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Standard Partial Molar Volumes of Electrolytes and Ions in Nonaqueous Solvents

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1. Introduction

The standard partial molar volumes, $V°$, occupied by electrolytes and their constituent ions at infinite dilution in nonaqueous solutions at (or close to) 298.15 K are the subject of this review. A critical compilation of the reported data is made, and a selection of recommended values and their interpretation are presented. A similar service was performed

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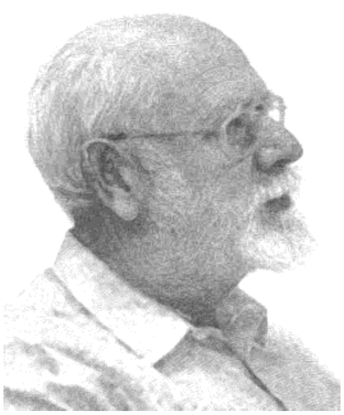
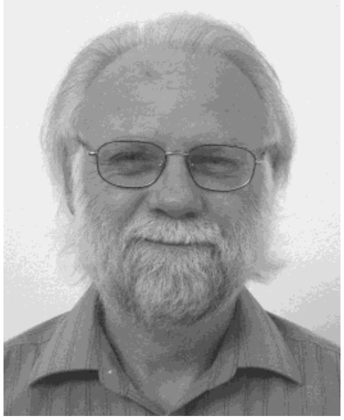


Yizhak Marcus was born in Germany and, having immigrated to Israel as a child, obtained his M.Sc. Degree in 1952 and Ph.D. degree in 1956 in chemistry from the Hebrew University of Jerusalem. He was professor of inorganic and analytical chemistry there from 1965 to his retirement (to emeritus status) in 1999, but he continues to be active. For a dozen years, Professor Marcus was with the Israeli Atomic Energy Commission laboratories and a visiting scientist and professor in various countries: Australia, England, Germany, Japan, Turkey, and USA. His research interests concern solution chemistry, and he has published in this and neighboring fields 6 books and over 250 papers in refereed journals.



Glenn Hefter received his B.Sc. (in 1969) and Ph.D. (in 1973) degrees from the University of Melbourne. He worked as a high school teacher and then at Stirling University in Scotland, the University of Malaya in Malaysia, and the Marine Science Laboratories in Australia before joining Murdoch University in 1982, where he is currently Associate Professor in Chemistry. His main research interests are in solution chemistry, including the thermodynamics of ion solvation and the nature of ion pairs in aqueous, nonaqueous, and mixed solvents, as well as chemical speciation in complex hydrometallurgical and environmental solutions. He has had a long-standing involvement with the IUPAC–NIST *Solubility Data Series* and recently coedited and contributed to a book: *The Experimental Determination of Solubilities* (2003).

by Millero[1] over 30 years ago for electrolytes and ions in aqueous solutions, which included a table of “conventional” $V°$ values of ions, based on the arbitrary convention that $V°(H^+,aq) \equiv 0$. Conway[2] discussed for aqueous solutions the change from “conventional” volumes to “absolute” values, which represent more realistically the actual $V°$ values and can therefore be interpreted in terms of ion−solvent interactions. The present authors discussed such issues with regard to nonaqueous solutions,[3] a discussion that is augmented and supplemented here.

The $V°$ of an electrolyte is the limiting value of its partial molar volume as the concentration of the electrolyte, c, approaches infinite dilution in the solvent. By analogy with other standard partial thermodynamic quantities, $V°$ is also the limiting value of the corresponding apparent molar volume, ${}^{\phi}V$. The latter is the volume, V, of a solution containing n_2 moles of solute minus the volume attributed to the n_1 moles of solvent present, considered as pure solvent of molar volume V_1*, per mole of solute:

$$ {}^{\phi}V = (V - n_1V_1^*)/n_2 \qquad (1)$$

(Henceforth, the subscripts 1 and 2 designating solvent and solute are not employed unless necessary.) Apparent molar volumes are commonly derived from solution densities or, more accurately but less frequently, from dilatometry. The methods for the determination of ${}^{\phi}V$ are briefly reviewed in section 2.

The apparent molar volume of a solute (in $cm^3\ mol^{-1}$) depends on the density of the solution at solute concentration, c in mol dm^{-3} (molarity, M), or molality, m [mol (kg solvent)$^{-1}$] as

$$ {}^{\phi}V = (M/\rho^*) - 1000(\rho - \rho^*)/\rho^* c \qquad (2a)$$

$$ {}^{\phi}V = (M/\rho) - 1000(\rho - \rho^*)/\rho\rho^* m \qquad (2b)$$

where M is the molar mass of the electrolyte solute (in g mol^{-1}) and ρ and ρ^* are respectively the densities of the solution and the pure solvent (in g cm^{-3}). Note that the values of ${}^{\phi}V$ are independent of the concentration *scale* and that the designation “molar volume” (sometimes referred to as “molal volume”) does not refer to the concentration scale used for the measurements. Both “molar” and “molal” are, in this context, merely alternative adjectives that describe volumes expressed on a per mole basis.

The ${}^{\phi}V$ values are in a sense artificial quantities, in that they invoke the pure solvent, with molar volume V^*, rather than the actual volume of the solvent in the solution. They are therefore not suitable for interpretation in terms of molecular-level interactions. The partial molar volume V_2,

$$ V_2 = {}^{\phi}V + m_2(\partial\, {}^{\phi}V/\partial m_2)_{T,P} \qquad (3)$$

does not have this drawback. At infinite dilution the partial molar volume, $V°$ (the subscript 2 is not needed), is called the *standard partial molar volume* and is exactly equal to the apparent molar volume:

$$ V° = {}^{\phi}V^{\infty} = \lim_{m \text{ or } c \to 0} {}^{\phi}V \qquad (4)$$

The extrapolation of experimental ${}^{\phi}V$ values to infinite dilution is further discussed in section 2.4. The value of $V°$ defines the volume of the solution ascribable to the solute itself. It is a reflection of ion−solvent interactions alone. It is this quantity that is the subject of this review.

1.1. Historical Background

A detailed review of the historical development of the concept of apparent and partial molar volumes of electrolytes and ions in solution was presented by Millero in 1971.[1] Most of the earlier work concerned aqueous solutions, with very few studies in nonaqueous or even mixed solvents. Since then, however, the publications in this area have proliferated, which is one of the justifications for the present review.

Possibly the earliest study of electrolyte volumes in nonaqueous solvents was that of Carrara and Levi,[4] who reported $^{\phi}V$ values of electrolytes in methanol, ethanol, and acetone. At that time, and for several years subsequently, the usual solution composition quantity reported was the dilution, that is, "V" (V/n_2 in current notation), the number of liters (L, dm^3) per mole of solute, equaling $1/c$, where c is the solute concentration in M ($\equiv$ mol dm^{-3}, molarity). The data of Carrara and Levi covered a dilution range of ~0.6−90 M^{-1}. The electrolytes studied included HCl, CCl_3COOH, LiCl, NaI, KI, KOH, $CuCl_2$, $CuSO_4$, and CdI_2, but not all in each of the three solvents or over exactly the same dilution range. In 1907 Walden[5] reported $^{\phi}V$ values for KI, Et_4NI, and Pr_4NI in methanol, ethanol, nitromethane, acetonitrile, propionitrile, ethylene glycol, and acetone, albeit at not very high dilutions, "V" $\leq$ 50. The incomplete dissociation of the electrolytes in these solvents was recognized in these two studies.[4,5]

Relatively few measurements of $^{\phi}V$ of electrolytes in nonaqueous or mixed solvents were reported over the next 50 years or so. The papers that did appear dealt mainly with salts in methanol[6−13] but also in ethylene glycol,[10] ethylenediamine,[14] and aqueous ethanol.[15−17] Most of the data reported in those papers have been remeasured subsequently with greater accuracy, but they are mentioned in the appropriate tables in section 5. The state of research on "apparent volumes in nonaqueous solutions" up to 1940 was reviewed in a not-generally-available paper by Filipova.[18] That review showed graphically the linear dependence of $^{\phi}V$ on $c^{1/2}$ in dilute solutions of the salts in the solvents studied up until then. In the 1960s there was a resurgence of interest in molar volumes in nonaqueous solvents. Some 40 years on this shows no sign of abating, as for studies of other thermodynamic quantities (see for instance Figure 1 of ref 19). Papers on the interpretation and modeling of these data also appear regularly, attesting to the ongoing importance of molar volumes in solution chemistry, kinetics, and so on.

The early paper by Redlich and Rosenfeld[7] merits particular recognition in this connection. These authors showed that extrapolation of $^{\phi}V$ to infinite dilution, yielding $V°$, should be made at high dilutions and in accordance with the theoretical expression they derived from the Debye−Hückel theory,

$$V° = \lim_{c\to 0}[^{\phi}V - S_V{}^{DH}c^{1/2}] = \lim_{c\to 0}[^{\phi}V - w^{3/2}kc^{1/2}] \quad (5)$$

where w is a valency factor and k is the Debye−Hückel limiting law slope for volumes (obtained by taking the derivative of the Debye−Hückel equation for activity coefficients with respect to pressure). Specifically, Redlich and Rosenfeld obtained published density data for $CaCl_2$ in MeOH at 12.9 °C, estimated the coefficient k for methanol at this temperature as 16.9 $cm^3\ dm^{3/2}\ mol^{-3/2}$, and calculated a value for $V° \approx -55\ cm^3\ mol^{-1}$ that is similar to current estimates. In 1940 Redlich[20] again stressed the need to use the limiting law slope k for extrapolation of the $^{\phi}V$ values to infinite dilution rather than the empirical Masson equation and illustrated this by means of the data of Vosburg et al.[8] for LiCl, NaCl, NaI, and KI in MeOH. The choice of solvent was based on the expectation that dissolved salts would be dissociated in dilute solutions and because MeOH was the only solvent (apart from water) for which the pressure derivative of the relative permittivity $(\partial\epsilon/\partial P)_T$, required for the calculation of k according to Debye−Hückel theory, was available at the time.

Notwithstanding the admonitions of Redlich on the need to use dilute solution measurements and the limiting law slope for the extrapolation of $^{\phi}V$ to infinite dilution to yield $V°$, most authors at the time (and indeed, since) used instead the Masson expression. This dependence had been proposed originally by Masson[21] in 1929 on a purely empirical basis for electrolytes in aqueous solutions:

$$^{\phi}V = {}^{\phi}V^{\infty} + S_V{}^{M}c^{1/2} \quad (6)$$

The slope $S_V{}^{M}$, specific for each electrolyte, substitutes the theoretical slope $w^{3/2}k$ of eq 5. The Masson expression (eq 6) has been applied by many authors since, in both aqueous and nonaqueous solutions (mainly due to lack of the required value of k for the latter), at concentrations generally ranging from 0.1 to 1.0 M and often higher.

The review by Redlich and Meyer of 1964[22] contained only a very short section on electrolyte volumes in nonaqueous solvents. However, Millero[1] included virtually all the extant data for nonaqueous solutions available in his 1971 review. Since then a large body of information has accumulated, but no systematic compilation or assessment of the data has appeared apart from an unpublished thesis.[23] A review by Kolker and Safonova[24] listed $V°$(electrolyte) and $V°$(ion) values in tables for several solvents, but it was not comprehensive, nor were the data critically assessed. The same is true of the brief review in the book by Popovych and Tomkins.[25]

It has long been realized that a proper interpretation of the $V°$ values of electrolytes requires their splitting into the individual ionic contributions, $V°$(ion). This is because at infinite dilution each ion is surrounded by solvent molecules only, interacting with them in a manner that directly affects the partial molar volume. A detailed review of the methods that have been commonly employed subsequent to the Millero review[1] to obtain the individual ionic contributions to $V°$(electrolyte) in nonaqueous solvents is presented in section 3.

Naturally, the interpretation of $V°$(ion) values was applied at first to aqueous solutions, with various empirical[26] and semiempirical expressions being proposed. The latter, due to Hepler[27] and to Mukerjee,[28] were based on the assumption that $V°$ is the sum of a positive term expressing the intrinsic volume of the ion and a negative term reflecting the electrostriction of the solvent surrounding the ion arising from the pressure exerted by its high electrical field. Developments in the interpretation of the

$V°$(ion) values since the review by Millero[1] are discussed in section 6.

1.2. Scope and Coverage

This review aims to compile and critically assess the data available in the open literature for the standard partial molar volumes of electrolytes, $V°$, and their ionic constituents, $V°$(ion), in nonaqueous solvents at 298.15 K. The literature has been covered to near the end of 2003.

While efforts have been made to be comprehensive, some publications, mostly in the Russian literature, that have been cited in other publications, could not be obtained within the time frame of this review. In such (very few) cases the $V°$ values have been taken from the secondary sources. All other $V°$ values were either taken as reported from the original papers or derived by the present reviewers from reported apparent molar volumes, ${}^{\phi}V$, or, as a last resort, calculated by the reviewers from reported density data.

The solvent systems for which data are compiled have been restricted to the common molecular substances (other than water and heavy water) that are liquid at near-ambient temperatures and that are practical solvents for electrolytes. Very few data exist for systems other than those presented here. Solvents for which data were insufficient to justify compilation into individual tables are recorded for convenience in Table 38. Mixed solvents, both aqueous and nonaqueous, have been excluded. This is a sensible limitation of the present review, but it is also appropriate because relatively few systematic studies have been made of such systems and even fewer have been duplicated, making critical assessment of the data difficult.

As in previous publications[19,29] the focus of the present review has been on electrolytes composed of simple (monatomic and symmetrical polyatomic) ions although salts containing ions such as triflate (trifluoromethanesulfonate, $CF_3SO_3^-$) and acetate (ethanoate, $CH_3CO_2^-$), which are often utilized in nonaqueous studies because of their favorable solubilities, are also included whenever available.

The overwhelming majority of the volume data available for electrolytes refer to 1:1 salts. Some results have also been reported for 2:1 (MX_2) and, to a lesser extent, 3:1 (MX_3) electrolytes, but apparently none have been reported for salts containing multivalent anions. Data for the higher valent salts have rarely been duplicated, and because of the difficulties in obtaining $V°$ values that are free from ion pairing effects, which become acute for salts containing multivalent ions and in solvents of lower permittivity, such results need to be considered with great caution. Indeed, very few studies on salts with multivalent ions have been done at sufficiently low concentrations, with sufficient accuracy, with a sufficient range of counterions (to check for additivity), and with sufficiently sophisticated data processing[30] to ensure that the $V°$ values really refer to the fully dissociated electrolyte solution. Some rare examples where this has been done are mentioned in the comments on the tabulated data in section 5.

Only data at 298.15 K and atmospheric pressure have been included except for some data for solvents such as ethylene carbonate, tetramethylene sulfone, and *N*-methylacetamide, that have melting points above this temperature. The closely related subjects of electrolyte partial molar expansivities and compressibilities have also been excluded from the present review, again since hardly any systematic and independently confirmed data are available.

Understanding of the dependence of $V°$(electrolyte) values on the properties of their constituent ions and of the solvents they are dissolved in depends on the ion–solvent interactions that are manifested by the standard partial molar volumes of the ions, $V°$(ion). Hence, it is mandatory to obtain the latter quantities, for which extrathermodynamic assumptions ("extra-" in the sense of "outside of") are required. Commonly employed assumptions are discussed in section 3. The "least objectionable" approaches, for which the required data were available, have been used to obtain ionic volumes. These $V°$(ion) values are tabulated in section 5 and interpreted in section 6.

