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Ionic volumes in solution

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Abstract

The volumetric properties of electrolytes in solutions indicate the interactions of the constituent ions with their environment: the solvent and other ions. The interactions with the solvent alone are manifested at infinite dilution by the standard partial molar volume, V^∞(salt), obtained from density measurements. To study the interactions, it is necessary to split V^∞(salt) into the additive ionic contributions, V^∞(ion), using an extra-thermodynamic assumption. Values of V^∞(ion) for small ions depend cardinally on the electrostriction of the solvent that can be obtained from an iterative shell-by-shell calculation from a continuum model of the solvent. The solvent shrinkage per mol of ions is ΔV_{el}(ion)<0. Also, the molar electrostriction of the solvent S, $\Delta V_{el}(S)<0$, is calculable. The ratio ΔV_{el}(ion)$/\Delta V_{el}(S)=n^\infty$ is the solvation number of the ion in S at infinite dilution. The calculated V^∞(ion)$_{calc}$ are compared with the experimental values, showing good agreement for many univalent ions in both single solvents and in some binary solvent mixtures, where no appreciable preferential solvation takes place. Ion pairing sets in under certain circumstances of ionic charge and solvent permittivity. The difference $\Delta V_{ip}=V_{ip}^\infty-[V_+^\infty+V_-^\infty]>0$ is obtained experimentally from the pressure derivative of the association constant. The ratio $\Delta n_{ip}=\Delta V_{ip}/\Delta V_{el}(S)$ represents the number of solvent molecules released to the bulk on ion pairing by the diminution of the electrostriction.

Keywords: Standard partial molar volume; Ionic molar volume; Electrostriction; Solvation number; Ion pairing

1. Introduction

Among the various properties of ions, encountered in physiological environments as well as in laboratory and industrial practice, are their sizes. The sizes of ions, like those of non-electrolytic molecules [1], can be described by a radius, if nearly spherical, or by two linear dimensions, if approximating an oblate or prolate ellipsoid of revolution. However, independent of the shape, the volume of an ion gives a good indication of its size. The sizes of ions in an isolated (ideal gaseous) state are ill defined, since the electron density extends indefinitely except during a collision with another particle. But in a condensed phase, whether a crystalline solid, a molten salt, or a solution, the neighboring particles limit this extension and confine the ion within definite boundaries, so that its volume can be assessed.

An ion is said to have an intrinsic volume, V_{intr} per mol of ions, which represents its volume in a crystalline phase, where the electric fields of the neighboring ions and their hard cores confine it. At absolute zero, an ion occupies a definite position in the crystal lattice and its volume can be assessed from the crystal structure [2]. This intrinsic volume is considered to be incompressible by external pressures, even very high ones, since the electric field of the neighboring ions has already compressed the electron shells to the utmost. It is thus an invariant property of the ion and is independent of its environment, whether a crystal, a melt, or a solution.

In solution, an ion interacts with the surrounding solvent – is solvated by it – and the volume ascribable to it reflects not only its intrinsic value but also its interactions. Volume is occupied in the solution by the ions and by the solvent, but there is also some "free volume" that permits diffusion of ions and molecules. Since the ions and the solvent molecules are assumed to have some intrinsic volume that is not compressible, external pressure exerted on the solution compresses the 'free volume' only. Interactions between the ions and the solvent, likewise, compress what would otherwise be 'free volume' rather than the solvent molecules themselves. Hence, the volumetric properties of the solution, i.e., the apportioning of

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the total volume of the solution to the parts occupied by the ions and by the solvent, is indicative of the interactions that take place. The more intense these are, the smaller the total volume of the solution. However, the diminution of the volume is limited by the sum of the intrinsic volumes of the ions and solvent molecules and by their mutual packing.

Ions in solutions interact with:

1. The solvent; if more than one solvent is present then preferential solvation can occur.
2. Other ions: all other ions in terms of the ionic atmosphere; eventually ions of opposite charge, to form ion pairs.

However, at infinite dilution of an electrolyte in the solution no interactions of a given ion with other ions take place, so that this ion is surrounded by solvent molecules only (its counter-ion being at an infinite distance from it) and its interactions are with the molecules of the solvent(s) alone.

Volume is an extensive thermodynamic quantity and, therefore, is measurable only for entire electrolytes (abbreviated in the following to ‘salts’) and not for individual ions that cannot be added to a solution without their counter-ions. Theoretical considerations of the interactions, on the other hand, pertain to individual ions. Calculated volumes for an ion and its counter-ion can be added (weighted stoichiometrically) for comparison with the measured volume of the salt. Contrarily, splitting of the measured volume of a salt into the individual ionic contributions, for comparison with theoretically derived values, can be done only by the use of an extra-thermodynamic assumption, as will be shown below.

