶⁷ The volume change of splitting the duplex into two strands is positive; hence salts that increase the internal pressure of water (such as NaCl and KCl) increase the transition temperature, whereas those that decrease it (such as KSCN, NaClO₄, and NaCF₃CO₂) diminish it. Again, electrostriction cannot be invoked to explain the effect of the latter three salts.

Salts may accelerate reactions that involve a negative activation volume not only in aqueous solutions but in nonaqueous ones too. For instance in acetone, the reaction between 2,3-dimethylbutadiene and 1,4-naphthoquinone ($\Delta V^\ddagger = -22 \text{ cm}^3 \cdot \text{mol}^{-1}$) is accelerated by sodium, lithium, barium, and magnesium perchlorates with increasing effectivity in this order.¹⁶⁸ This parallels their internal pressures (Table 10) and probably also their electrostriction, as expected from the ionic radii and charges.

Negative activation volumes are manifested also in purely inorganic reactions, such as that of IrCl₆²⁻ with I⁻ in aqueous acid or salt solutions.¹⁶⁹ In addition to catalysis by K⁺ ions, there are secondary medium effects attributable to the anions of the accompanying salts. Although “electrostriction” was mentioned in the title of this paper, it was not actually invoked in the discussion of the results.

Electrochemical reactions may also involve a reaction volume for the (half-cell) reaction, ΔV_{cell} , which depends on the electrostriction of the solvent. In one study, the decamethylferrocene(1/0) electrode reaction¹⁷⁰ and in another the electrochemistry of metal phthalocyanines in organic solvents¹⁷¹ was shown to involve electrostriction. In the former of these, the relationship

$$\Delta V_{\text{cell}} = A - [(N_A e^2 / 8\pi\epsilon_0) \Delta(z^2) r^{-1}] \epsilon_r^{-1} (\partial \ln \epsilon_r / \partial P)_T \quad (56)$$

was established, where A is a constant depending on the reference electrode. This dependence on the change of the square of the charge and on the pressure derivative of the relative permittivity is what is required from application of the Drude–Nernst eq 2 for the electrostriction.

Several other studies invoked electrostriction in order to explain the dependence of reaction rates, isomer yields, electrode reactions, charge transfer rates, etc. on the electrostriction caused by nonreacting ions or salts. In many cases, other explanations can be as effective or better (ion solvation, hydrophobic and donor–acceptor interactions, etc.), so these papers are not reviewed here.

8. DISCUSSION AND CONCLUSIONS

Drude and Nernst¹ laid the foundation for the concept of electrostriction, the compression of the solvent surrounding ions in consequence of their electric field. It was only after the actual sizes of ions in condensed media were established, on the order of 0.05–0.5 nm, that it was realized how huge the electric field strength in the immediate vicinity of ions is, being on the order of 10–100 GV·m⁻¹. Such field strengths cannot so far be achieved in ordinary laboratory experiments (0.1 GV·m⁻¹ appears to be the limit), so the consequences of the fields around ions need to be established by theory or computer simulation, as recently reviewed by Fulton.⁶² A large dielectric decrement, down to dielectric saturation, results from such enormous fields (section 4.3). The pressures exerted by such fields are on the order of 0.1–1 GPa, so high compression of the solvent ensues (section 4.2).

The actual compression of the solvent in electrolyte solutions can be determined from the partial molar volume of the solvent or of the electrolyte, obtained experimentally from the densities of its solutions. Most of the attention was naturally directed at aqueous solutions, but the methods used apply to any solvent. A comparison of the experimentally derived electrostriction with expectations from the properties of the solvent and of the ions is best made at infinite dilution, where only ion–solvent but no ion–ion interactions need to be taken into account.

Thus, the first step is to obtain valid results for the standard (infinite dilution) partial molar volumes of the electrolytes, V_2^∞ . This ought to be done according to the Debye–Hückel limiting law, eq 12, which requires knowledge of the limiting slope, S_V^{DH} . This, in turn requires knowledge of the pressure derivative of the relative permittivity of the solvent, $(\partial \epsilon_r / \partial P)_T$, and of its isothermal compressibility, κ_T , at the relevant temperature, the former of which is known for relatively few solvents (see Table 1 for S_V^{DH}).

The next step is to split the V_2^∞ into the ionic contributions, V_i^∞ , but this cannot be done on a purely thermodynamic basis. It requires an extra-thermodynamic assumption concerning one ion, from which the values for other ions are obtained from the additivity principle that holds at infinite dilution. The most consistent results for aqueous solutions, as discussed by Conway,²¹ are obtained by using the suggestion by Millero.^{2,3} This leads to eqs 13 and 14 and yields $V^\infty(\text{H}^+, \text{aq}) = -5.4 \text{ cm}^3 \cdot \text{mol}^{-1}$ at 25 °C, estimated to be valid to $\pm 0.2 \text{ cm}^3 \cdot \text{mol}^{-1}$. For nonaqueous solvents, it was found expedient by Hefter and Marcus²² to apply the TPTB assumption: $V^\infty(\text{Ph}_4\text{P}^+) - V^\infty(\text{BPh}_4^-) = 2.0 \pm 2.0 \text{ cm}^3 \cdot \text{mol}^{-1}$, providing the least objectionable estimates. The ionic partial molar volume, V_i^∞ , describes the actual volume that can be assigned to the ion in the solution.