1.3. Applications of Molar Volumes of Electrolytes and Ions

The influence of solute volumes on a wide range of solution properties has long been recognized. A broad-ranging discussion of many of these effects is given in the book by McGowan and Mellors.[31] Although this work primarily focused on aqueous solutions, consideration was also given to the effects of electrolyte and/or ionic volumes on various phenomena in nonaqueous solvents such as solubilities, ion pairing, partition chromatography, and so on.[31]

In chemical engineering terms, solution densities are required for mass balance and mass transfer calculations for process control and optimization. With the increasing use of nonaqueous solvents for industrial processes involving (mostly organic) ionic species, knowledge of the molar volumes of electrolytes in such solvents will become increasingly important. In practice, apparent molar volumes of electrolytes are useful quantities in any situation that requires solution density to be known, since the latter can be calculated by combination of eqs 2 and 5 or 6:

$$\rho = \rho^*\{1 + [M/\rho^* - (V° + S_V c^{1/2})]c/1000\} \tag{2c}$$

where S_V is either the theoretically sound S_V^{DH} or an assumed S_V^M (presuming it has already been determined experimentally). This expression is valid in the concentration range where the square root dependence of ${}^{\phi}V$ on c holds, but it also often works surprisingly well even at high concentrations. As an approximation for dilute solutions, the $S_V c^{1/2}$ term can be neglected, simplifying eq 2c further to $\rho = \rho^*[1 + (M/\rho^* - V°)c/1000]$, which underlines the importance of knowing $V°$.

Densities of solutions containing complex mixtures of electrolytes can also be estimated with reasonable accuracy by applying Young's rule.[32] This rule, which in essence assumes ionic-strength-based pro-rata additivity of component properties in aqueous solutions, has been used by Millero[33] to calculate the density of seawater as a function of composition. It has also been shown by a number of workers[34,35] to work up to high concentrations in many salt solutions, even when a limited amount of ion pairing is present. No tests of Young's rule for volumes in nonaqueous solvents have been made to the best of the present reviewers' knowledge, but there is no reason to suppose that it will not apply, although perhaps not to the same level of accuracy.

Ionic volumes are used to interpret the effects of pressure on both equilibrium and rate constants.[36,37] In equilibrium studies, most attention has been directed toward evaluating volumes of complex species such as ion pairs. Measurement of the effect of pressure on the equilibrium constant under isothermal conditions, $(\partial \ln K°/\partial P)_T$, is a direct measure of the change in volume between reactants and products, $\Delta_r V°$. If the equilibrium involves ion pair formation, then $V_{ip}°$ can be obtained directly from the $\Delta_r V°$ and $V°$(ion) values (cf. eq 19 below). In kinetic studies, the measurement of pressure effects on rate constants is a powerful tool for elucidating reaction mechanisms for both organic and inorganic reactions. The effect of pressure at constant temperature on the rate constant of a reaction, $(\partial \ln k/\partial P)_T$, is a direct measure of the activation volume, $\Delta V^{\ddagger}$, the difference in volume between the transition state and the reactants. Knowledge of $\Delta V^{\ddagger}$ and $V°$(ion) values leads directly to the volume of the transition state. For both equilibrium and kinetic studies, it is often imperative to have the "absolute" ionic volumes, since the processes under consideration may not be charge symmetric. Numerous examples of measurements of volume effects on equilibria and kinetics in organic and inorganic chemistry in nonaqueous solvents are given in standard works.[36,37]

One application of electrolyte volumes in nonaqueous solvents that has received ongoing attention has been in the area of high energy batteries. Here the focus has been on salts such as $LiAsF_6$ in the neat and mixed solvent systems that have been used for lithium batteries. Since energy densities per unit volume may be just as significant as those per unit mass (for example, in heart pacemaker batteries), detailed knowledge of electrolyte volumes (solution densities) under practical conditions is important. Furthermore, as the charge/discharge cycles usually involve insertion or removal of solvated ions within the electrode materials, the volumes of such ions may exert considerable influence on battery performance. The first such detailed study in this area appears to be that of Atkins et al.[38] These authors measured ${}^{\phi}V$ for a number of salts at a single concentration (0.05 M) in a variety of mixed solvents containing propylene carbonate and were able to correlate these values with particular cell performance data.[39] More recent papers by others have focused on newer solvent mixtures.[40−42]

2. Methods

2.1. General Comments

Standard partial molar volumes of electrolytes in solution, $V°$, cannot be measured directly, since they refer to the electrolyte at zero concentration. Such quantities are usually determined by the extrapolation to infinite dilution of apparent molar volumes, ${}^{\phi}V$, measured at finite electrolyte concentrations, using an appropriate theoretical or (less desirably) empirical expression, as discussed in section 2.4 below. There are two broad ways of determining ${}^{\phi}V$ for electrolytes in solution: by measuring densities of solutions relative to those of the pure solvent and applying eq 2, and by measuring directly the volume change of solutions with changing concentration (dilatometry). Before describing these approaches in detail, there are two general comments that pertain to all the experimental methods that warrant comment.

Temperature control is critical for the reliable determination of ${}^{\phi}V$, and hence $V°$, assuming adequate electrolyte and solvent purity. This is not because either ${}^{\phi}V$ or $V°$ is particularly sensitive to temperature but rather because the two experimental quantities from which they are derived by difference, density and volume, are. For example, the isobaric expansivity of water, α_P, has a value of $\sim 0.25 \times 10^{-3}$ K^{-1} under ambient conditions.[43] Thus, for a precision of ~2 ppm in density (or volume) a temperature control of *at least* ±0.01 K is required. For nonaqueous solvents, which often have much higher expansivities, even this is insufficient. For example, measurements with MeOH ($\alpha_P \sim 1.2 \times 10^{-3}$ K^{-1})[43] would require ±0.001 K temperature control for 2 ppm precision.

The second general problem that besets all measurements of ${}^{\phi}V$, albeit in somewhat different ways according to the technique, is the presence of microbubbles. These must be scrupulously avoided, as they can quickly destroy the accuracy of the data. While most solvents are easily degassed, solutions are not. Sonication may be helpful for the latter, as is careful experimental technique, such as storing solutions before measurement at or slightly above the measurement temperature.

2.2. Density Determinations

2.2.1. Pycnometry

The measurement of density by pycnometry is a mature discipline. The apparatus required is simple and inexpensive: some glassware, a good analytical balance, and appropriate temperature control; it is therefore available to most laboratories. Pycnometry involves determining the mass of a liquid or solution occupying a known volume. The volume is invariably obtained by measuring the mass of pure water (and/or mercury) held by the pycnometer at a given temperature and pressure, rather than from geometric calculation. A variety of designs are available, but only some are useful for high precision work.[44,45] Pycnometer capacities are usually around 30 mL, which represents a convenient balance of cost, ease of measurement, and accuracy.

To achieve anything like the potential precision of pycnometry, it is essential that many precautions be taken and that scrupulous procedures be followed. Reliable mass measurements are not as straightforward as they seem. For example, the adsorption of moisture and induced electrical charges (a particular but mostly overlooked problem for modern electronic balances) on the external surfaces of the glass pycnometer may introduce significant errors. Filling the pycnometer reproducibly may be problematic, and for high precision work with volatile solvents, allowance must be made for evaporation, including that into the cap space. The use of uncapped pycnometers cannot be justified.

If sufficient care is taken, pycnometry is capable of a precision of ±5 ppm (i.e., $\pm 5\ \mu g\ g^{-1}$ in terms of weighing) or better. However, it is difficult to achieve such precision in the study of electrolyte solutions in nonaqueous solvents, and it has been noted that a general problem with pycnometry is that its accuracy is much less than its precision.[44,45] Researchers regularly make strong claims for the precision of their pycnometric data, and reasonable precision in ${}^{\phi}V$ can undoubtedly be obtained at relatively high electrolyte concentrations. However, conventional pycnometry is less satisfactory for measuring the small density *differences* (between solvent and solution) at low solute concentrations that are necessary for the determination of reliable $V°$ values (section 2.4). Consequently, the values of $V°$ obtained from pycnometry often do not compare well with those obtained by more reliable techniques (section 5). Other drawbacks of pycnometry for the measurement of density are that for results of high accuracy it is particularly time-consuming, is difficult to automate, and requires relatively large samples.

Given the ready availability nowadays of better and faster methods of density measurement, as discussed below, the determination of apparent molar volumes by pycnometry should only be considered if no other choice is available. Intending investigators are referred to the literature[44,45] for details of the procedures required for obtaining reliable densities from pycnometry. Values of $V°$ obtained from pycnometry are designated with "pyc" in the footnotes of the tables in section 5.

2.2.2. Buoyancy and Magnetic Floats

The buoyancy or hydrostatic method is based on Archimedes' principle that the upward (buoyant) force on a body, known as a buoy, float, or sinker, immersed in a fluid is exactly equal to the mass of the displaced fluid. There are various types of hydrostatic balance, and a number of excellent summaries of their construction and operation have appeared.[44−46] Many of the published designs, particularly those of more recent years,[46] have been developed to measure densities under extreme conditions and do not have the sensitivity desirable for precise determination of the apparent molar volumes of electrolytes in typical nonaqueous solvents under near ambient conditions. Nevertheless, some of these designs can be adapted for such measurements.

At its simplest, a hydrostatic balance consists of a suitable glass or metal sinker suspended by a thin metal (usually Pt) wire suspended from underneath an analytical balance. The sinker is immersed into the sample liquid or solution and its apparent mass recorded. The sample density is obtained from the relationship

$$\rho = (m_s{}^* - m_s)/V_s \qquad (7)$$

where $m_s{}^*$ is the true (vacuum) mass of the sinker and m_s is its apparent mass when immersed in the sample. The volume of the sinker, V_s, is best measured by weighing in pure water, and $m_s{}^*$ is best measured by weighing in air with appropriate correction for buoyancy in air. Other corrections such as surface tension effects on the wire must also be made for highly accurate work. Researchers should consult standard works for further details.[44−46]

The attainable precision depends on many factors but is of the order of a few parts per million. It is possible to minimize many of the sources of error in the buoyancy method by using a differential buoyancy balance[44] in which the solution is compared directly against the solvent. A sensitivity of <1 ppm and a precision of 3 ppm have been claimed for one such balance used for apparent molar volume determinations in aqueous solutions, with sufficient attention to detail.[47] Values of $V°$ obtained from buoyancy measurements are designated with "buo" in the footnotes of the tables in section 5.

Magnetic floats are a variant of hydrostatic methods that are capable of very high precision.[44,45] They are most suitable for measurements over small ranges of densities and, as such, are particularly apt for the determination of ${}^{\phi}V$. This method involves the use of a buoy, typically consisting of a permanent magnet encased in glass, the density of which is less than that of the liquid it is to measure. The float is placed in the thermostated liquid sample and is then submersed by application of a magnetic force, produced by passing a current through a solenoid appropriately located outside the sample cell. The solenoid current and float combination is calibrated against liquids of known density.

Reproducibilities of ~0.1 ppm have been reported by many workers, but of course there are many precautions that must be followed. Particular care must be taken to ensure that the float surface is free from bubbles. A number of designs of magnetic floats have been published;[45,46] that of Millero[48] has been extensively used for the determination of ${}^{\phi}V$ of electrolytes in both aqueous and nonaqueous solutions. Researchers should consult the literature for further details. Values of $V°$ obtained from measurements employing magnetic floats are designated with "mgf" in the footnotes of the tables in section 5.

2.2.3. Vibrating Tube Densimeters

The vibrating tube densimeter is part of a larger class of density measuring devices that have been referred to as acoustic resonance densimeters, which includes wires, plates, and so forth.[45,49] In essence, a hollow U- or V-shaped tube, typically made from glass or a stiff metal with an internal diameter of 1−2 mm and clamped at its ends, is made to vibrate by the application of an electromagnetic force. The resonance period, which is typically a few milliseconds, is detected electrically or optically. Very high precision is achieved by averaging the period over several thousand vibrations.

As a rather complex electromechanical system, the vibrating tube is difficult to describe in exact terms.[49] Nevertheless, consistent with theory, it can be shown that there is a relationship between the period of vibration of the tube τ and its mass. The latter is in turn dependent on the mass (and, hence, the density, since the volume of the tube is constant at constant T and P) of the fluid contained within the tube. This produces a working equation of the form

$$\rho = K_1 + K_2\tau^2 \tag{8}$$

where K_1 and K_2 are constants that can be calculated approximately from first principles but are better determined empirically by measurements on substances with accurately known densities. Pure water and dry nitrogen are generally used for this purpose. For measurements with denser solutions, D_2O or NaCl(aq) can be used. The densities of most organic liquids are not known with sufficient accuracy to be suitable for this purpose. The vibrating tube densimeter (vtd) is particularly suited for accurate measurement of density differences and, hence, ${}^{\phi}V$ (cf. eq 2), since, from eq 8,

$$\rho_A - \rho_B = K_2({\tau_A}^2 - {\tau_B}^2) \tag{9}$$

where the subscripts A and B refer to two different samples, for example, a solvent and a solution.

It is fair to say that the vtd has revolutionized the measurement of densities. Under favorable circumstances a precision of a few parts per million can be obtained with an accuracy of probably a few tens of parts per million. Commercial apparatus covering wide temperature and pressure ranges is available from several manufacturers. Purpose-built vtd designs are available in the literature that extend measurements to a variety of extreme temperatures and pressures.[49] Measurements with a vtd are rapid, ranging from ~1 min for a flow system to ~10 min for a static system (most of which is related to temperature stabilization). Only small volumes are required: from about 1 mL for static systems to ~10 mL for flowing systems.

The major requirements to realize the inherent precision of a vtd are the absence of even the smallest of microbubbles and rigorous thermostating (preferably better than ±0.01 K (section 2.1)). Because of its electromechanical nature, the readings obtained with a vtd are prone to drift with time. Fortunately, it is only the τ values that vary whereas the densimeter constant K_2 is particularly stable. Thus, all that is required is that the period of an appropriate standard be continually checked; in measurements of ${}^{\phi}V$, the solvent is very convenient for this purpose. Due to the relatively high area/volume ratio of a vtd, scrupulous cleaning of the inner walls of the tube is important; surface adsorption may lower both the precision and accuracy achievable for some solutions.[50] In principle, changes in viscosity can affect the accuracy of the results (by altering the *amplitude* of the tube's vibration, which in turn can affect the *period* of vibration used in the measurement of density),[49] but in most solvents of interest this effect will be negligible. Values of $V°$ obtained from vibrating tube density measurements are designated with "vtd" in the footnotes of the tables in section 5.

2.3. Dilatometry

Dilatometry involves the direct measurement of the volume change that occurs when a solution is diluted into its solvent.[44,45,51−55] As such, it is probably the most sensitive means of measuring apparent molar volumes. For example, Bottomley et al.[52] were able to measure volume changes that corresponded to density changes of *less* than ±0.1 ppm. However, purpose-built apparatus is required, and very careful attention has to be paid to experimental design and to thermostating.[45,52] For the highest precision, quite large volumes of solvent (~500 mL) are required and, depending on the design, there may be other requirements such as nonreactivity of the solvent and solutions with mercury. Nevertheless, dilatometers are inexpensive, although the thermostating may not be. Bottomley et al.[52] have suggested employment of a dummy dilatometer to minimize thermostating errors.