2. Standard partial molar volumes of salts

To deal with ion–solvent interactions only, the proper measure is the standard partial molar volume of the salt, V^{∞}(salt). Although this quantity is experimentally obtainable, the procedure for doing so is not so simple. The usual method employed is to measure at a carefully controlled temperature the densities of the solvent, ρ^*, and of a series of dilute solutions of the salt at concentrations c, $\rho(c)$. The apparent molar volume of the salt, ${}^{\varphi}V$, is the difference, per mol of salt present, between the total volume of the solution, V, and the volume ascribable to the solvent if it were not affected by the presence of the salt. The latter quantity is the product of the molar volume of the pure solvent, V^*, and the number of moles of it present in V. Values of ${}^{\varphi}V(c)$, are calculated from [3]:

$$ {}^{\phi}V(c) = (M/\rho^*) - 1000[\rho(c) - \rho^*]/\rho^* c \qquad (1) $$

where M is the relative molar mass of the salt. The numerical coefficient, 1000, is used for densities in g cm^{-3}, concentrations in mol dm^{-3}, and molar masses in g mol^{-1}, yielding the volume in cm^3 mol^{-1}. High accuracy of the density data is needed: an accuracy of $\pm 1\times 10^{-4}$ g cm^{-3} is inadequate! Data down to at least $c=0.01$ mol dm^{-3} are required.

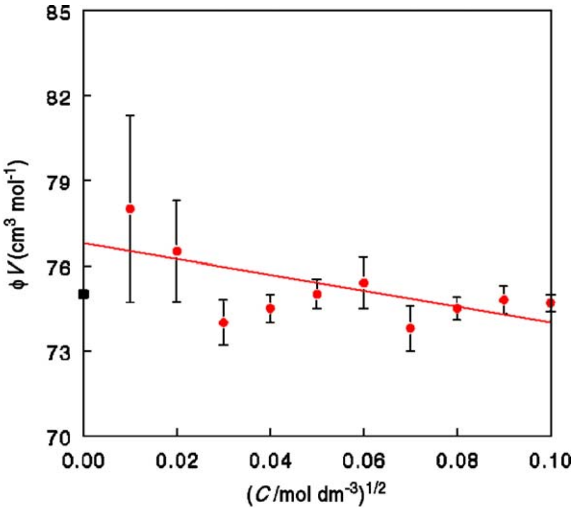

Fig. 1. A Masson plot of the apparent molar volume of a salt (having a standard partial molar volume of 75.0 cm^3 mol^{-1}, the small black square) against the square root of the molar concentration. The values pertain to a hypothetical combination of a salt and a solvent with randomly assigned uncertainties in the density of $\pm 1\times 10^{-4}$ g cm^{-3}. Note that the uncertainties in the volume increase appreciably as the concentration diminishes.

The infinite dilution value of the apparent molar volume of the salt equals its standard partial molar volume [3]:

$$ {}^{\phi}V^{\infty}(\text{salt}) = \lim(c\rightarrow 0)\,{}^{\phi}V(\text{salt}) = V^{\infty}(\text{salt}) \qquad (2) $$

However, the $c\rightarrow 0$ extrapolation of ${}^{\phi}V(c)$ against $c^{1/2}$ needs to be done properly, i.e., according to the theoretical limiting slope:

$$ {}^{\phi}V(\text{salt}) = {}^{\phi}V^{\infty}(\text{salt}) + S_{\text{V}}^{\text{DH}} c^{1/2} + \cdots \qquad (3) $$

The slope, S_{V}^{DH}, obtained from the Debye–Hückel theory [3], requires data of the pressure derivative of the solvent permittivity: $(\partial \ln\varepsilon/\partial P)_T$. Unfortunately, these data are not available for all solvents of interest, but are known for a fair number of them [4].

It is inadvisable to use Masson [5] plots instead of using the theoretical slope, S_{V}^{DH}, although this is commonly done. Masson plots, i.e., plots of ${}^{\phi}V(c)$ against $c^{1/2}$, are linearly extrapolated to $c=0$ with an empirical slope of S_{V}^{M}. Doing so as well as having large uncertainties in ρ at low c can lead to serious errors, as large as 1 cm^3 mol^{-1}, in the desired value of V^{∞}(salt), see Fig. 1. However, with the most careful work and proper extrapolation, an accuracy of ± 0.01 cm^3 mol^{-1} in V^{∞}(salt) can be achieved.

3. Ionic molar volumes

Since it is individual ions that interact with their surrounding solvent at infinite dilution, ionic molar volumes, V^{∞}(ion), are required for studying these interactions. Therefore, it is necessary to split V^{∞}(salt) into the individual ionic contributions:

$$ V^{\infty}(\text{salt}) = \nu_{+}V_{+}^{\infty} + \nu_{-}V_{-}^{\infty} \qquad (4) $$

the v being the stoichiometric coefficients of the ions designated by the charges + for cations, − for anions. An extra-thermodynamic assumption is required for this splitting, because V^∞(ion) ($\equiv V^\infty_+$ or V^∞_-) cannot be measured.

Marcus and Hefter [6] pointed out that the claimed direct measures by ultrasonic vibration potentials of V_+ and V_- values also require an extra-thermodynamic assumption. This assumption equates the measured hydrodynamically significant ionic volume to the thermodynamically significant V^∞(ion) value. Therefore, the usefulness of the ultrasonic vibration potentials method should be assessed by comparison with other assumptions.