A further step is to derive the ionic electrostriction volume, $V_{i\text{ elec}}$, from the ionic partial molar volume V_i^∞ by subtraction from the latter of the intrinsic volume of the ion, $V_{i\text{ intr}}$, according to eq 17. The problem is how this quantity is to be defined and estimated, since it became obvious that the value for the “bare” ion, $(4\pi N_A/3)r_i^3$, does not lead via eq 17 to valid electrostriction volumes, which need to be negative (the solvent is compressed). The various suggestions that have been made to correct this situation are discussed in section 3.2. Table 3 compares results for the intrinsic volumes of several ions according to some approaches that may be useful. It should be remembered that $V_{i\text{ intr}}$ ought to be independent of the solvent, of the concentration, and practically also of the temperature.

A different approach estimates the electrostriction volume, $V_{i\text{ elec}}$, from electrostatic considerations and not from the partial molar volumes as described above. Two methods for doing this are reviewed in section 4.4, that of Desnoyers et al.¹⁷ and that of Marcus and Hefter.¹⁸ There are several properties of the solvents that are required in order to apply these methods; those for aqueous solutions are shown in Table 4 for a range of temperatures and two pressure values, and those for water and nonaqueous solvents at 25 °C are shown in Table 8, as far as data are available. The first of these methods¹⁷ leans on the thermodynamics of fluids in electric fields as discussed by Frank¹⁴ to calculate the pressure exerted by the ionic field at the middle of the solvation shell of the ion. Then, with the mean electrostriction per mole of solvent (section 4.6) and the number of moles of solvent exposed to the field in the solvation shell, the total electrostriction volume is obtained. The second method¹⁸ leans on an electrostatic calculation proposed by Landau and Lifshitz⁷² and computes the electrostriction around the ion shell-by-shell with narrow shell widths. Iterative computation is required because of the mutual dependence of the permittivity of the solvent and the electric field, the nonlinear dielectric effect being taken into account.

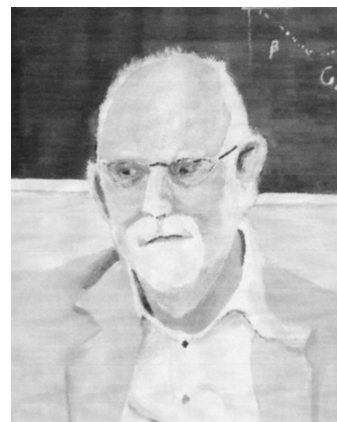
The results of such calculations pertain to infinite dilution, but at finite concentrations the ion–ion interactions enormously complicate the picture. What is clear is that these interactions cause the electrostriction volume to become less negative, until such large concentrations are reached at which practically all the solvent is included in the solvation shells with no bulk (“free”) solvent remaining, at which stage no further electrostriction is possible (section 4.5). When at infinite dilution, the thermodynamic states (temperature or pressure) depart from ambient; then again appreciable changes in $V_{2\text{ elec}}$ are to be expected. It becomes more and more negative as the temperature is increased at constant pressure above about 50 °C, where its absolute value is minimal (section 4.4.1).

Most of what is dealt with in sections 3 and 4 pertains to ions that have a spherically symmetrical electric field around them: monatomic ions and pseudoglobular ones, such as $(\text{CH}_3)_4\text{N}^+$ and ClO_4^- . Complications arise in the cases of other kinds of ions or of charges distributed on different parts of molecules, as discussed in section 5. Of major importance is the electrostriction at the surfaces of biomolecules, such as proteins (section 5.4). The surface charge density of proteins is $\sigma = 0.08\text{--}0.48\text{ C}\cdot\text{m}^{-2}$ ¹²⁶ and the relative permittivity of water ϵ_r is reduced (at 20 °C) from 82 at zero charge density to 11 at $0.3\text{ C}\cdot\text{m}^{-2}$ and to 4 at $0.4\text{ C}\cdot\text{m}^{-2}$. The density of the water at the surface layer of the protein increases to $1.087\text{ g}\cdot\text{cm}^{-3}$ at $\sigma = 0.3\text{ C}\cdot\text{m}^{-2}$ and to $1.417\text{ g}\cdot\text{cm}^{-3}$ at $\sigma = 0.4\text{ C}\cdot\text{m}^{-2}$.¹²⁸ The physiological implications

of these effects on the water include the behavior of ion channels and other manifestations.

Despite such implications, in other situations electrostriction may be involved but other causes of the observed phenomena cannot be discounted. This is briefly discussed in section 7.

BIOGRAPHY



Yizhak Marcus was born in Germany but received all his education in Jerusalem, where he obtained his Ph.D. from the Hebrew University in 1956. He was a researcher at the Soreq Nuclear Research Institute, dealing mainly with actinide chemistry, ion exchange, and solvent extraction. From there, he was called in 1965 and appointed Professor of Inorganic and Analytical Chemistry at the Hebrew University. There he taught and did research until his retirement in 1999, but he continues with research as Professor Emeritus. His main interest is solution chemistry: aqueous, nonaqueous, and mixed solvents and solutions of electrolytes and nonelectrolytes. He has published in this and neighboring fields 6 books and over 290 papers in refereed journals. Since six years ago, he has taken up painting, and the photo is a recent self-portrait.

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