In dilatometry, a small volume v' of a concentrated electrolyte solution is added to a much larger volume v (usually $>100v'$) of solvent to produce a solution of volume v''. The expansion/contraction of the solution Δv that occurs during the dilution process is then

$$\Delta v = v'' - (v' + v) \tag{10}$$

Combination of this expression with the definition of apparent molar volume, eq 1, gives the working equation for dilatometry:

$${}^{\phi}V_f = {}^{\phi}V_i + \Delta v/n_2 \tag{11}$$

where the subscripts i and f refer to the initial (concentrated) and final (diluted) states of the electrolyte solution and n_2 is the number of moles of the electrolyte added to the solvent. Note that because it is only the *change* in volume that has to be measured, no unattainable accuracy in (absolute) volume measurement is required. By making the titrant sufficiently concentrated, ${}^{\phi}V_i$ can be measured with high precision (±0.01 $cm^3\ mol^{-1}$) using any reasonable density method such as pycnometry or vibrating tube densimetry. Then, if Δv can be measured with sufficient accuracy, and the published designs achieve this, ${}^{\phi}V_f$ can be determined with similar accuracy to that for ${}^{\phi}V_i$ down to very low concentrations (<0.001 M).

The chief disadvantages of dilatometry are that it is rather slow, especially for high precision work, labor intensive, and difficult to automate. Related devices such as volumometers, expansimeters, and piezometers[55,56] that also measure volume changes directly under conditions of varying temperature or pressure are also particularly useful for measuring changes in ${}^{\phi}V$ (for obtaining $V°$) as functions of T and P. However, such properties are beyond the scope of the present review. Values of $V°$ obtained from dilatometric measurements are designated with "dil" in the footnotes of the tables in section 5.

2.4. Obtaining the $V°$ of an Electrolyte

The standard partial molar volume of an electrolyte is the limiting value of its partial (or apparent) molar volume as its concentration, c or m, approaches zero, corresponding to infinite dilution in the solvent (eq 4). At this limit, ions are surrounded only by the solvent, with other ions being infinitely distant. It follows, therefore, that $V°$ is unaffected by ion−ion interactions and is a measure *only* of the mutual influence of the ion and the solvent upon each other. As for other thermodynamic quantities, the standard values for cations and anions (and, hence, for electrolytes) are additive in a given solvent and at a specified temperature and pressure. These features make $V°$ an important quantity in the interpretation of electrolyte behavior in solutions.

In practice, the value of $V°$ of an electrolyte is obtained from the extrapolation of its apparent molar volume, ${}^{\phi}V$, to infinite dilution. The various methods that have been used for this purpose will now be discussed in detail.

2.4.1. Theoretical and Semiempirical Extrapolations

Redlich, Rosenfeld, and Meyer (RRM)[7,20,22] showed that a theoretically rigorous extrapolation of ${}^{\phi}V$ to infinite dilution can be achieved using an expression obtained from the pressure derivative of the Debye−Hückel theory for the activity coefficients of electrolyte solutions. The expression obtained, which is strictly valid only at reasonably low concentrations, has the form

$$ {}^{\phi}V = V° + S_V^{\mathrm{DH}} c^{1/2} \tag{12} $$

so that $V° = {}^{\phi}V - S_V^{\mathrm{DH}} c^{1/2}$.

It is worthwhile to note here that there is a common (albeit usually unstated) misconception that the concentration limit of the validity of the Debye−Hückel limiting law (DHLL) for volumes must be the same as that for activity coefficients, which is generally considered to be ~0.001 M for typical 1:1 electrolytes at 25 °C (ref 57, pp 230 ff). There is no a priori reason for this to be so, and the highest quality experimental (dilatometric) evidence in water[51,58,59] shows that linear plots of ${}^{\phi}V$ versus $c^{1/2}$ with the correct (DHLL) slope are obtained for fully dissociated 1:1 electrolytes up to $c \approx 0.04$ M. Redlich[20,22] has summarized data for a number of 1:1 electrolytes that appear to follow the DHLL up to even higher concentrations, but these have been based on the less accurate (see section 2) densimetric methods. Surprisingly, multivalent electrolytes often exhibit DHLL slopes up to concentrations similar to those for 1:1 salts.[52,59]

The slope S_V^{DH} has a predictable value for all electrolytes of a given charge type in a given solvent and at a given temperature:

$$ S_V^{\mathrm{DH}} = (0.5[\nu_+ z_+^2 + \nu_- z_-^2])^{3/2} k \tag{13} $$

where the subscripts + and − denote the cation and the anion of the electrolyte and ν is the number of ions of charge z into which the electrolyte dissociates. The value of k (in SI units but for c in M) is given by

$$ k = N_A^2 e^3 (8\pi^2 \epsilon_0^3 RT)^{-1/2} \epsilon^{-3/2} [(\partial \ln \epsilon/\partial P)_T - \kappa_T/3] \tag{14} $$

where N_A is Avogadro's number, e is the unit (proton) charge, ϵ_0 is the permittivity of free space, ϵ is the relative permittivity of the solvent, $(\partial \ln \epsilon/\partial P)_T$ is its pressure dependence, and κ_T is its isothermal compressibility, with other symbols having their usual meanings. Similar but somewhat different expressions are found in the literature, arising from differences in units, including those for concentration. Values of k for various solvents at $T = 298.15$ K derived from contemporary values of $(\partial \ln \epsilon/\partial P)_T$ and κ_T have been tabulated.[60]

To allow for departures from the limiting law behavior at higher electrolyte concentrations, Redlich and Meyer[22] added an additional empirical term to give

$$ {}^{\phi}V = V° + S_V^{\mathrm{DH}} c^{1/2} + b_V c \tag{15} $$

which is usually referred to as the RRM equation. This expression satisfactorily represents ${}^{\phi}V$ data up to ~1 M for most systems. Plots of $({}^{\phi}V - S_V^{\mathrm{DH}} c^{1/2})$ versus c are usually linear and readily yield $V°$ and b_V as the intercept and slope, respectively.

With the ongoing development of electrolyte theories (mostly for aqueous solutions), a variety of extrapolation expressions has become available. Undoubtedly, the most popular of these is that due to Pitzer,[61−63] which for the volumes of 1:1 electrolytes takes the form[62] of the following set of equations:

$$ {}^{\phi}V = V° + (A_V/b) \ln(1 + bm^{1/2}) + 2RT(B^V m + C^V m^2) $$

$$ A_V = 4RT(\partial A_\phi/\partial P)_T $$

$$ A_\phi = (2\pi N_A \rho^*/9000)^{1/2} (e^2/4\pi\epsilon_0\epsilon k_B T)^{3/2} $$

$$ B^V = \beta^{V(0)} + 2\beta^{V(1)} f(\alpha m^{1/2}) $$

$$ \mathrm{f}(x) = [1 - (1 + x)\exp(-x)]/x^2 \tag{16} $$

where $b = 1.2$, $\alpha = 2.0$, and $\beta^{V(0)}$, $\beta^{V(1)}$, and C^V are the pressure derivatives of the corresponding Pitzer parameters for activity or osmotic coefficients. Note that for the use of these expressions the solution concentrations are to be given in molalities (moles per kg of solvent). These derivatives (and the original parameters) are purely empirical and are generally unknown for nonaqueous solutions, so not surprisingly, little use has been made of them to date. A recent exception[64] used an abbreviated form of the Pitzer model

$$ {}^{\phi}V = V° + (A_V/b) \ln(1 + bm^{1/2}) + 2RT\beta^{V(0)} m \tag{17} $$

to obtain $V°$. Note, however, that there is no conclusive evidence that the extra complexity of the Pitzer

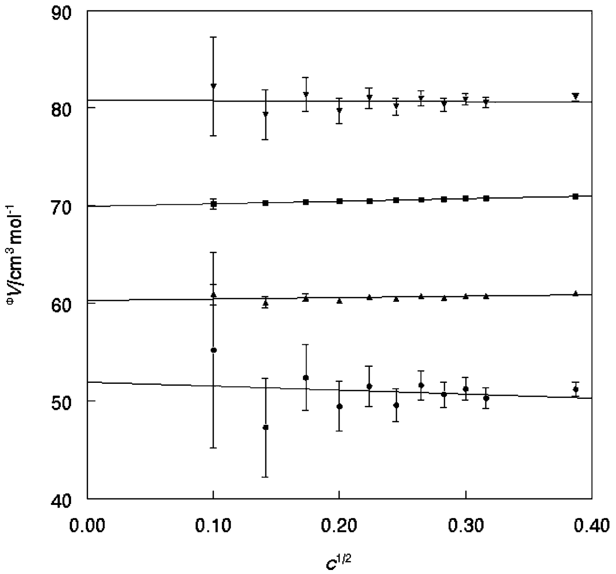


Figure 1. Masson plots (${}^{\phi}V$ vs $c^{1/2}$) of the concentration dependence of apparent molar volumes of electrolytes. The "true" $V°$ values (in cm^3 mol^{-1}) and the density difference uncertainties $\delta\rho = (\rho - \rho^*)$/(g cm^{-3}) are, from bottom to top, as follows: (a) 50.00, 1×10^{-4}; (b) 60.00, 1×10^{-5}; (c) 70.00, 2×10^{-6}; (d) 80.00, 5×10^{-5}. Random deviations in ${}^{\phi}V$ of magnitude $\leq 0.5\delta\rho/c$ have been introduced.

equations (or other models) produces significantly more reliable estimations of $V°$. Indeed, even in aqueous solutions where reliable data are plentiful, the $V°$ values produced by extrapolations based on the Pitzer and RRM equations are essentially identical,[65,66] providing that data are restricted to $c \leq 1$ M. In nonaqueous solutions, where ion pairing is more common (see below), the Pitzer expressions become particularly unwieldy.

2.4.2. Empirical Extrapolations

Because of the absence or inadequacy of the requisite data for calculating S_V^{DH} in nonaqueous solvents and the difficulty of measuring accurate densities at sufficiently low concentrations, it has been common practice to extrapolate ${}^{\phi}V$ to infinite dilution using the *purely empirical* equation

$$ {}^{\phi}V = {}^{\phi}V^{\infty} + S_V^{M} c^{1/2} \tag{6} $$

There are, however, longstanding misconceptions about the proper significance[1] of the eponymous eq 6, proposed by Masson in 1929,[21] in which the slope, S_V^M, is derived from a (presumed linear) plot of ${}^{\phi}V$ against $c^{1/2}$, as shown in Figure 1, and has a characteristic value for every electrolyte. Values of S_V^M are generally positive but may be negative (in the range of c values studied), particularly for tetraalkylammonium salts.[68−70] The Masson equation is generally able to describe ${}^{\phi}V$ data at $c \leq 1.0$ M in both water and nonaqueous solvents, but at higher concentrations a further empirical term linear in c may be required.

The dangers of using Masson plots, eq 6, rather than the DHLL (eq 4), RRM (eq 15), or other theory-based equations for the extrapolation of ${}^{\phi}V$ to infinite dilution have been discussed on many occasions and reviewed several times.[1,20,22] Extrapolations from relatively high concentrations, often associated with pycnometric measurements, may yield $V°$ values that are in error by several cubic centimeters per mole, *even if the plots are linear*. Masson plot extrapolations even using relatively low concentration data may still produce errors of up to ~1 cm^3 mol^{-1} in $V°$.

One of the reasons for the apparent success of the Masson equation in describing ${}^{\phi}V(c)$ data arises from the effects of errors. Figure 1 shows plots of ${}^{\phi}V$ against $c^{1/2}$ in which *random* uncertainties in $(\rho - \rho^*)$/(g cm^{-3}) of 2×10^{-6}, 1×10^{-5}, 5×10^{-5}, and 1×10^{-4} have been introduced in curves c, b, d, and a (so ordered to avoid overlap). These errors produced deviations of −0.10, +0.26, +0.80, and +1.9 cm^3 mol^{-1} respectively in ${}^{\phi}V$. Clearly, density determinations to $\pm 1 \times 10^{-4}$ g cm^{-3} (~100 ppm) are entirely inadequate for obtaining reliable values of $V°$. Furthermore, it is necessary to make measurements of the densities down to at least 0.01 M in order not to let data at high concentrations, say $c \geq 0.25$ M, exert too great an influence on the extrapolation of the ${}^{\phi}V$ versus $c^{1/2}$ curve. However, such measurements are not trivial: in water for an electrolyte with ${}^{\phi}V = 100$ cm^3 mol^{-1}, the density change at $c = 0.01$ M is ~3 ppm! Reliable measurement of such small changes is beyond the abilities of most techniques (see previous sections). Given that systematic errors are likely to be at least as important as random errors, especially at low c, it is not surprising that many authors are able to produce linear plots of ${}^{\phi}V$ versus $c^{1/2}$.

Of course, for many solvents, there is no alternative but to employ the Masson equation, as the solvent data required for extrapolation (eq 14) are either unavailable or not known with sufficient accuracy[60] to justify their use. The likely errors associated with the determination of $V°$ in this manner should be kept in mind.

Occasionally, an even cruder approximation has been used. This is for systems in which, within the measured concentration range and the limits of experimental error, the densities of the solutions are linear with concentration: $\rho = \rho^* + bc$. Introduction of this relationship into eq 2a yields ${}^{\phi}V = (M_2 - 1000b)/\rho^* =$ constant. That is, ${}^{\phi}V$ is independent of c over the range of measurement, implying (hopefully) that it remains so also to infinite dilution, so that $V° = {}^{\phi}V° = (M_2 - 1000b)/\rho^*$.

2.4.3. Ion-Pairing Effects

A particular complication, which occurs in many nonaqueous solvents whose relative permittivities are significantly lower than that of water (cf. eqs 12−14), is the effect of ion pairing. This effect arises because in general the sum of the $V_i° = V°$(ion) values of free (dissociated) ions is smaller than that of their ion pair, V_{ip}, due to the greater electrostrictive effect of the ions on the solvent molecules (section 6.1.2). Note that $V°_{ip}$ is (like the standard association constant for an electrolyte in solution $K_A°$) a virtual quantity, since at infinite dilution the electrolyte is completely dissociated.

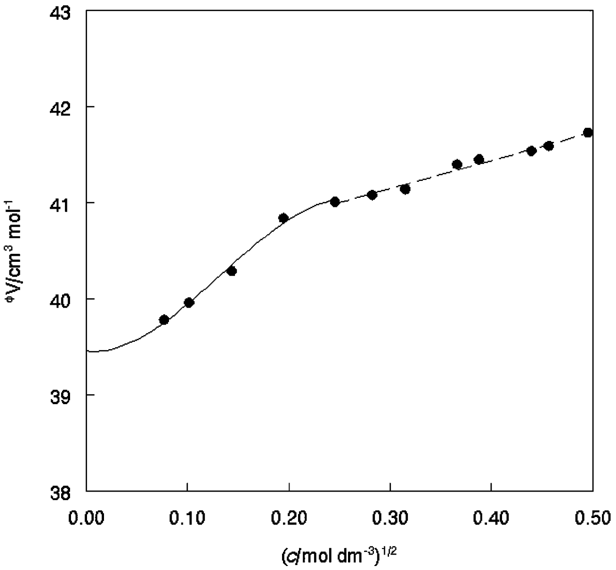


Figure 2. Concentration dependence of the apparent molar volume of $TlNO_3$ in water.[67] The dashed line represents the region where ion pairs predominate.