For non-aqueous solvents, S, Hefter and Marcus [7] found that the TPTB assumption:

$$V^\infty(\mathrm{Ph_4P^+},S) = V^\infty(\mathrm{BPh_4^-},S) + 2\ \mathrm{cm^3\ mol^{-1}} \tag{5}$$

is the least objectionable among several extra-thermodynamic assumption that had been proposed. The assumption is that the volumes of the very similar ions of tetraphenylphosphonium tetraphenylborate (TPTB) are nearly the same in all solvents, but for the small (<0.7%) specified difference. The numerical addend is valid for 298.15 K and the claimed validity is ±2 $\mathrm{cm^3\ mol^{-1}}$. Some other viable assumptions can also be applied, as shown by Marcus and Hefter [6]. For aqueous solutions, W, the Conway assumption [8] that $V^\infty(\mathrm{H^+},\ \mathrm{W}) = -5.5\ \mathrm{cm^3\ mol^{-1}}$ (at 298.15 K) appears to be the best. It ought to be stressed that these assumptions cannot be put to a proof, and their acceptance is in view of agreement of the resulting values with theoretically derived values (see below), but that the validity of these theories themselves cannot be proved.

It should be remembered that the V^∞(ion) values in a given solvent are independent of each other: only ion–solvent interactions occur at infinite dilution. Therefore, once the V^∞(ion) of just one ion is known, those of other ions can be obtained from measured values of V^∞(salt) of salts involving this ion by additivity, using Eq. (4). For example, the following hierarchical procedure can be employed [7]:

1. Measure $V^\infty(\mathrm{Ph_4PBr})$, $V^\infty(\mathrm{NaBPh_4})$, and $V^\infty(\mathrm{NaBr})$.
2. From additivity, $V^\infty(\mathrm{Ph_4PBPh_4}) = V^\infty(\mathrm{Ph_4PBr}) + V^\infty(\mathrm{NaBPh_4}) - V^\infty(\mathrm{NaBr})$.
3. Then, from the TPTB assumption, $V^\infty(\mathrm{Ph_4P^+}) = \frac{1}{2}V^\infty(\mathrm{Ph_4PBPh_4}) + 1\ \mathrm{cm^3\ mol^{-1}}$; $V^\infty(\mathrm{BPh_4^-}) = \frac{1}{2}V^\infty(\mathrm{Ph_4PBPh_4}) - 1\ \mathrm{cm^3\ mol^{-1}}$.
4. Hence, $V^\infty(\mathrm{Br^-}) = V^\infty(\mathrm{Ph_4PBr}) - V^\infty(\mathrm{Ph_4P^+})$; $V^\infty(\mathrm{Na^+}) = V^\infty(\mathrm{NaBPh_4}) - V^\infty(\mathrm{BPh_4^-})$.
5. And for other cations (from $V^\infty(\mathrm{Br^-})$) and anions (from $V^\infty(\mathrm{Na^+})$).

The solubility of $\mathrm{Ph_4PBPh_4}$ in most solvents is too small for permitting the direct measurement of its apparent molar volume, hence the round-about method of item 2 is employed for obtaining its standard partial molar volume on extrapolation.

Extensive critically evaluated compilations of standard partial molar volumes of ions, V^∞(ion), at 298.15 K were published for aqueous solutions [9,10] and more recently for non-aqueous ones [6].

4. Molar ionic electrostriction

An ion in solution exerts an enormous electric field around it. For example, at the distance of 0.158 nm from the center of a $\mathrm{K^+}$ ion (of radius 0.138 nm) in dimethylsulfoxide (DMSO) the field is $E = 2.3\times10^{10}\ \mathrm{V\ m^{-1}}$. Such a large field corresponds to a huge pressure, P, of 4.6 GPa, and has a strong compressive effect on the solvent surrounding the ion, “electrostriction”, a term coined already by Drude and Nernst in 1894 [11].

The electrostriction around an ion can be calculated in a shell-by-shell manner according to Marcus and Hefter [4], using a continuum model of the solvent. Iterations are required in the calculation, due to the mutual dependence of the field and the permittivity of the solvent, and non-linear dielectric effects for the solvent have to be taken into account. The molar electrostriction near ion I in solvent S is obtained from summing over increasing values of the running index j of the electrostriction occurring in each j-th shell at the distance $r(j)$ from the center of the ion. A conveniently small constant shell thickness, $\Delta r = r(j+1) - r(j)$ is used, the summation starting with the radius of the bare ion $r(1) = r(I)$:

$$\Delta V_{\mathrm{el}}(I,S) = -(8\pi^2 N_{\mathrm{A}}\varepsilon_0)\sum[r(j+1)^3 - r(j)^3]\{\varepsilon(j)[(\partial\ln\varepsilon/\partial P)_T - \kappa_T] + \kappa_T\}E(j)^2 \tag{6}$$

Here N_{A} is Avogadro's number, ε_0 is the permittivity of vacuum, T is the temperature, and ε is the relative permittivity and κ_T is the isothermal compressibility of the solvent S. The latter quantity is assumed to be independent of the electric field and equal the value for the neat solvent, $\kappa_T{*}$. The non-linear dielectric effect for solvent S is characterized by the coefficient β describing the electric field dependence of the relative permittivity of S:

$$\varepsilon(E) - \varepsilon(0) = \beta E^2 \tag{7}$$

Here $\varepsilon(0) \equiv \varepsilon{*}$ is the relative permittivity of the solvent in the absence of an electric field, i.e., of the bulk solvent at a large distance from the ion. The field strength in the j-th shell around an ion at the distance $r(j)$, where a relative permittivity $\varepsilon(j)$ prevails, is therefore:

$$E(j,\varepsilon,r) = z(I)e/\{4\pi\varepsilon_0[\varepsilon(0) + \beta(S)E(j,\varepsilon,r)^2]r(j)^2\} \tag{8}$$

where e is the unit charge. As mentioned, $E(j,\varepsilon,r)$ must be calculated iteratively from Eq. (8) for use in Eq. (6). The calculation of $\Delta V_{\mathrm{el}}(I,S)$, therefore, requires for the ion I:

- the charge z,
- the radius r.

and for the solvent S:

- the isothermal compressibility κ_T,
- the permittivity ε,
- its pressure derivative $(\partial\ln\varepsilon/\partial P)_T$,
- the non-linear dielectric effect $\beta = (\partial\varepsilon/\partial E^2)_T$.

A direct result from this calculation is the dielectric saturation near the ion. This means that the relative permittivity near the ion has a value much smaller than in the bulk solvent, the limit being the square of the refractive index. This means that the polarization of the solvent by the electric field is electronic and atomic but has no longer an orientational component for the dipoles of the solvent molecules.

As the distance from the center of the ion increases, the electric field diminishes. Therefore, the solvent shrinkage is largest near the ion and decreases at larger distances. The sum in Eq. (6) as $r(j) \to \infty$ converges readily and yields the electrostriction per mol of ions, $\Delta V_{el}(I,S) < 0$, i.e., a negative quantity. The lower the permittivity of the solvent, the farther away from the center of the ion summation needs to extend, as is seen in Figs. 2 and 3. As is seen further below, the calculated $\Delta V_{el}(I,S)$ values can be used for the theoretical estimation of the V^{∞}(ion) values for ions I in solvents S.

5. Molar solvent electrostriction

The molar volume of the solvated ion, $V_s(I,S)$, with its (already compressed) solvation shell, can be defined at any concentration c and be expressed by either of two sums, according to Padova [12]:

$$V_s(I,S) = V_{intr} + nV_{el}(S) = {}^{\varphi}V + nV^* \tag{9}$$

On the one hand $V_s(I)$ is the sum of the intrinsic molar volume of the ion itself, V_{intr}, and n, the solvation number, times the molar volume of the electrostricted solvent, $V_{el}(S)$. On the other hand $V_s(I)$ is the sum of the apparent molar volume, ${}^{\varphi}V$, and n times the molar volume of the neat solvent, V^*. Eq. (9) couples the molar volume of the electrostricted solvent (its mean over the entire volume where electrostriction takes place), $V_{el}(S)$, and the solvation number n. The one is meaningful only with respect to the other. The already electrostricted solvent near an ion is considered as incompressible. Therefore, if a c molar solution has a measured compressibility κ_T, the incompressible fraction of the solution is:

$$1 - \kappa_T/\kappa_T^* = (c/1000)V_s(I) \tag{10}$$

where κ_T^* pertains to the neat solvent.

The limiting expressions (at low concentrations) for the concentration dependences of the apparent molar volume and apparent molar compression are:

$${}^{\varphi}V = {}^{\varphi}V^{\infty} + S_V c^{1/2} = V^{\infty} + S_V c^{1/2} \tag{11a}$$

$${}^{\varphi}K = {}^{\varphi}K^{\infty} + S_K c^{1/2} \tag{11b}$$

where S_V and S_K are the limiting slopes and Eq. (11a) is the same as Eq. (3).

From Eqs. (9) (10) (11a) and (11b), following Padova [12] further, with elimination of the solvation number n, the expression:

$$V_{el}(S) = V^*[1 - (S_V/S_K)\kappa_T^*] \tag{12}$$

results [13]. The theoretical limiting slopes according to Debye and Hückel are [3]:

$$S_V = 0.5\nu RTS_f X \tag{13a}$$

$$S_K = 0.25\nu RTS_f[X^2 - 2(\partial X/\partial P)_T] \tag{13b}$$

where S_f is the limiting slope for the activity coefficients and the variable X is:

$$X = 3(\partial \ln\varepsilon/\partial P)_T - \kappa_T^* \tag{14}$$

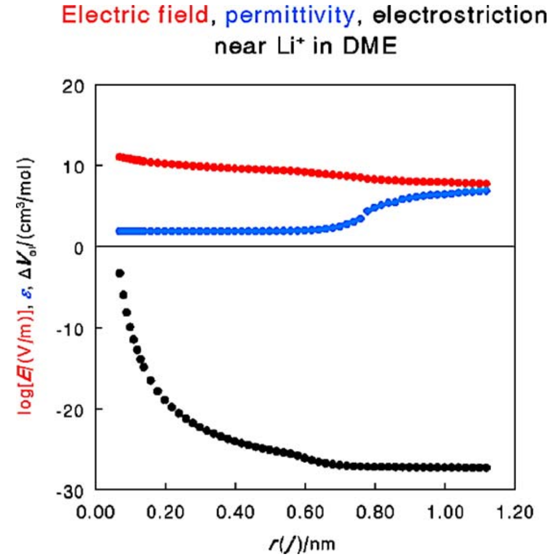

Fig. 3. Shell-by-shell calculation of the electric field strength (note the logarithmic scale), the relative permittivity, and the electrostriction around a lithium ion in 1,2-dimethoxyethane.