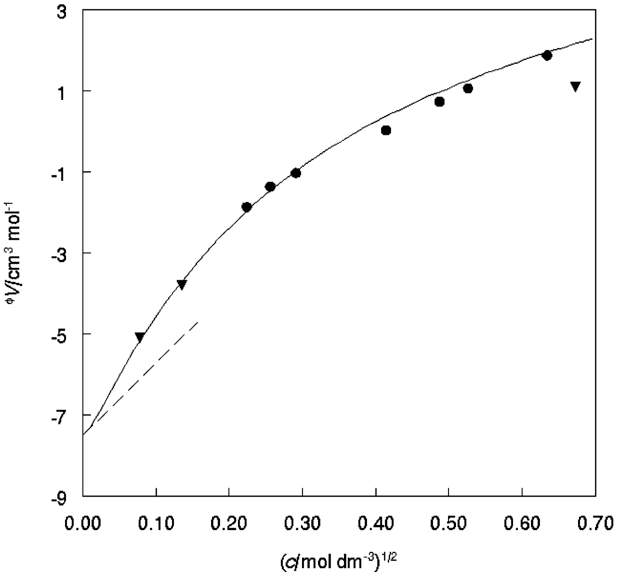


Figure 3. Concentration dependence of the apparent molar volume of LiCl in methanol. The experimental values (●) are from ref 8; the dashed line is the limiting slope; the continuous line was calculated iteratively for α, the fraction dissociated,[71] with $K_A = 68$ dm³ mol⁻¹ and $\Delta V°_{ip} = 13$ cm³ mol⁻¹.

At finite concentrations, the observed ${}^{\phi}V$ is made up of contributions from the ions and ion pairs:

$$ {}^{\phi}V = \alpha\, {}^{\phi}V_i + (1 - \alpha)\, {}^{\phi}V_{ip} \qquad (18) $$

where α is the fraction (degree) of dissociation of the ion pair. Typical consequences of ion pairing on ${}^{\phi}V$ versus $c^{1/2}$ curves are shown in Figures 2 and 3. Linear extrapolation of these data according to eq 6 clearly leads to an incorrect $V°$ value. It is also apparent that ${}^{\phi}V$ continues to increase with c even in the range where α is small, indicating that ${}^{\phi}V_{ip}$ varies with c. It is possible to estimate the molar volume increase on ion pairing, ΔV_{ip}, if the pressure dependence of the association constant K_A is known (e.g., from high pressure conductivity data). Then

$$ \Delta V_{ip} = V_{ip} - V = -RT(\partial \ln K_A/\partial P)_T \qquad (19) $$

(V being the partial molar volume of the ionized part, as it is for nonassociated electrolytes dealt with above). Knowledge of K_A at ambient pressure permits the iterative calculation of α. This is required because the mean ionic activity coefficients of the dissociated part of the electrolyte are inherent in the relation between K_A and α. These, in turn, depend on the ionic strength, which depends on the concentration of the ions and hence on αc.[71] The resulting expression for uni-univalent electrolytes is

$$ {}^{\phi}V = \alpha[-\Delta V°_{ip} + k(\alpha c)^{1/2}] + V°_{ip} + hc \qquad (20) $$

where k is the Debye–Hückel slope factor from eq 5 and h is an empirical constant describing the deviations of ${}^{\phi}V$ from a linear dependence on $c^{1/2}$ at high concentrations. From such concentrations where $\alpha \rightarrow 0$

$$ \lim_{c\rightarrow\infty} {}^{\phi}V = V°_{ip} + hc \qquad (21) $$

is obtained and finally $V°_i$ from a combination of eqs 19–21. This should represent the "true" value of $V°$.

A more complete treatment of the effects of ion pairing has been presented subsequently by Côté et al.[30,72] in terms of the Bjerrum theory of ion pairing. The expression given is

$$ {}^{\phi}V = V° + \mathrm{Bjerrum}(K_A,T,P,\epsilon) + hc \qquad (22) $$

The Bjerrum function is evaluated from the right-hand-side of eq 19,[30] where K_A is specified as the association constant according to the Bjerrum theory:

$$ K_A = (4\pi N_A/1000)\int_a^q r^2 \exp(2q/r)\, \mathrm{d}r \qquad (23) $$

In this expression, the lower limit of integration a is the Debye–Hückel "distance of closest approach" and the upper limit is the Bjerrum association distance $q = |z_+z_-|e^2/8\pi\epsilon_0\epsilon kT$. For electrolytes with significant ion pairing, this procedure should in general produce more reliable values of $V°$ than empirical extrapolations or those based on the DH theory alone (which assume complete dissociation). Unfortunately, the calculations using the Bjerrum model are more complex, but a computer program is available from the original authors[30,72] that enables evaluation of both $V°$ and $K_A°$.

It is probable that the effects of ion pairing are second only to measurement errors in producing inaccurate values of $V°$ for electrolytes in nonaqueous solvents. Attention to this aspect of the determination of $V°$, by careful experimental design (the use of highly dissociated salts, use of appropriate methods, etc.) and by appropriate theoretical treatments such as the above, is required to produce reliable $V°$ values. Such practices are likely to be far more fruitful than the use of more complicated extrapolation equations such as the Pitzer expressions that do not specifically allow for ion pairing.

Unfortunately, it has been tacitly assumed in many measurements that ion pairing does not affect the partial molar volume of an electrolyte even in relatively concentrated solutions where it is unlikely that $\alpha \rightarrow 1$. The mere observation of a linear plot of ${}^{\phi}V$ against $c^{1/2}$ does not, contrary to widespread belief, prove that ion-pairing effects are negligible. Such an observation is critically dependent on the errors (random and systematic) in the data, the concentration range studied, and the magnitudes of ΔV_{ip} and K_{A}. For the reasons outlined in section 2.4.2, the majority of the $V°$ data compiled in the tables of this review have been obtained by the use of the Masson equation, eq 6, from density data with uncertainties of the order of $\pm 1 \times 10^{-5}$ g cm^{-3} or worse. Although $V°$ values have been reported by some authors to two decimal places (with an implied uncertainty of $\pm(0.01-0.05)$ cm^3 mol^{-1}), their probable error is not better than $\pm(0.1-0.5)$ cm^3 mol^{-1} and in many cases will be considerably worse.

3. Individual Ionic Volumes

3.1. Background

For the purpose of tabulation of standard partial molar volumes, it is convenient to have ionic values, since there are many more salts than ions. Whole salt volumes are then readily recovered by appropriate ionic combinations on the thermodynamically correct basis of the additivity of the standard quantities. For such purposes, it is sufficient to employ a convention to split the electrolyte values into ionic contributions. The choice of convention is purely arbitrary; it is akin to defining the $E°$ of the standard hydrogen electrode as zero. For volumes, the most commonly employed convention has been to define $V°(\mathrm{H}^+) \equiv 0$ in all solvents at all temperatures (cf. ref 1 concerning aqueous solutions). In effect, this produces an infinite set of unrelated scales: one for each solvent (or solvent mixture) at each temperature.

While satisfactory for tabulation, conventional ionic volumes provide practically no information about the actual volumetric properties of ions in solution. As was recognized many years ago: "the interpretation of partial molar properties of salts on an absolute ionic basis cannot be avoided if such measurements are to be of any value in developing and understanding of ion−solvent interactions quantitatively".[47] Since ions are the species present in dissociated electrolyte solutions, such actual or "absolute" ionic volumes are also essential for theoretical and computational modeling purposes.

Due to the additivity of the ionic contributions to $V°$(electrolyte), it is necessary only to know $V°$(ion) for just one ion in a given solvent at a given temperature and pressure in order to obtain all other values, provided an appropriate chain of additions and subtractions of $V°$(electrolyte) and $V°$(ion) is available.

Herein lies a problem because, as is well-known, it is impossible within the framework of thermodynamics to apportion a measurable whole salt thermodynamic quantity into its ionic components. This can only be done by making an appropriate extrathermodynamic assumption ("extra-" in the sense of "outside of"). This difficulty has been considered in depth for other thermodynamic quantities, and many ingenious proposals have been developed for estimating ionic Gibbs energies, enthalpies, and so forth. However, for volumes, the situation has been somewhat clouded by the apparent existence of direct methods for measuring ionic volumes (see below).

Numerous extrathermodynamic assumptions for estimating $V°$(ion) have been proposed over the years; those employed up to approximately 1970 have been summarized by Millero.[1] The reviews by Panckhurst,[73] Curthoys and Mathieson,[74] and Conway[2,75] also cover many methods but again mostly those pertaining to aqueous solutions. Only the subsequent reviews by Krumgalz,[76] Kolker and Safonova (to a limited extent),[24] and Hefter and Marcus[3] deal specifically with procedures for obtaining absolute $V°$(ion) values in nonaqueous solvents. Many of the earlier methods for estimating $V°$(ion) are unique to water or are only of historical interest. Accordingly, only those methods that have been employed extensively since Millero's review[1] are discussed here.

3.2. "Direct" Methods

Following an earlier suggestion of Debye,[77] Yeager and co-workers[78,79] detected the existence of ultrasonic vibration potentials (uvp's) and showed that they can be used to obtain ionic volumes in solution. They applied their method to aqueous solutions of a number of 1:1, 1:2, and 2:1 electrolytes at 22 °C and at concentrations from 0.001 to 0.1 M and in some cases up to 1 M. The working expression of Zana and Yeager[79] can be rewritten as

$$\Phi_0/a_0u = (1.037 \times 10^{-6})[(t_+/z_+)(M_+ - V_+\rho^*) - (t_-/|z_-|)(M_- - V_-\rho^*)] \quad (24)$$

where Φ_0 is measured in microvolts, a_0 is the velocity amplitude, u is the velocity of the ultrasound in centimeter per second, ρ^* is the density of the solvent in grams per cubic centimeter, the subscripts + and − denote the cation and anion, t is the transference number, z is the charge number, M is the molar mass in grams per mole, and V is the ionic volume in cubic centimeters per mole. The values of Φ_0/a_0u were found to be independent of the concentration in reasonably dilute solutions. Individual ionic transference numbers $t_+ = 1 - t_-$ can be determined experimentally. So too can $V°(\text{electrolyte}) = \nu_+V_+ + \nu_-V_-$, where the ν are the stoichiometric coefficients and $\nu_+z_+ = \nu_-z_-$. Thus, there are two equations with just two unknowns, V_+ and V_-, and so the method yields single ion volumes (these are noted as "uvp" in the footnotes of the tables in section 5). The precision of this method can be judged by the constancy of the derived V_+ or V_- values for a given ion from a series salts containing different counterions. In aqueous solutions,[79] mean deviations were no more than ±2 cm^3 mol^{-1} for univalent ions and

±4 $cm^3 mol^{-1}$ for divalent ions. The resulting value of $V(H^+,aq) = -5.4$ $cm^3 mol^{-1}$ (at 22 °C) agrees well with the authoritative estimates (at 25 °C) of −4.7 ± 1.1 $cm^3 mol^{-1}$ (ref 1) and −5.5 ± 0.5 $cm^3 mol^{-1}$ (ref 75, p 375).

This method was subsequently employed by Zana, Kawaizumi, and co-workers to obtain V_+ and V_- values in nonaqueous solvents. In contrast with the case of aqueous solutions, Φ_0 was found to depend on concentration, although only minimally in the range 3×10^{-4} to 3×10^{-3} M. Values in this range were used to calculate V(ion) in MeOH,[80] EtOH,[111] DMF,[111] DMSO,[81] MeCN,[82] EG,[83] and PC.[84] However, the results obtained were much less satisfactory than those in aqueous solution. Thus, the value of a_0 was not known in the nonaqueous solvents, so that an estimate had to be used and variations of ±5 cm^3 mol^{-1} or sometimes worse were found for a given ion with different counterions, even for 1:1 electrolytes. There is no way of knowing if an even wider spread of V(ion) values would be obtained from a more comprehensive investigation. This uncertainty often forced Zana et al. into arbitrary data selection, thus destroying any claim of the method to be "direct". A more detailed critique of the method and the results obtained with it in nonaqueous solvents is given elsewhere.[3,76] The values obtained by this method are listed in the tables in section 5, when available.

Hirakawa[85] devised an apparatus providing an oscillating accelerating field to solutions, from which sedimentation potentials (spt's) could be determined. The resulting expression is analogous to eq 24. This method was applied to aqueous electrolyte solutions at concentrations from 0.001 to 0.1 M at 25 °C. Unfortunately, the expected independence of V_+ or V_- from the nature of the counterion was not observed, with the values varying systematically with counterion size within a range of ±4 $cm^3 mol^{-1}$. This method was subsequently applied to solutions in MeOH,[86] again with rather large limits of errors (the resulting values are noted as "spt" in the footnotes of the tables in section 5).

There is no doubt that the uvp and spt methods unambiguously yield V_+ and V_- values, albeit with rather large uncertainties, from the measurable quantities of V(electrolyte), t_+ and t_-, and the appropriate Φ_0/a_0u values or spt's. Unfortunately, it has been presumed widely that the values so obtained can be equated with the standard partial molar volumes; that is, V_+ or $V_- = V°$(ion). This is incorrect: as with all single ion thermodynamic properties, $V°$(ion) *cannot* be measured. As pointed out by Conway,[2] the quantity obtained from uvp or spt measurements is a *hydrodynamically significant* volume; equating it to the *thermodynamically significant* $V°$(ion) value is an extrathermodynamic assumption. Like all such assumptions, however appealing it may be intuitively, the usefulness of the uvp or spt methods can only be assessed by comparison with other assumptions. An analogy here is with the application of Stokes' law to (measurable) ionic conductivities. The resulting "directly measured" hydrodynamic ionic volumes show little relevance to $V°$(ion) values.

3.3. Methods Based on Crystal Ionic Radii

Many authors have proposed methods that ultimately can be related to the semiempirical expression due to Hepler[27]

$$V°(\text{ion}) = Ar^3 - Bz^2/r \qquad (25)$$

where r is the crystal ionic radius of the ion and A (which may be r dependent) and B are coefficients. Estimates of A and B from theoretical considerations yield $V°$(ion) values that when combined appropriately do not reproduce measured $V°$(electrolyte) values. Consequently, A and B have to be obtained from fitting the latter quantities. As originally proposed by Hepler,[27] the $V°$(ion) values were obtained by the arbitrary choice of $V°(Cl^-)$ in water. A number of methods essentially based on eq 25, and the proper choice of the r values for obtaining V(ion) values for aqueous solutions, have been reviewed.[1,73,74]

An early method for obtaining $V°$(ion) values based on crystal ionic radii, which was originally devised for aqueous solutions but later employed for nonaqueous solutions, was proposed by Mukerjee.[28] This method consisted of plotting conventional ($V°(H^+,aq) \equiv 0$) values of $V°$(ion) of the alkali metal and halide ions against the cubes of the Pauling crystal ionic radii. Two more or less parallel (but not strictly linear) curves resulted, one for the cations and the other for the anions. Since strict additivity of the ionic values should hold, Mukerjee then added/subtracted a constant quantity (which in essence corresponded to selection of the "absolute" value of $V°(H^+,aq)$) to/from the conventional $V°$(ion) values of the cations/anions to produce a single smooth (curved) line. Consistent with eq 25, this implies that $V°$(ion) of these monatomic univalent ions in aqueous solutions does not depend significantly on the sign of the charge, as had been suggested by Couture and Laidler.[26] In water the constant quantity added/subtracted was equivalent to $V°(H^+,aq) = -4.5$ cm^3 mol^{-1}. As noted by Mukerjee,[28] even for aqueous solutions, not all the adjusted ionic volumes of the alkali metal and halide ions conformed exactly to the final (curved) plot but most did so within ±0.5 cm^3 mol^{-1}. The major outliers were Li^+, Na^+, and F^-.