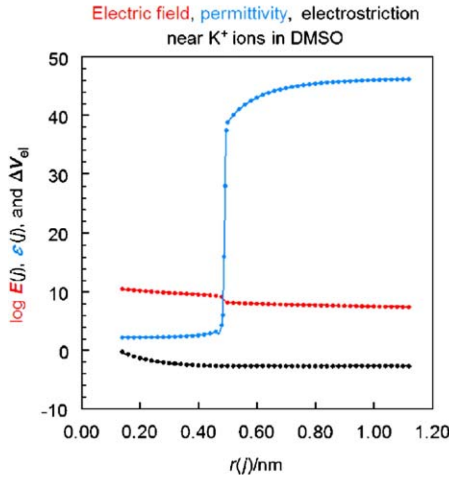

Fig. 2. Shell-by-shell calculation of the electric field strength (note the logarithmic scale), the relative permittivity, and the electrostriction around a potassium ion in dimethylsulfoxide.

Table 1
The molar solvent electrostriction of some solvents [13]

Solvent	X (GPa^{-1})	$(\partial X/\partial P)_T$ (GPa^{-2})	$-\Delta V_{\mathrm{el}}$ (cm^3 mol^{-1})
Water	0.97	−2.27	2.91
Methanol	2.47	−17.49	5.99
1-Propanol	1.66	−3.94	14.41
1,2-Ethanediol	1.29	−1.74	9.46
Propylene carbonate	0.99	−5.56	7.12
4-Butyrolactone	0.80	−2.87	9.26
Acetonitrile	2.40	−25.24	4.93
Dimethyl sulfoxide	0.40	−2.78	4.98

Since only the ratio S_V/S_K is needed, the factor $vRTS_f$ is immaterial. The operative expression used to obtain the molar electrostriction of the solvent is thus [13]:

$$-\Delta V_{\mathrm{el}}(S) = \{2X/[X^2 - 2(\partial X/\partial P)_T]\}\kappa_T^* V^* \qquad (15)$$

This calculation requires the following data for the solvent S: V^*, κ_T^*, X, and $(\partial X/\partial P)_T$ with X according to Eq. (14). Hence, the first and second pressure derivatives of the permittivity ε^* and the density ρ^* of the solvent S are required ($\kappa_T^* = (\partial \ln\rho^*/\partial P)_T$). Unfortunately, the second derivatives have been reported for only a limited number of solvents that are used for electrolyte solutions. Some representative values of the quantities involved and the resulting molar solvent electrostriction values are shown in Table 1 [13].

6. Solvation numbers

The actual molar volume of an ion at infinite dilution, that is the volume ascribable to it out of the total volume of the solution, is its standard partial molar volume, $V^\infty(I,S)$. This can be equated with the intrinsic volume of the ion diminished by the electrostriction of the solvent in its solvation shell:

$$V^\infty(I,S) = V_{\mathrm{intr}}(I) + \Delta V_{\mathrm{el}}(I,S) \qquad (16)$$

remembering that $\Delta V_{\mathrm{el}}(I,S)$ is a negative quantity. According to Eq. (9) this volume can be equated with the volume of the solvated ion, $V_s(I,S)$. Now, that the total molar electrostriction near an ion, $\Delta V_{\mathrm{el}}(I,S)$, as well as the molar electrostriction of the solvent, $\Delta V_{\mathrm{el}}(S)$, are known, their ratio represents the solvation number of the ion (at infinite dilution) according to Eqs. (9) and (16):

$$n^\infty(I,S) = \Delta V_{\mathrm{el}}(I,S)/\Delta V_{\mathrm{el}}(S) \qquad (17)$$

Table 2
Solvation numbers from electrostriction for representative ions in some solvents [13]

Ion	Solvent				
	Water	Methanol	Propylene carbonate	Acetonitrile	Dimethylsulfoxide
Li^+	2.3	3.3	1.4	4.3	1.0
Na^+	2.9	3.7	0.6	4.1	0.0
K^+	0.8	2.5	0.0	3.3	
Ag^+	3.5		1.7	4.9	2.0
Mg^{2+}	10.5		4.5		5.6
Ca^{2+}	10.0		3.7		
Sr^{2+}	11.8		3.8		
Ba^{2+}	9.8		3.1		
Ni^{2+}	14.2				7.0
Cl^-	1.7	1.8	1.4	4.7	3.4
Br^-	1.2	1.5	0.8	4.5	3.0
I^-	0.5	2.2	1.4	3.7	2.4
ClO_4^-	0.5	1.5	0.7	3.1	1.0

Representative values of the solvation numbers obtained in this manner are shown in Table 2. They are comparable with values obtained from other approaches [9,10]. Some approaches, however, such as structural ones like neutron diffraction, count the total number of solvent molecules geometrically adjacent to an ion in the solution, not necessarily associated with it. On the whole, solvation numbers are defined operationally. The hydration numbers obtained by the present approach may therefore be smaller than those reported by authors using such approaches [10].

7. Calculated standard partial molar ionic volumes

Addition of the theoretically calculated negative electrostriction at infinite dilution, $\Delta V_{\mathrm{el}}(I,S)$, Eq. (6), to the intrinsic volume of the ion, $V_{\mathrm{intr}}(I)$ [2], should yield according to Eq. (16) a calculated value of standard partial molar volume of the ion. The resulting calculated $V^\infty(I,S)_{\mathrm{calc}}$ can be compared with the experimental $V^\infty(I,S)_{\mathrm{expt}}$ values (experimental in the sense that $V^\infty(\mathrm{salt},S)$ is from experimental density data and an extra-thermodynamic assumption is applied for the splitting). There are sufficient data for univalent ions in many solvents for this comparison [6], as shown in Fig. 4 for protic solvents and in Fig. 5 for dipolar aprotic solvents [14]. There are, however, insufficient data for testing this for multivalent ions.

In cases where there are more than one solvent in the solution, preferential solvation of the ions by one of the solvents

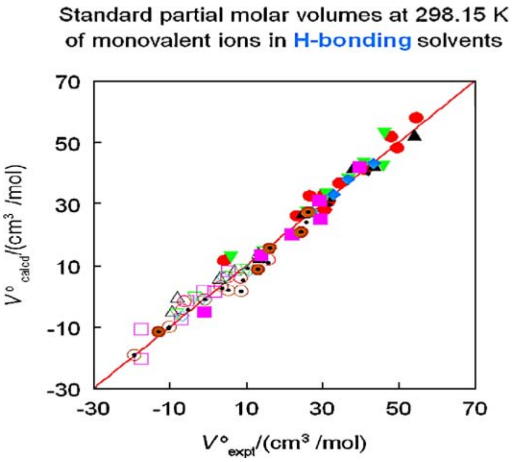

Fig. 4. Calculated vs. experimental standard partial molar volumes of univalent ions in protic solvents at 298.15 K. Filled symbols: anions, empty symbols: cations in water (●, ○), methanol (■, □), ethanol (dotted circles), formamide (▲, △), *N*-methylformamide (▼, ▽), and *N*-methylacetamide (♦, ◇). (Reprinted from Marcus [14] by permission from the publisher, Elsevier.)

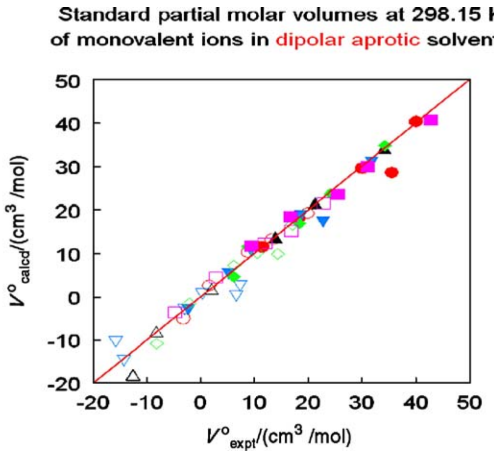

Fig. 5. Calculated vs. experimental standard partial molar volumes of univalent ions in dipolar aprotic solvents at 298.15 K. Filled symbols: anions, empty symbols: cations in propylene carbonate (●, ○), dimethylsulfoxide (■, □), nitromethane (▲, △), acetonitrile (▼, ▽), and *N*,*N*-dimethylformamide (◆, ◇). (From Marcus [14] by permission from the publisher, Elsevier.)

present is to be expected. The ion then interacts more strongly with molecules of this one solvent component, hence is surrounded by its molecules at a higher proportion than its bulk concentration. Nevertheless, if the solvents interact similarly with the ion, no preferential solvation takes place, and the surroundings of the ion reflect the bulk. This would be the case if the interactions are mainly of the charge–dipole type and the two solvents S_1 and S_2 have similar dipole moments or if donor–acceptor relationships prevail with similar donor and acceptor centers in the solvents. For the calculation of $V^\infty(I,S_1+S_2)_{calc}$ according to Eq. (16) when there is no preferential solvation it may be assumed that the solvent properties are prorated according to the bulk composition. In some cases of binary mixed solvents, such as propylene carbonate (PC)+acetonitrile (MeCN) and water (W)+methanol (MeOH), agreement of the calculated $V^\infty(I,S_1+S_2)_{calc}$ with the experimental $V^\infty(I,S_1+S_2)_{expt}$ could be noted, as shown in Figs. 6 and 7 [15].