Mukerjee's method has been used to derive $V°$(ion) values for 2-aminoethanol (MEA), *N*-methylacetamide (NMA), *N*-methylpropanamide (NMP), and anhydrous formic acid (HCOOH), where other methods could not be employed, as well as ethanol (EtOH), ethylene glycol (EG), formamide (FA), and dimethylformamide (DMF). These values are given in the tables in section 5 and are denoted as "muk" in the footnotes.

The present reviewers have reapplied Mukerjee's method[28] using current values of the crystal ionic radii r_i of the alkali metal and halide ions[87] and the "selected" $V°$(electrolyte) values from the tables in section 5. As the starting point for such calculations is arbitrary, initial $V°$(ion) values were obtained from the tetraphenylarsonium tetraphenylborate (TATB) or tetraphenylphosphonium tetraphenylborate (TPTB) assumption (see section 3.5 below). This method was applied to all solvents where suitable data were

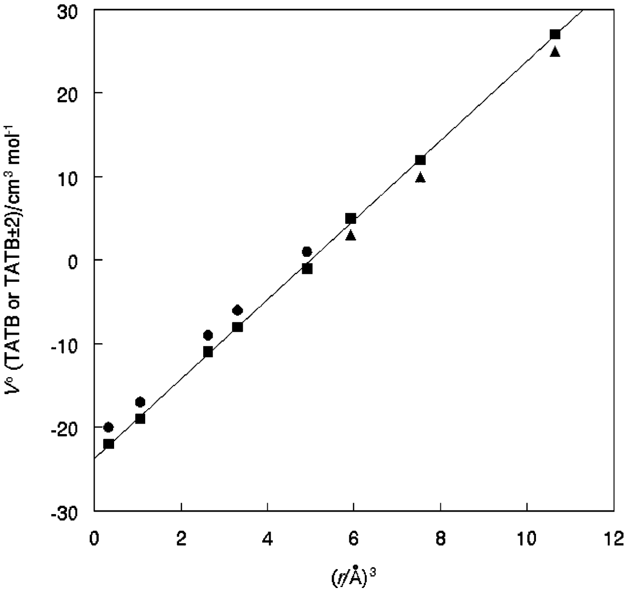


Figure 4. Mukerjee-type plots for the alkali metal and halide ions in MeCN (obtained using the TATB assumption). The cation values (●) were then adjusted by -2 cm^3 mol^{-1} and the anion values (▲) by $+2$ cm^3 mol^{-1} to give the values (■) situated on a single line.

available: water (w), MeOH, EtOH, EG, propylene carbonate (PC), MeCN, FA, NMF, DMF, nitromethane (NM), and DMSO. The adjustment of the TATB/TPTB values of $V°$(ion) required to produce a smooth single line for the alkali metal and halide ions was from 1 to 4 cm^3 mol^{-1} ($-$ for cations and $+$ for anions) for most of the solvents. Larger adjustments were required for EtOH (± 6 cm^3 mol^{-1}), DMSO (± 8 cm^3 mol^{-1}), and DMF (± 10 cm^3 mol^{-1}), giving an overall average of ± 4 cm^3 mol^{-1} for the 10 nonaqueous solvents. A typical plot (for MeCN) is shown in Figure 4. For some of the solvents — EG, PC, *N*-methylformamide (NMF), and DMSO — Mukerjee plots against r^3 are smooth but notably curved. For such solvents plots against r^2 produce straight lines (using the same adjustments). All of the plots, whether against r^3 or r^2, show one or two outliers among the nine ions. These are always Li^+ or Na^+ and F^- or I^- but differ for different solvents.

It may be concluded that Mukerjee's method is broadly on a par with the TATB/TPTB assumptions, showing an average difference of ± 4 cm^3 mol^{-1}, with those for EtOH, DMSO, and DMF being rather larger. This is surprising in view of the small size of the ions employed. Such ions would be expected to show significant differences in their electrostriction effects. Further, the ion−dipole interactions with the solvent molecules would have the latter oriented oppositely for cations and anions. It may be significant that the two solvents showing the largest deviations (DMSO and DMF) have rather different steric crowding at their dipolar sites.

3.4. Extrapolation Methods

The $V°$(electrolyte) values for partly or completely alkyl-substituted ammonium halides, $(CH_3(CH_2)_n)_mH_{4-m}NX$, where $n = 0...5$, $m = 1...4$, and X = Cl, Br, and I,[47,88] show a constant increment per $-CH_2-$ group in a homologous series. A similar observation was made for the tetraalkylammonium (R_4N^+; R = $CH_3(CH_2)_n$) chlorides and bromides in methanol.[89,90] For the large, substantially nonelectrostricting R_4N^+ salts, plots of $V°(R_4NX)$ against M, the molar mass of R_4N^+, proposed by Conway et al.,[47] or against $N = 4(n + 1)$, the number of the carbon atoms, attributable to Verrall[88] in aqueous solutions and Jolicoeur and co-workers[90] in MeOH solutions, were found to be linear. That is

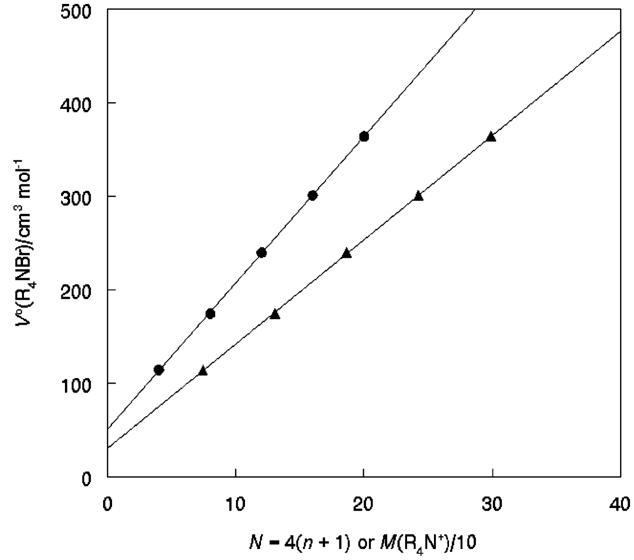


Figure 5. Extrapolation of standard partial molar volumes of tetraalkylammonium bromides in water[47] at 25 °C: (▲) against the cation molar masses M divided by 10 [intercept $\equiv V°(Br^-) = 30.6$ cm^3 mol^{-1}]; (●) against the number of carbon atoms N [intercept $\equiv V°(Br^-) = 50.7$ cm^3 mol^{-1}].

$$V°(R_4NX) = V°(R_4N^+) + V°(X^-)$$
$$= bM + V°(X^-) \qquad (26a)$$
$$= b'N + V°(X^-) \qquad (26b)$$

The slope of plots according to eq 26 corresponds to the volume increment of four $-CH_2-$ groups. For eq 26a, $b = 1.112$ for the bromides in water at 25 °C.[47] According to the proponents of this method, when the $V°(R_4NX)$ values are extrapolated to zero M or N, the intercept on the ordinate should yield $V°(X^-)$.

The problem here is that there is no compelling reason to prefer plots against M or against N, yet the two plots yield different $V°(X^-)$ values (Figure 5). The intercept of plots against N is larger than that of those against M by $18.0b$, where 18.0 cm^3 mol^{-1} is the volume of the "virtual" ammonium ion "NH_4^+".[3] It turns out that in aqueous solutions plots against M yield $V°$(ion) values in agreement with those obtained by other plausible methods[2,3] whereas those against N do not. If $V°(R_4NX)$ values are plotted against $N + 1$, including the nitrogen atom,[91] the discrepancy would decrease to 4.5 rather than 20.1 cm^3 mol^{-1} in water. However, this has not usually been done, and anyway, the discrepancy is still uncomfortably large.

In nonaqueous solutions, the opposite is true. Plots against N produce $V°(X^-)$ values (noted as "*N*ex" in the footnotes of the tables in section 5) in reasonable agreement with those determined by other methods,[3] while plots against M^{76} (noted as “*M*ex” in the footnotes of the tables in section 5) differ markedly. Criticism of the use of the extrapolation against M has also been made by Panckhurst,[73,92] and although partly rebutted by Conway et al.,[91] the problem was not fully settled. It should also be noted that the extrapolation to obtain $V°(X^-)$ is rather long, which introduces considerable uncertainty. Furthermore, at least in nonaqueous solvents, there is evidence that the values of $V°(R_4NX)$ for $R = CH_3$ do not lie strictly on a straight line for either plot,[3] creating further uncertainty.

3.5. Reference Electrolyte Methods

An ideal reference electrolyte would have the following characteristics:

It would consist of univalent (i.e., low charged) spherical cations and anions of exactly the same size.

The size of the ions would be large enough so that their charge did not cause significant electrostriction of the surrounding solvent.

The size of the ions would be small enough so that their presence did not appreciably disrupt the structure of the solvent.

The charges of the ions would be as delocalized as possible (or shielded from the solvent by a cage of weakly interacting atoms), so that there would be virtually no difference in their interaction with the solvent due to the difference in their sign.

It would have a partial molar volume that could be measured to high precision in all solvents.

For such an electrolyte it could be assumed with considerable confidence that the value of $V°$(reference electrolyte) could be split equally between $V°_+$ and $V°_-$.

It is clear that some of the above requirements are mutually exclusive and that no real electrolyte can meet all of these desiderata. Still, such a reference electrolyte can be approximated sufficiently well by either tetraphenylarsonium tetraphenylborate (TATB) or tetraphenylphosphonium tetraphenylborate (TPTB), which have been extensively employed for the splitting of other thermodynamic quantities of electrolytes into ionic components.[19,29,43,93]

Inevitably, there are some drawbacks with the use of these salts. The first is that, because of the necessarily large size of their ions, it is difficult to determine their $V°$(electrolyte) values with sufficient precision to avoid large (relative) errors in the $V°$(ion) values of common small ions. This situation is exacerbated by the fact that, except for a few solvents, both TATB and TPTB are too sparingly soluble for their volumes to be measured directly. Instead, $V°$(TATB or TPTB) values must be determined from a combination of at least three salts involving the constituent ions of TATB/TPTB, with the unavoidable propagation of experimental errors. For instance,

$$V°(\mathrm{TATB}) = V°(\mathrm{TAX}) + V°(\mathrm{MTB}) - V°(\mathrm{MX}) \quad (27)$$

where X^- is a univalent anion (generally halide) and M^+ a univalent cation (generally sodium). Since ionic volumes are then derived additively (ultimately from TATB/TPTB and other salts), the uncertainty in $V°$(ion) increases even further.

The second drawback involves the difficulty of fixing the relative sizes of the component ions of the reference electrolyte. There is general recognition that the sizes are not equal, with the cation being somewhat larger than the anion, as indicated by their van der Waals volumes. Accordingly, the splitting of their $V°$(TATB or TPTB) values should not be exactly equal.

Millero[94] used TATB-based data to estimate $V°(H^+,aq)$, obtaining values in the range −4.1 to −6.6 $cm^3\ mol^{-1}$ by using three independent methods for assessing the intrinsic sizes of the TA^+ and TB^- ions. The methods used the covalent radii of the central atoms, the ratio of the Stokes radii of the ions in solution, and of the van der Waals volumes of the isolated ions. Unfortunately, as shown by Hefter and Marcus,[3] all the methods used by Millero were flawed to some extent.

First, significant errors occurred in the calculation using the covalent radius of the central atom. A transposed value, 1.81 Å instead of the correct value of 1.18 Å, was used for the covalent radius of arsenic, and an incorrect expression was used for the difference in the sizes of cation and anion. Second, the Stokes radii method was found[3] to be solvent dependent, with an unacceptably high uncertainty: a mean value of 1.0712 was obtained for the cube of the Stokes radius ratio for six solvents with a standard deviation of 6.7% (corresponding to ∼20 $cm^3\ mol^{-1}$ in $V°$(ion)). Finally, it was shown that the van der Waals volumes of the ions reported in the literature also vary significantly:[3] those for the TA^+ cation by 1.33% and those for the TB^- anion by 0.53% (standard deviations from the mean). Although not large in percentage terms, these uncertainties amount to several cubic centimeters per mole in $V°$(ion). It should also be noted that $V°$(TATB) values in solution are ∼50% larger than the van der Waals volumes, which makes the assumption of the equivalence of their ratios (i.e., $V°(TA^+)/V°(TB^-) = V_{vdW}(TA^+)/V_{vdW}(TB^-)$) somewhat speculative.

The alternative reference electrolyte, TPTB, has the advantage that its cation, TP^+, is smaller than TA^+ and nearer in size to TB^-. The ratios $V°(TP^+)/V°(TB^-)$ have the mean value 1.0072 ± 0.0003 (compared with $V°(TA^+)/V°(TB^-) = 1.0461$) for eight solvents, including water, when $V°(TP^+) - V°(TB^-) = 2\ cm^3\ mol^{-1}$ (see below) is used.[3] However, since $V°$(ion) values must be obtained additively, the *difference* between the reference cation and anion volumes is more pertinent than their ratio. A comparison using the Mukerjee, extrapolation, and reference electrolyte methods led to the conclusion[3] that the TATB method, with

$$V°(\mathrm{TA}^+) - V°(\mathrm{TB}^-) = 8 \pm 2\ \mathrm{cm}^3\ \mathrm{mol}^{-1} \quad (28)$$

and the equivalent TPTB method, with

$$V°(\mathrm{TP}^+) - V°(\mathrm{TB}^-) = 2 \pm 2\ \mathrm{cm}^3\ \mathrm{mol}^{-1} \quad (29)$$

are the least objectionable splits available at the present time.

The reference electrolyte, TATB or TPTB, method has been employed for many solvents, and in many cases, agreement with results from other methods has been found. This was the preferred method used in the relevant tables in this review. However, if the required $V°$(TATB) or $V°$(TPTB) had not been measured but $V°$ values for the alkali halides were available, then Mukerjee's method was used instead.

4. Data Treatment

4.1. Organization of the Data

Separate tables for the standard partial molar volumes of electrolytes, $V°$ (in $cm^3\ mol^{-1}$), have been compiled for all solvents for which appreciable amounts of data were available. The ordering of the presentation of data with respect to the solvents, and to the electrolytes in a given solvent, follows that used in previous reviews in related areas.[19,29] The abbreviations used for solvents are standard[19,29] and are given in the relevant section and table headings. For compounds containing R_4N^+ ions, the abbreviations Pr, Bu, Pe, Hx, Hp, Oc, and Dc refer to *n*-alkyl substituents (*i*- is used as a prefix for isoalkyl substituents). Abbreviations of complex salts are given in the appropriate footnotes of the tables.

In the data tables, the second column presents the reported $V°$ values with footnotes to the references and the experimental methods used. References with an oblique line (/) between two entries denote values calculated in the second reference from data in the first. In a few cases it was necessary to recalculate or extrapolate data given in the original publications (against either concentration or temperature); this is indicated by an appropriate footnote. Values of $V°$(electrolyte) were listed to a maximum of two decimal places where so reported or as was consistent with the claimed accuracy. In this context it should be noted that many authors claim higher accuracies than are justified by a realistic consideration of experimental uncertainties. The reviewers have exercised their judgment accordingly, rounding data to the nearest 0.1 or 1 $cm^3\ mol^{-1}$ as appropriate. Data obtained by pycnometry particularly fall into this category. The third column presents the $V°$ value selected by the reviewers as the optimal one for a given electrolyte according to the criteria in section 4.2.

The estimated values of $V°$ for ions are presented in a separate table immediately following that containing the electrolyte data for each solvent. Ions are arranged as previously:[19] with cations listed, in order of increasing charge, before anions. The values in the second and third columns of the $V°$(ion) tables were derived from the "selected" electrolyte data in the immediately preceding table as part of the present review, using the TATB/TPTB assumption (see section 3.5) wherever possible and assuming ionic additivity. The appropriate salt/ion combinations employed are indicated in parentheses, and as many alternative routes as possible were used. Where TATB/TPTB data were unavailable, Mukerjee's method (section 3.3) was employed to obtain $V°$(ion) values. The third column of the $V°$(ion) tables contains the "selected" values, that is, those values which in the judgment of the reviewers are the best available estimate of $V°$(ion) at the present time. These are usually the mean of the $V°$(ion) values in column two. Also included, in the fourth column, are $V°$(ion) values reported by other authors where available, with a footnote indicating the extrathermodynamic assumption used.

The following abbreviations have been used for the various assumptions (most of which are discussed in detail in section 3): muk (Mukerjee's method[28]); vdW (Millero's method[94] involving van der Waals radii); cor (the correspondence method of Criss[95]); *M*ex (extrapolation of $V°(R_4NX)$ against M[47,91]); *N*ex (extrapolation of $V°(R_4NX)$ against N[90]); uvp (the ultrasonic vibration potential method of Yeager et al.);[78,79] spt (sedimentation potential method of Hirakawa et al.);[85] ext (other extrapolation methods); TATB or TPTB (reference electrolyte method, recognizing the differences in the volumes of TA^+ or TP^+ and TB^-, or else TA = TB and TP = TB are used). To minimize the loss of information for whole salts (obtainable by applying additivity to appropriate cation and anion data), values of $V°$(ion) are given to integer values, while recognizing that the uncertainty of the extrathermodynamic assumption is greater than the $\pm 1\ cm^3\ mol^{-1}$ that this might imply.

4.2. Selection Criteria

Critical assessment of the $V°$ data of electrolytes in nonaqueous solvents has relied in general on the existence of independently determined values from the literature. The availability of such data varies considerably among solvents. For some solvents only one data source was available; in others several references were known but with almost no overlap of salts. In general, data reported by authors from the same laboratory, even if publishing separately, have not been regarded as independent. For reasons outlined in detail in section 2, where serious disagreements among independent determinations exist, values were given preference (assuming all other factors to be equal) in the order dilatometry > magnetic float or vibrating tube densimetry > pycnometry.

Where data were deemed unreliable, they were still generally included in the tables for completeness but are enclosed in square brackets [ ] and were not used further. Data were so rejected because of obvious flaws in the determinations, because of calculation errors in the original report, because they flagrantly violated the ionic additivity established with reliable data (see below), or because they differed markedly from apparently reliable data The reasons for rejection of such data are usually included in the comments on the relevant solvent system in section 5 or in appropriate footnotes to the tables.

Standard partial molar volumes of electrolytes deemed reliable, that is, those for which *independent* determinations of $V°$ differ by $\leq \pm 1\ cm^3\ mol^{-1}$, were obtained by unweighted averaging. The means so obtained are classed as "recommended" and are printed in **bold** in the "selected $V°$" column. Other values may be regarded as "tentative" unless other-

Table 1. Hierarchy Used in Deriving $V°$(ion,DMSO) Values

ordinal number	electrolyte used to derive ionic value	ion	electrolyte used to derive ionic value	ion	electrolyte used to derive ionic value	ion
1	Ph_4PBPh_4	$Ph_4P^+{=}BPh_4^- + 2$	Ph_4AsBPh_4	$Ph_4As^+{=}BPh_4^- + 8$		
2	$NaBPh_4$	Na^+	Ph_4PBr	Br^-	Ph_4AsCl	$Cl^{-\,a}$
3	NaX^b	$X^{-\,b}$				
4	KX^c	$K^{+\,c}$	RbX^d	$Rb^{+\,d}$	Me_4NX^d	$Me_4N^{+\,d}$
5	$MNO_3{}^e$	$NO_3{}^{-\,e}$	$NaClO_4{}^f$	$ClO_4{}^{-\,f}$		
6	$AgNO_3$	Ag^+	$R_4NClO_4{}^g$	$R_4N^{+\,g}$	$NH_4ClO_4{}^h$	$NH_4{}^{+\,h}$
7	Bu_4NBBu_4	$BBu_4{}^-$				

[a] F^- and I^- were also obtained for this ordinal number; the latter obtained using Ph_4AsI was rejected because of doubts about the accuracy of the primary data. [b] X = Cl, Br, I; averaged with values from ordinal number 2 where appropriate. [c] Results for X = Cl, Br, I were averaged. [d] Results for X = Br, I were averaged; similarly for LiX/Li^+ and CsX/Cs^+. Other single R_4NX data were used to derive R_4N^+ (R = Et to Hp) [e] Results for M = Na, K, Rb, Cs were averaged. [f] R_4NClO_4 (R = Me, Et) data were also used and results averaged. [g] Results for R = Et to Bu averaged with values from ordinal number 4. [h] Values for M^{n+} ($n > 1$) derived from $M(ClO_4)_n$ data.

wise designated. Values obtained by additivity were not used in the averaging process. The recommended/tentative $V°$ values are rounded off to the nearest 0.1 (or 1 if appropriate) $cm^3\ mol^{-1}$, in view of the uncertainties in the data.

For many salts the only $V°$ values reported were obtained by additivity. This was most commonly because limited solubility prevented direct measurement but also because of the limited range of directly investigated salts. So as not to lose possible information, such values are included in the tables in section 5 but are printed in *italics*. Such values have not in general been classified, since it was considered that additive values obtained using the present larger database should in general be more reliable. The latter are printed in the selected $V°$ column in *italics*, with an appropriate footnote, and are always considered as "tentative".

Accurate values of $V°$ must be additive. Thus, differences in $V°$ between sets of electrolytes having a common ion should be independent of the nature of the common ion. This approach was used wherever possible to assess the quality of doubtful data. The failure of additivity to worse than $\sim \pm 2\ cm^3\ mol^{-1}$ is prima facie evidence that the data contain significant errors. But note that unless sufficient data are available it is not always possible to determine which of the $V°$ values are aberrant; see, for example, the cases of NH_4Br in MeOH and of Et_4NI in MeCN.

Ionic volumes were estimated via the TATB/TPTB extrathermodynamic assumption as described in section 3.5. Extra care was taken to derive the most reliable $V°$ values for the salts required for calculating the TATB/TPTB values (eqs 28 or 29), although this task was often rendered moot by the absence of the required data. Both TATB and TPTB are sufficiently soluble in a few solvents, so that their $V°$ values can be measured directly.[96] Unfortunately, the quality of the studies performed to date has not been sufficient to produce reliable directly determined values, and thus the additivity values have been preferred. Once the values for $V°(Ph_4(As,P)^+)$ and $V°(BPh_4^-)$ were fixed, they were then used to calculate volumes for other ions in the hierarchical manner illustrated in Table 1 for dimethylsulfoxide. Values of $V°$(ion) were calculated in the successive stages of the hierarchy, so that errors are expected to accumulate. Averaging was applied when data for more than one counterion were available for any given ion. In those solvents for which the data required for implementation of the TATB/TPTB assumption were not available, the Mukerjee method (section 3.3) was used. As shown above, this assumption usually, but not always, produces $V°$(ion) values that are consistent with the TATB/TPTB approach to within $\pm 4\ cm^3\ mol^{-1}$. The accuracy of the $V°$(ion) values is largely dependent on the validity of the extrathermodynamic assumption used to obtain them. This can ultimately be assessed only by comparison with the results obtained from other assumptions or, perhaps in the future, by appropriate theoretical calculations or realistic computer simulations.

5. Detailed Presentation of the Data

The standard partial molar volumes of electrolytes and ions mostly at 25 °C in those solvents for which sufficient information was found to justify compilation are shown in Tables 2−37. The even-numbered tables pertain to $V°$(electrolyte) while the adjacent odd-numbered tables give the corresponding $V°$(ion) values. Tables 38 and 39 list $V°$ values for electrolytes and ions in other solvents for which there were insufficient data for a separate table. For the $V°$(electrolyte) tables, the footnotes give the source of the data and the method used (see sections 2.2 and 2.3 for abbreviations) to determine the ${}^{\phi}V$ values from which the $V°$ values were obtained by extrapolation to zero concentration (section 2.4). Selected values were chosen according to the criteria discussed in section 4.2. The $V°$(ion) values in each solvent were obtained by splitting the selected $V°$(electrolyte) values into their ionic contributions by means of the methods discussed in section 3. The TPTB or TATB method (section 3.5) was used whenever the required data were available. If no such information existed, then the best alternative, usually Mukerjee's method (section 3.3), was employed. The $V°$(ion) tables also list previously reported $V°$(ion) values for comparison. These are again annotated in the footnotes.

5.1. Salt and Ion Volumes in Methanol (MeOH)

The extensive array of standard partial molar volumes of electrolytes reported in methanol (MeOH) at 25 °C is shown in Table 2. Some tests of ionic additivities are (in $cm^3\ mol^{-1}$) as follows: $V°(Br^-)$ −

Table 2. Standard Partial Molar Volumes, *V*°/(cm^3 mol^{-1}), of Electrolytes in Methanol (MeOH) at 25 °C[aa]

electrolyte	*V*° reported	*V*° selected[bb]
HCl	−1.5,[a] −2.7[b]	**−2.1**
LiCl	−3.8,[c] −4.9,[d] −4.5,[e] −4.0,[x] −5.1[z]	**−4.5**
LiBr	5.7,[f] 3.5,[g] 2.3,[x] 0.8[z]	3.1
LiI	10.7[z]	10.7
LiOMe	[−4.3][e]	
LiBBu$_4$	267.8[u]	268
NaCl	−3.3,[d] [2.0],[b] −4.5,[h] −3.8,[e] −5.5[x]	**−3.9**
NaBr	5.1,[h] 3.5[x]	**4.3**
NaI	[16.2],[f] 11.8,[d] 11.3,[g] 10.8[e]	**11.3**
NaNO$_3$	11.3[i]	11.3
NaClO$_4$	21.6[y]	21.6
NaOMe	[2.1],[b] [−8.8][e]	
NaBPh$_4$	241,[j] [245.0][u]	241
KF	−8.6,[g] −6.8[x]	**−7.6**
KCl	7.3,[k] 5.7,[g] 5.6,[e] 8.5[l]	**7.0**
KBr	15.2,[l] 15.7,[m] 13.1[x]	**14.7**
KI	21.9,[d] 20.8,[m] 21.5,[n] 20.8,[e] 22.8,[l] 22.3[x]	**21.7**
KSCN	28.2[m]	28.2
KNO$_3$	19.8[h]	*22*
KOMe	[0.6][e]	
RbCl	11.3[h]	11
RbNO$_3$	*26.1*[o]	*26*
RbOMe	[1.6][e]	
CsF	2.0[x]	2
CsCl	17.8[h]	18
CsI	32.9[h]	33
CsNO$_3$	(*32.6*)[o]	*33*
CsOMe	[1.5][e]	
NH$_4$Cl	17.1,[h] 8.1[l]	**17.5**
NH$_4$Br	20.1,[p] 20.8,[q] 22.0[r]	*25*
NH$_4$I	32.1[h]	32
NH$_4$NO$_3$	31.0,[i] 32.6[m]	31.8
AgNO$_3$	21.8[w]	21.8
Me$_4$NCl	83.7,[p] 83.0[q]	*80*
Me$_4$NBr	88.2[r]	*88*
Et$_4$NCl	142.3,[p] 140.7[q]	**141.5**
Et$_4$NBr	149.6,[p] 148.0,[q] 146.6,[r] 149.3[s]	**148.4**
Et$_4$NI	161.9,[s] 154.4[t]	*155*
Pr$_4$NBr	222.1,[p] 222.0,[q] 216.7,[r] 220.0[s]	**222.0**
Pr$_4$NI	232.6[s]	*229*
Bu$_4$NBr	286.5,[j] 285.9,[p] 286.2,[q] 285.4,[r] 286.2,[s] 287.0[x]	**286.1**
Bu$_4$NI	[300.5][s]	*293*
Pe$_4$NBr	359.5[u]	360
Hp$_4$NBr	495.7[u]	496
Et$_4$PI	156.6[t]	157
Bu$_4$PBr	302.9[u]	303
Ph$_4$PCl	277[j]	277
Ph$_4$PBr	284.9[u]	285
Ph$_4$AsCl	283[j]	283
CaCl$_2$	−55[v]	
Ca(NO$_3$)$_2$	8.7[w]	

[a] Reference 97, 20 °C. [b] Reference 98, buo. [c] Reference 15, 18 °C, pyc. [d] Reference 8, pyc. [e] Reference 99, mfl. MOMe data are original; others are recalculated from the literature. [f] Reference 10/13, dil. [g] Reference 10/1, dil. [h] Reference 80, vtd. [i] Reference 13, pyc. [j] Reference 90, buo, vtd. [k] References 8 and 9/1. [l] Reference 9. [m] Reference 11, pyc. [n] Reference 12, mfl. [o] Reference 80, add. [p] Reference 89, pyc /calculated by compilers from ρ. [q] Reference 89/1, pyc. [r] Reference 100, buo, dil. [s] Reference 101, pyc. [t] Reference 64, vtd. [u] Reference 102, vtd. [v] Reference 7, from figure, at 12.87 °C. [w] Reference 103, vtd. [x] Reference 104, vtd. [y] Reference 105, pyc. [z] Reference 53, dil. [aa] Values in square brackets [ ] are rejected. Recommended values are shown in **bold** type. Values obtained by additivity are given in *italic* type. [bb] No value was selected where electrolyte data were dubious. Values in *italics* in this column are calculated by present reviewers by additivity using the selected *V*°(ion) values in Table 3.