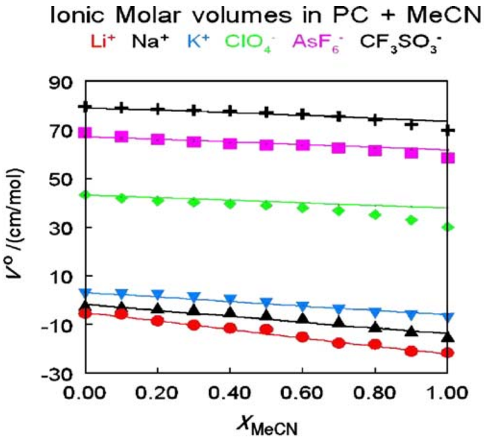

Fig. 6. Calculated ionic volumes (curves) and experimental values (points) in mixtures of propylene carbonate (PC) and acetonitrile (MeCN) plotted against the mole fraction of the latter. (From Marcus [15], by permission of the publisher, Springer.)

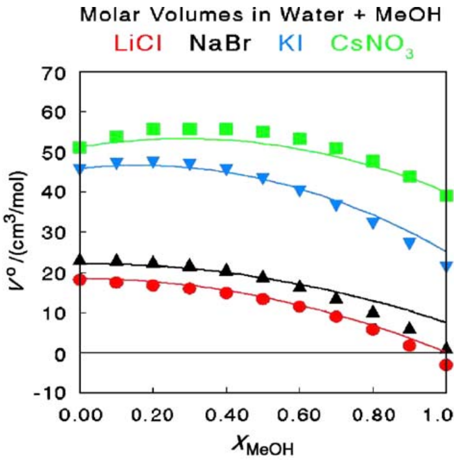

Fig. 7. Calculated volumes (curves) and experimental values (points) in mixtures of water (W) and methanol (MeOH) plotted against the mole fraction of the latter. (From Marcus [15], by permission of the publisher, Springer.)

In other cases, preferential solvation does occur, and the calculated $V^\infty(I,S_1+S_2)_{calc}$ values need to take this into account. If the preference is large, i.e., when selective solvation of an ion occurs, this ion is surrounded exclusively by the preferred solvent. In water (W)+dimethylsulfoxide (DMSO), there is evidence that the anions are selectively hydrated but the cations are solvated by both solvents, but preferentially by DMSO. Calculated values, $V^\infty(I,S_1+S_2)_{calc}$, on this basis [16] are compared with the experimental values in Fig. 8.

8. Ionic volumes at finite concentrations

The considerations presented here so far pertain to infinite dilution of the salt and its ions in the solution. In practice, however, solutions with finite concentrations are employed and

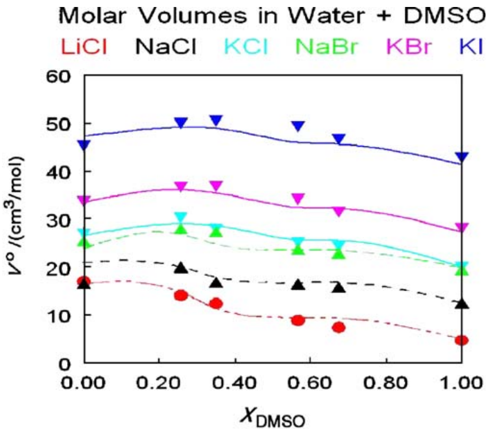

Fig. 8. Calculated volumes (curves) and experimental values (points) in mixtures of water (W) and dimethylsulfoxide (DMSO) plotted against the mole fraction of the latter. (From Marcus [16] by permission the publisher, Springer.)

the volumes occupied by the ions in them are of interest. The limiting expression (3) of the apparent molar volume of a salt is extended at higher concentrations c with a linear term:

$$^{\phi}V\,(\text{salt}) = {}^{\phi}V^{\infty}\,(\text{salt}) + S_{\text{V}}^{\text{DH}}c^{1/2} + b_{\text{V}}c + \cdots \tag{18}$$

Such an empirical extension is able to describe the densities of the salt solutions (obtained from inversion of Eq. (2)) up to fairly high concentrations, as found long ago by Redlich [17] for aqueous solutions. There are currently no generally accepted theories for the estimation of the coefficient b_{V} that necessarily remains as an empirical fitting parameter. There are indications that b_{V} is additive in terms of the ions constituting the salt [17].

At higher salt concentrations, and in particular for salts consisting of multivalent ions and/or in solvents of relatively low permittivity, ion pairing may set in, entailing interesting volume changes. Consider two ions of opposite charges coming together to form an ion pair as shown schematically in Fig. 9.

An ion pair has a lower net charge than the partner ions and therefore produces less electrostriction than the individual ions do. The difference

$$\Delta V_{\text{ip}} = V_{\text{ip}}^{\infty} - (V_{+}^{\infty} + V_{-}^{\infty}) > 0 \tag{19}$$

is thus positive. Values of ΔV_{ip} are obtainable from the measured pressure derivative of the association constant $K_{\text{ip}(c)}$ expressed on the molar scale (dm^3 mol^{-1}):

$$\Delta V_{\text{ip}} = -RT[(\partial \ln K_{\text{ip}(c)}/\partial P)_T - \kappa_T^*] \tag{20}$$

The lowered electrostriction is accompanied by the release of some solvent molecules from the solvation shells to the bulk.