V°(Cl$^-$) = 7.6 (Li$^+$), 8.2 (Na$^+$), 7.7 (K$^+$); *V*°(I$^-$) − *V*°(Cl$^-$) = 15.2 (Na$^+$), 14.7 (K$^+$); *V*°(Na$^+$) − *V*°(Li$^+$) = 0.6 (Cl$^-$), 1.2 (Br$^-$); *V*°(K$^+$) − *V*°(Na$^+$) = 10.9 (Cl$^-$), 10.4 (Br$^-$), 10.4 (I$^-$), 8.5 (NO$_3^-$); *V*°(NH$_4^+$) − *V*°(K$^+$) = 10.5 (Cl$^-$), 5.5 (Br$^-$), 10.3 (I$^-$), 12.0 (NO$_3^-$); *V*°(Me$_4$N$^+$) − *V*°(K$^+$) = 77.2 (Cl$^-$), 72.7 (Br$^-$); *V*°(Et$_4$N$^+$) − *V*°(K$^+$) = 134.5 (Cl$^-$), 133.7 (Br$^-$), 140.5 (I$^-$); *V*°(Pr$_4$N$^+$) − *V*°(Et$_4$N$^+$) = 73.6 (Cl$^-$), 70.7 (Br$^-$); *V*°(Bu$_4$N$^+$) − *V*°(Et$_4$N$^+$) = 137.6 (Cl$^-$), 138.6 (Br$^-$). Comments on the reliability of the values in Table 2 now follow.

The *V*°(HCl) value reported[97] is rather uncertain, as it was obtained from $^{\phi}V$ data at $c \geq 0.41$ M. The other value of *V*°(HCl)[98] was said to have been "interpolated from the densities of methanolic HCl solutions". However, the reference cited does not contain such data. The resulting mean of the two reported values is therefore much less certain than the apparent agreement suggests. Some of the *V*°(LiCl) and *V*°(LiBr) values are from very old (1930s) determinations. Although the density and $^{\phi}V$ values were measured accurately enough, in some cases[10,15] *V*° values were obtained only from later recalculations.[1,13] Nevertheless, the difference *V*°(Br$^-$) − *V*°(Cl$^-$) = 8.2 cm^3 mol^{-1} derived from the tentatively selected mean values for the lithium salts is in good agreement with the values obtained from the sodium and potassium salts, 8.2 and 7.7 cm^3 mol^{-1}, lending credence to the selection.

Some of the reported values for the sodium halides appear to be wrong. These include a positive value for NaCl[98] and a high value for NaI (recalculated[13] from earlier data[10]). These values are rejected, since they deviate grossly from additivity requirements. Values for NaCl and NaBr listed in Table I of ref 80, cited as "other works", are wrongly reported, since they do not appear in the quoted references. They are therefore not included in the present compilation. The other values for the sodium halides are accepted, as are those for the potassium halides, since they obey the additivity requirement within ±1 cm^3 mol^{-1}. The mean values are recommended as the best available. (Note that, for KI, the dependence[9] of density on *c* has an obvious misprint: the coefficient of *c* should be 0.148096 rather than 1.48096.) The *V*° values of the nitrates of the alkali metals appear to be reliable but have not been independently confirmed. On the other hand, the methoxide values[99] appear to be beset by errors; as they do not show the expected cationic differences, they are rejected. The few values reported for rubidium and cesium salts show the expected ionic additivities, those of the nitrates having been calculated on this basis in the first place. For NH$_4$Br, two independent determinations[89,100] are in fair agreement. However, their average is ~5 cm^3 mol^{-1} lower than the value demanded by *V*°(Br$^-$) − *V*°(Cl$^-$) ≈ 8 cm^3 mol^{-1} and *V*°(I$^-$) − *V*°(Br$^-$) ≈ 6 cm^3 mol^{-1} from the alkali halide data. The *V*°(NH$_4$Cl) and *V*°(NH$_4$I) values,[80] on the other hand, conform to the difference *V*°(I$^-$) − *V*°(Cl$^-$) ≈ 14 cm^3 mol^{-1}.

The tetraalkylammonium salts are more soluble in MeOH than their alkali metal counterparts. Those *V*° values that have been determined independently,

Table 3. Standard Partial Molar Volumes, $V°/(\mathrm{cm^3\ mol^{-1}})$,[o] of Ions in Methanol (MeOH) at 25 °C, Calculated Assuming $V°(Ph_4P^+) = V°(BPh_4^-) + 2\ \mathrm{cm^3\ mol^{-1}}$

		$V°$(ion)	
ion	$V°$(electrolyte) used	selected	reported
H^+	−17 (Cl^-)	−17	−17,[a] −15[b]
Li^+	−19 (Cl^-)	−19	−18,[a] −19,[c] −18,[d] −16,[e] −21,[f] −17,[g] −14[b]
Na^+	−19 (BPh_4^-)	−19	−17,[a] −18,[c] −20,[h] −16,[d] −17,[e] −17,[u] −20,[v] −16,[w] −13,[b] −20[f]
K^+	−8 (Cl^-)	−8	−7,[a] −8,[c] −7,[d] −7,[e] −6,[f] −6,[g] −3[b]
Rb^+	−4 (Cl^-)	−4	−2,[a] 0[f]
Cs^+	3 (Cl^-), 3 (I^-)	3	5,[a] 2,[d] 5,[f] 3[g]
Ag^+	−8 (NO_3^-)		−15[g]
NH_4^+	2 (Cl^-), −2 (Br^-), 2 (I^-)	2	4,[a] 2[d]
Me_4N^+	68 (Cl^-), 65 (Br^-),	65	70,[a] 70,[i] 68[d]
Et_4N^+	125 (Br^-), 132 (I^-)	125	160,[j] 130,[a,k] 125,[h] 127,[d] 129[i]
Pr_4N^+	199 (Br^-), 203 (I^-)	199	230,[j] 202,[a] 197,[d] 198,[h] 199[i]
Bu_4N^+	263 (Br^-), 271 (I^-)	263	267,[d,l] 270,[j] 268,[a] 262,[h] 268,[i] 297[j]
Bu_4P^+	280 (Br^-)	280	284[i]
Pe_4N^+	336 (Br^-)	336	340[d]
Hp_4N^+	473 (Br^-)	473	476[d]
Bu_4P^+	281 (Br^-)	281	284[i]
Ph_4P^+	262 (Ph_4PCl, $NaBPh_4$, NaCl), 264 (Ph_4PBr, $NaBPh_4$, NaBr)	262	264,[l] 268,[c] 266,[i] 264,[d] 261[h]
Ph_4As^+	268 (Cl^-)	268	270,[l] 268[c]
Ca^{2+}	−51 (NO_3^-)		−65[g]
F^-	−1 (K^+), −1 (Cs^+)	−1	−1,[a] 0,[d] −3[f]
Cl^-	15 (Ph_4PCl)	15	13,[a] 15,[c] 16,[h] 13,[d] 12,[e] 12,[f] 12,[g] 9,[m] 9[b]
Br^-	23 (Li^+), 23 (Na^+), 23 (K^+)	23	19,[n] −9,[j] 18,[a] 19,[c] 20−22,[d] 21,[f] 17[b]
I^-	31 (Na^+), 29 (K^+)	30	2,[j] 28,[a] 30,[c] 29,[d] 32,[f] 24[b]
SCN^-	36 (K^+)	36	
NO_3^-	30 (Na^+), 28 (K^+), 30 (NH_4^+)	30	28,[a] 37[g]
ClO_4^-	41 (Na^+)	41	42[h]
BPh_4^-	260 ($NaBPh_4$, Ph_4PCl, NaCl), 261 ($NaBPh_4$, Ph_4PBr, NaBr)	260	259,[c] 257,[l] 261,[d,h] 262[i]

[a] Reference 80, uvp. [b] Reference 106, calculated from unpublished data. [c] Reference 96, TA = TB. [d] Reference 102, $V°(Br^-) = 22$ for TPTB, 20 for the model calculation. [e] Reference 108, spt, ±3. [f] Reference 86, spt, ±4. [g] Reference 93, spt. [h] Reference 105, TP = TB. [i] Reference 109, model, also 20, 40 °C. [j] Reference 101, *M*ex. [k] The reported 12.9 is obviously a misprint; the value here is obtained from the differences between columns b and d in Table 3,[80] for other ions. [l] Reference 90, *N*ex. [m] Reference 110, spt. [n] Reference 89/90, *N*ex. [o] Estimated uncertainty ±2 $\mathrm{cm^3\ mol^{-1}}$.

often by several authors, are generally in good agreement. The most extensive series (R = Me to Pe), is available for the bromides, and a plot[90] of their $V°$ values against their numbers of carbon atoms is linear. The standard error is pretty high, ±2.9 $\mathrm{cm^3\ mol^{-1}}$, mainly due to a too-high value for the tetramethylammonium bromide and a too-low value for the tetraethylammonium bromide. The slopes of the plots of n_C against $V°(R_4NX)$ for the three halide series are independent of the anion: $68.8 \pm 0.8\ \mathrm{cm^3\ mol^{-1}}$ per four methylene groups. As expected, the intercepts differ by the above-mentioned values: $V°(Br^-) - V°(Cl^-) \approx 9$, $V°(I^-) - V°(Br^-) \approx 6$, and $V°(I^-) - V°(Cl^-) \approx 15\ \mathrm{cm^3\ mol^{-1}}$, if it is accepted that $V°(Me_4NCl)$ is 7 $\mathrm{cm^3\ mol^{-1}}$ too high.

Only two values were found for divalent salts. That for $CaCl_2$, −55 $\mathrm{cm^3\ mol^{-1}}$, was derived[7] from older density data at 12.87 °C, mainly as a demonstration of the need to use the limiting law for the extrapolation of ${}^{\phi}V$ to infinite dilution. From $V°(NO_3^-) - V°(Cl^-) \approx 15\ \mathrm{cm^3\ mol^{-1}}$, established for the alkali metal and ammonium salts, and accepting the value for $Ca(NO_3)_2$, $V°(CaCl_2)$ at 25 °C should be −21 $\mathrm{cm^3\ mol^{-1}}$. This difference cannot be accounted for by the lower temperature.

The splitting of the $V°$(electrolyte) values into their individual ionic contributions was done via the reference electrolyte method (section 3.5). Values of Ph_4PCl,[90] Ph_4PBr,[102] or Ph_4AsCl[90] and $NaBPh_4$,[90,102] and the selected value for NaCl or NaBr, yielded $V°(BPh_4^-) = [V°(NaBPh_4) + V°(Ph_4PCl) - V°(NaCl)]/2 - 1$ (or $[V°(NaBPh_4) + V°(Ph_4AsCl) - V°(NaCl)]/2 - 4$, cf. section 3.5). The resulting $V°$(ion) values, calculated additively from various combinations of salts, are shown in Table 3.

The selected value for H^+ is dubious due to the uncertain status of the $V°$(HCl) values noted above. The values for the alkali metal cations and ammonium are better established and should be accurate to within the accuracy of the reference electrolyte assumption: ±2 $\mathrm{cm^3\ mol^{-1}}$ or better. Table 3 also shows values of $V°$(ion) reported by other authors. These are generally in agreement with the selected values, with some notable exceptions. The estimates,[106] based on unpublished $V°$(electrolyte) data, were obtained from eq 25 and are too positive/negative by ~5 $\mathrm{cm^3\ mol^{-1}}$ for the cations/anions. This indicates the quantitative inadequacy of this expression, if improper values of the coefficients *A* and *B* are employed. An uncertainty of ±5 $\mathrm{cm^3\ mol^{-1}}$ was assigned[90] to the intercept, $V°(Br^-)$, obtained by the *N*-extrapolation method (section 3.4). The resulting values for the other ions[90] are within this uncertainty of the selected ones. However, the values reported from application of the *M*-extrapolation method[101] (section 3.4) are ~30 $\mathrm{cm^3\ mol^{-1}}$ too large for the R_4N^+ cations and too small for Br^- and I^- and must be rejected. On the other hand, the estimates from application of the uvp method (section 3.2) are within the expected limits of error of the selected values (note that there is a misprint in the value given for Et_4N^+).[80] Since $V°(R_4NBr)$ values are better established than those of the iodides, the former have been preferred for obtaining $V°(R_4N^+)$ by means of the well established $V°(Br^-)$ value.

5.2. Salt and Ion Volumes in Ethanol (EtOH)

Data for the standard partial molar volumes at 25 °C for a large number of mostly 1:1 electrolytes in ethanol (EtOH) are given in Table 4. However, it should be noted that just a few of these values have been satisfactorily replicated, many have been obtained only via additivity, and some were taken by the compilers from a review without sighting the (inaccessible) original data. Of the results obtained from experimental data, only a few additivity tests are possible (all values in cm^3 mol$-^1$): $V°(Br^-) - V°(Cl^-) = -0.3$ (Li^+), 3.6 (Et_4N^+); $V°(CF_3SO_3^-) - V°(I^-) = 45.3$ (Na^+), 39.2 (Cs^+); $V°(I^-) - V°(Br^-) = 7.4$ (Na^+), 3.3 (Et_4N^+), 10.5 (Bu_4N^+); $V°(Et_4N^+) - V°(NH_4^+) = 128.8$ (Cl^-), 122.5 (I^-); $V°(Bu_4N^+) - V°(Et_4N^+) = 135.9$ (Br^-), 143.1 (I^-).

The $V°$ values of only four salts — LiCl, LiBr, NaI, and KI — have been independently confirmed to a sufficient level of precision such that their means can be recommended. Indeed, the limited database means that it is not possible at present to adjudicate between alternative values differing for some salts by up to 7 $cm^3\ mol^{-1}$, which is most unsatisfactory. As can be seen from the data in Table 4, most of the "selected" volumes have a rather high uncertainty and, hence, must be regarded as tentative.