The molar solvent electrostriction, $-\Delta V_{\text{el}}(S)$, being known, can be used to obtain [13] the number of solvent molecules released from electrostriction on ion pairing, Δn_{ip}, from the ratio:

$$\Delta n_{\text{ip}} = \Delta V_{\text{ip}}/[-\Delta V_{\text{el}}(S)] \tag{21}$$

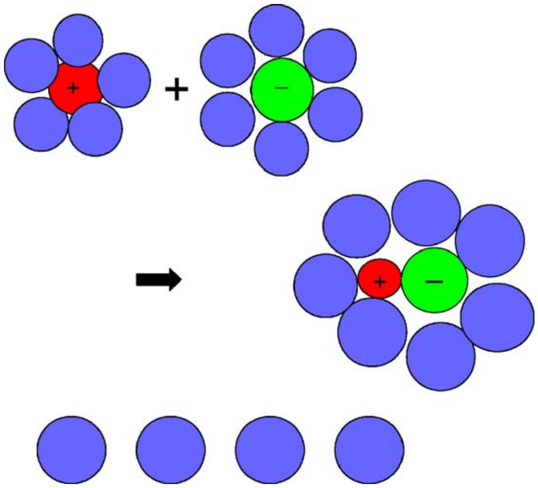

Fig. 9. Schematic representation of the formation of an ion pair and concomitant release of solvent molecules from the solvation shells to the bulk solvent.

Table 3
Volume change on ion pairing and the number of solvent molecules released [13]

Solvent	Salt	ΔV_{ip} (cm^3 mol^{-1})	Δn_{ip} from ΔV_{ip}	Δn_{ip} from ΔS_{ip}	$n_{+}+n_{-}$
Water	LiF	7.9	2.5		5.7
	$NaB(OH)_4$	8.4	2.9		11.3
	KSO_4^-	5.9	2.1		11.1
	$RbNO_3$	6.0	1.9		2.1
	$MgSO_4$	7.4	2.3	4.9	20.0
	$LaSO_4^+$	21	6.8	6.3	31.0
Methanol	LiBr	17	2.8		4.8
2-Propanol	NaI	15	0.4		
Acetone	NaI	25	1.0	1.9	4.9
Benzene	$Bu_4NPicrate$	62	2.8		

Representative values of Δn_{ip} are shown in Table 3. Most of the available data pertain to aqueous solutions, for which the ΔV_{ip} have been measured, whereas for several non-aqueous solvents for which ΔV_{ip} is known $\Delta V_{\text{el}}(S)$ is not and vice versa.

The number of released solvent molecules, Δn_{ip}, is necessarily smaller than the sum of the solvation numbers of the individual ions, $n_{+}+n_{-}$, as is seen in Table 3 to be the case for some representative ion pairs and solvents. A further comparison can be made between Δn_{ip} obtained from electrostriction with a similar number of solvent molecules released on ion pair formation from being translationally immobilized adjacent to the separate ions, obtained from the standard molar entropy change on ion pairing [18], also shown in Table 3. Measuring different properties of the solution on ion pairing, these numbers need not be the same, since whether the pairs are present as solvent-separated or -shared ion pairs or contact ion pairs may affect differently the numbers obtained from the volume and entropy considerations.

9. Conclusions

The interactions of the constituent ions of electrolytes in solutions with the solvent and other ions are studied in terms of their volumetric properties. At infinite dilution the interactions are with the solvent alone as measured by the standard partial molar volume. It is necessary, however, to split the V^{∞}(salt) obtained from density measurements into the additive ionic contributions, V^{∞}(ion). This requires an extra-thermodynamic assumption, such as the tetraphenylphosphonium tetraphenylborate (TPTB) one, the salt having nearly identical cationic and anionic volumes. For small ions the V^{∞}(ion) depend cardinally on the electrostriction of the solvent S near the ion I, $\Delta V_{\text{el}}(I,S) < 0$, that can be calculated from a continuum model of the solvent with an iterative shell-by-shell computation. The molar solvent electrostriction $\Delta V_{\text{el}}(S) < 0$, is also calculable. The solvation number of the ion I in S at infinite dilution is then given by $n^{\infty}(I,S) = \Delta V_{\text{el}}(I,S)/\Delta V_{\text{el}}(S)$. The calculated values of

$V^{\infty}(I,S)_{\mathrm{calc}} = V_{\mathrm{intr}}(I) + \Delta V_{\mathrm{el}}(I,S)$, where $V_{\mathrm{intr}}(I)$ is the solvent-independent intrinsic volume of the ion, are compared with the experimental values. Good agreement is obtained for many univalent ions in both single solvents and in some binary solvent mixtures, where no appreciable preferential solvation takes place. Under certain circumstances of high ionic charge and/or low solvent permittivity ion pairing sets in. The molar volume of the ion pair is larger then the sum of the volumes of the ion partners because of the lower net charge on the pair. The difference $\Delta V_{\mathrm{ip}} = V^{\infty}{}_{\mathrm{ip}} - [V^{\infty}{}_{+} + V^{\infty}{}_{-}] > 0$ is obtained experimentally from the pressure derivative of the association constant. The number of solvent molecules released to the bulk on ion pairing by the diminution of the electrostriction can be estimated as the ratio $\Delta n_{\mathrm{ip}} = \Delta V_{\mathrm{ip}} / \Delta V_{\mathrm{el}}(S)$.

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