For the important reference electrolyte volumes, required for implementation of the TATB or TPTB assumptions, only the unpublished values of Pang[23] for TPTB were available (Table 5). With the exception of the case of $V°(H^+)$, there is broad agreement (±2 $cm^3\ mol^{-1}$) between the present estimates of $V°$(ion) and those based on both the Mukerjee and uvp assumptions and indeed with the ionic radius-based extrapolation method of Krestov et al.[112]

Table 4. Standard Partial Molar Volumes, $V°/(cm^3\ mol^{-1})$, of Electrolytes in Ethanol (EtOH) at 25 °C[m]

	$V°$	
electrolyte	reported	selected
HCl	3.0^{a}	3.0
HBr	[*−0.4*]^{k}	*6*^{e}
LiCl	−4.4,^{b} −5.2,^{c} −5.2,^{d} [−13.0]^{l}	**−4.9**
LiBr	−4.1,^{d} −6.2^{l}	**−5.2**
LiI	3.6^{l}	3.6
$LiNO_3$	5.1,^{c} [−2.4]^{l}	5
NaCl	*4.0*^{c}	*5*^{e}
NaBr	6.1,^{c} 11.5^{d}	*9*^{e}
NaI	17.2,^{c} 15.9,^{l} 15.6,^{f} 15.9^{d}	**16.2**
$NaNO_3$	*15.3*^{c}	*16*^{e}
$NaCF_3SO_3$	61.5^{d}	61.5
$NaBPh_4$	254.8^{d}	254.8
KCl	[*12.6*]^{c}	*14*^{e}
KBr	[*15.8*]^{k}	*18*^{e}
KI	25.8,^{c} 26.4,^{f,k} 24.2^{d}	**25.5**
KNO_3	*23.9*^{c}	*25*^{e}
KOAc	42.7^{g}	42.7
RbCl	[*18.4*]^{c}	*20*^{e}
RbBr	[*20.6*]^{k}	*24*^{e}
RbI	31.6	31.6
$RbNO_3$	*29.7*^{c}	*31*^{e}
CsF	0.2^{d}	0.2
CsCl	*26.2*^{c}	*28*^{e}
CsBr	[*28.4*]^{k}	*32*^{e}
CsI	39.4^{c}	39.4
$CsNO_3$	*37.5*^{c}	*39*^{e}
$CsCF_3SO_3$	78.6^{d}	78.6
NH_4Cl	21.8^{c}	21.8
NH_4Br	[*24*]^{k}	*27*^{e}
NH_4I	35.0^{c}	35.0
NH_4NO_3	33.1^{c}	33.1
Me_4NCl	*87.9*^{k}	*87*^{e}
Me_4NBr	91.5^{f}	91.5
Me_4NI	[*102.0*]^{k}	*99*^{e}
Et_4NCl	150.6^{f}	150.6
Et_4NBr	154.2^{f}	154.2
Et_4NI	157.5,^{i} [*164.6*]^{k}	157.5
Et_4PI	158.6^{i}	158.6
Pr_4NCl	*218.7*^{k}	*218*^{e}
Pr_4NBr	222.3^{f}	222.3
Pr_4NI	*232.8*^{k}	*230*^{e}
Bu_4NCl	*286.5*^{k}	*287*^{e}
Bu_4NBr	290.1^{f}	290.1
Bu_4NI	300.6^{f}	300.6
Pe_4NCl	*353.0*^{k}	*352*^{e}
Pe_4NBr	356.6^{f}	356.6
Pe_4NI	[*367.1*]^{k}	*364*^{e}
Ph_4PBr	278.4^{d}	278.4
$SrBr_2$	3.2^{h}	3.2
$CuCl_2$	−16.4^{j}	−16.4

[a] Reference 1, method unknown. [b] From ref 1. [c] Reference 111, vtd. [d] Reference 23, vtd. [e] Calculated by the present reviewers by additivity using the $V°$(ion) values from Table 5. [f] Reference 112, bou. [g] Reference 113, pyc, in 99.6 wt % EtOH. [h] Reference 114, vtd. [i] Reference 64, vtd. [j] Reference 115, vtd, value somewhat dependent on the choice of the extrapolating equation. [k] Reference 93, review of literature data, original data not accessible. [l] Reference 53, dil. [m] Values in square brackets [ ] are rejected. Recommended values are shown in **bold** type. Values obtained by additivity are given in *italic* type.

5.3. Salt and Ion Volumes in 1,2-Ethanediol (Ethylene Glycol, EG)

Few studies of $V°$(electrolyte) values in ethylene glycol (EG) at 25 °C have been reported (Table 6), and several of the quoted values have been derived only from ionic additivities. Some tests of the expected ionic additivities based on experimental values are (in $cm^3\ mol^{-1}$) as follows: $V°(Li^+) - V°(H^+) = 3.4$ (Cl^-), 2.2 (Br^-), 4.2 (I^-); $V°(Na^+) - V°(Li^+) = 4.5$ (Cl^-), 5.4 (Br^-), 4.4 (I^-); $V°(K^+) - V°(Na^+) = 10.3$ (Cl^-), 9.1 (Br^-), 8.9 (I^-); $V°(Rb^+) - V°(K^+) = 5.8$ (Cl^-), 5.8 (Br^-), 6.1 (I^-); $V°(Cs^+) - V°(Rb^+) = 7.7$ (Cl^-), 9.0 (Br^-), 6.8 (I^-); $V°(Br^-) - V°(Cl^-) = 7.0$ (H^+), 5.8 (Li^+), 6.7 (Na^+), 5.5 (K^+), 5.7 (Rb^+), 7.0 (Cs^+); $V°(I^-) - V°(Br^-) = 9.5$ (H^+), 11.0 (Li^+), 10.0 (Na^+), 9.8 (K^+), 10.1 (Rb^+), 7.9 (Cs^+).

Most of the entries due to Sen[117] and Zana et al.[83] are in agreement to within ±1 $cm^3\ mol^{-1}$, and when they have been obtained from experimental data (rather than by additivity), their means can be recommended. Values for $V°(Et_4NX)$[118] must be rejected, because the bromide and iodide salts show wild fluctuations with temperature and because $V°(Et_4NCl)$ is higher than those of the larger halides.

The TATB assumption was employed for obtaining the $V°$(ion) values in EG (Table 7, column 3). These

Table 5. Standard Partial Molar Volumes of Ions, $V°(\mathrm{ion})/(\mathrm{cm^3\ mol^{-1}})$,[g] in Ethanol (EtOH) at 25 °C, Calculated Assuming $V°(Ph_4P^+) = V°(BPh_4^-) + 2\ \mathrm{cm^3\ mol^{-1}}$

ion	$V°$(electrolyte) used	$V°$(ion) selected	$V°$(ion) reported
H^+	−9 (Cl^-)	−9	−16[a]
Li^+	−20 (Br^-), −17 (Cl^-)	−18	−19,[a] −20,[b] −19[e]
Na^+	−6 (BPh_4^-)	−6	−10,[a] −11,[b] −10,[c] −11,[d] −6[e]
K^+	3 (I^-)	3	0,[a] −2,[b] −3,[c] 0,[d] 2[e]
Rb^+	9 (I^-)	9	6,[a] 4,[b] 7[c]
Cs^+	17 (I^-)	17	13,[a] 12,[b] 15,[c] 11[e]
NH_4^+	12 (I^-)	12	9,[a] 7,[b] 7[c]
Me_4N^+	76 (Br^-)	76	76[d]
Et_4N^+	139 (Br^-), 135 (I^-)	137	138[d]
Et_4P^+	136 (I^-)	136	
Pr_4N^+	207 (Br^-)	207	207[d]
Bu_4N^+	275 (Br^-), 278 (I^-)	276	275[d]
Pe_4N^+	341 (Br^-)	341	341[d]
Ph_4P^+	263 (Ph_4PBr, $NaBPh_4$, NaBr)	263	263[e,f]
Sr^{2+}	−27 (Br^-)	−27	
Cu^{2+}	−40 (Cl^-)	−40	
F^-	−17 (Cs^+)	−17	−11[e]
Cl^-	9 (NH_4^+), 14 (Et_4N^+)	12	13,[a] 15,[b] 12,[c] 12,[d] 13[e]
Br^-	15 (Ph_4P^+)	15	15,[a] 17,[b] 21,[c] 16,[d] 15[e]
I^-	23 (Na^+)	23	27,[a] 28,[b] 27,[c] 26,[d] 22[e]
OAc^-	40 (K^+)	40	
NO_3^-	23 (Li^+), 21 (NH_4^+)	22	24,[a] 24[c]
$CF_3SO_3^-$	68 (Na^+), 62 (Cs^+)	65	68[e]
BPh_4^-	261 (Ph_4PBr, $NaBPh_4$, NaBr)	261	261[e,f]

[a] Reference 111, uvp, based on a selected set of $V°$(ion) values. [b] Reference 111, muk. [c] Reference 111, uvp, averaged values. [d] Reference 112, ext. [e] Reference 23, TP = TB. [f] Based on data essentially the same as those of the present review. [g] Estimated uncertainty ±2 $\mathrm{cm^3\ mol^{-1}}$.

Table 6. Standard Partial Molar Volumes, $V°/(\mathrm{cm^3\ mol^{-1}})$, of Electrolytes in 1,2-Ethanediol (Ethylene Glycol, EG) at 25 °C[g]

electrolyte	$V°$ reported	$V°$ selected
HCl	12.5[a,b]	13
HBr	19.5[b]	20
HI	29.0[b]	29
LiCl	16.8,[b] 15.9[c]	**16.4**
LiBr	22.5,[d] 22.3,[b] 21.7[c]	**22.2**
LiI	33.1,[c] 33.2[b]	**33.2**
NaCl	21.5,[e] 20.2[c]	**20.9**
NaBr	28.0,[d] 28.1,[e] 26.7[c]	**27.6**
NaI	38.4,[d] 38.0,[b] 36.4[c]	37.6
$NaBPh_4$	280.3[c]	281
KCl	31.2[e]	*30*
KBr	37.8,[e] 35.6[c]	**36.7**
KI	47.8,[d] 47.5,[e] 44.1[c]	**46.5**
RbCl	36.8[e]	37
RbBr	*43.8*,[b] 41.1[c]	42.5
RbI	*53.3*,[b] 51.9[c]	**52.6**
CsF	26.2[c]	26
CsCl	44.5[e]	45
CsBr	51.5[b]	52
CsI	61.0,[b] 57.8[c]	59.4
Me_4NBr	109.9[c]	110
Et_4NCl	[215][f]	*162*
Et_4NBr	[189],[f] 168.7[c]	168.7
Et_4NI	[201][f]	*179*
Pr_4NBr	237.2[c]	237.2
Bu_4NBr	306.3[c]	306.3
Ph_4AsCl	315.4[c]	315.4

[a] Reference 116, pyc. [b] Reference 117, add. [c] Reference 83, vtd. [d] Reference 10/13, dil, calc from specific volume. [e] Reference 117, pyc. [f] Reference 118, 30 °C. [g] Values in square brackets [ ] are rejected. Recommended values are shown in **bold** type. Values obtained by additivity are given in *italic* type.

Table 7. Standard Partial Molar Volumes of Ions, $V°(\mathrm{ion})/(\mathrm{cm^3\ mol^{-1}})$,[c] in 1,2-Ethanediol (Ethylene Glycol, EG) at 25 °C, Calculated Assuming $V°(Ph_4As^+) = V°(BPh_4^-) + 8\ \mathrm{cm^3\ mol^{-1}}$

ion	$V°$(electrolyte) used	$V°$(ion) selected	$V°$(ion) reported
H^+	−11 (Cl^-), −11 (Br^-), −12 (I^-)	−11	−12[b]
Li^+	−8 (Cl^-), −9 (Br^-), −8 (I^-)	−8	−8,[b] −10[a]
Na^+	−3 (BPh_4^-)	−3	−3,[b] −5[a]
K^+	7 (Cl^-), 6 (Br^-), 6 (I^-)	6	7,[b] 4[a]
Rb^+	13 (Cl^-), 12 (Br^-), 12 (I^-)	12	12,[b] 9[a]
Cs^+	21 (Cl^-), 21 (Br^-), 18 (I^-)	21	20,[b] 16[a]
Me_4N^+	79 (Br^-)	79	
Et_4N^+	138 (Br^-)	138	
Pr_4N^+	206 (Br^-)	206	
Bu_4N^+	275 (Br^-)	275	
Ph_4As^+	292 (Ph_4AsCl, $NaBPh_4$, NaCl)	292	
F^-	5 (Cs^+)	5	10[a]
Cl^-	24 (Ph_4As^+)	24	25,[b] 26[a]
Br^-	31 (Na^+)	31	32,[b] 32[a]
I^-	41 (Na^+)	41	41,[b] 42[a]
BPh_4^-	284 (Ph_4AsCl, $NaBPh_4$, NaCl)	284	

[a] Reference 83, uvp. [b] Reference 117, muk. [c] Estimated uncertainty ±2 $\mathrm{cm^3\ mol^{-1}}$.

values are in agreement, within the likely uncertainties of the methods, with estimates using Mukerjee's method.[117] Values obtained by the uvp method[83] are somewhat lower (cations) and higher (anions).

5.4. Salt and Ion Volumes in Acetone (AC)

In acetone (AC), standard partial molar volumes at 25 °C have been reported in just three papers (Table 8). No duplicate data are available for any salt. The additivity tests (in $\mathrm{cm^3\ mol^{-1}}$) [$V°(BPh_4^-) - V°(ClO_4^-) = 231$ (Na^+), 236 (Bu_4N^+); $V°(Bu_4N^+) - V°(Na^+) = 284$ (ClO_4^-), 289 (BPh_4^-)] suggest the

Table 8. Standard Partial Molar Volumes, $V^{\circ}/(\mathrm{cm^3\ mol^{-1}})$, of Electrolytes in Acetone (Propanone, AC) at 25 °C[e]

electrolyte	reported V°	electrolyte	reported V°
LiBr	−37[a]	Et_4PI	167.9[c]
LiI	−31[a]	Pr_4NClO_4	218[b]
$LiNO_3$	−35[a]	Bu_4NCl	263[b]
NaI	−19[a]	Bu_4NClO_4	288[b]
$NaClO_4$	4[b]	Bu_4NBPh_4	524[b]
$NaBPh_4$	235[b]	Ph_4PCl	247[b]
Et_4NI	155.8[c]	$Cu(dmp)_2ClO_4$[d]	349[b]
Et_4NClO_4	145[b]		

[a] Reference 83, dil. [b] Reference 105, pyc. [c] Reference 64, vtd. [d] dmp = 2,9-dimethyl-1,10-phenanthroline. [e] All values are unconfirmed.

Table 9. Standard Partial Molar Volumes of Ions, $V^{\circ}(\mathrm{ion})/(\mathrm{cm^3\ mol^{-1}})$,[b] in Acetone (Propanone, AC) at 25 °C, Calculated Assuming $V^{\circ}(Ph_4P^+) = V^{\circ}(BPh_4^-) + 2$ cm^3 mol^{-1}

		V°(ion)	
ion	V°(electrolyte) used	selected	reported
Li^+	−62 (I^-)	−62	
Na^+	−18 (BPh_4^-)	−18	−19[a]
Et_4N^+	125 (ClO_4^-)	125	127[a]
Et_4P^+	137 (I^-)	137	
Pr_4N^+	198 (ClO_4^-)	198	200[a]
Bu_4N^+	271 (BPh_4^-), 271 (Cl^-)	271	270[a]
Ph_4P^+	255 (Ph_4PCl, Bu_4NBPh_4, Bu_4NCl)	255	254[a]
$Cu(dmp)_2^+$	329 (ClO_4^-)	329	331[a]
Cl^-	−8 (BPh_4^-)	−8	−7[a]
Br^-	25 (Li^+)	25	
I^-	31 (Et_4N^+)	31	
NO_3^-	27 (Li^+)	27	
ClO_4^-	17 (Bu_4N^+), 22 (Na^+)	20	18[a]
BPh_4^-	253 (Ph_4PCl, Bu_4NBPh_4, Bu_4NCl)	253	254[a]

[a] Reference 23, TP = TB, based on the same values presented in Table 8. [b] Estimated uncertainty ±2 cm^3 mol^{-1}.

reported values are consistent only to within 5 cm^3 mol^{-1}. All the V° values in Table 8 are considered as tentative in the absence of duplicate data.

Ionic volumes in AC based on the TPTB assumption are listed in Table 9. In the absence of a more extensive database, little can be said about these values at this time except that $V^{\circ}(Li^+)$ appears to be rather too negative, even though it was derived from what would be expected to be reliable dilatometric data.[53] Not surprisingly, the present V°(ion) values agree (to within 1 cm^3 mol^{-1}) with those reported by Pang, based on an equal split of V°(TPTB).[23]

5.5. Salt and Ion Volumes in Formic Acid (HCOOH)

Table 10. Standard Partial Molar Volumes, $V^{\circ}/(\mathrm{cm^3\ mol^{-1}})$, of Electrolytes in Formic Acid (HCOOH) at Various Temperatures[e]

	V°	
electrolyte	reported	selected
HCl	28.3[a]	28.3
$LiHCO_2$	[22.7][b]	
NaCl	15.5[a,c]	15
NaBr	20.4[a,c]	20
NaI	31.5[a,c]	31
$NaHCO_2$	[18.3][b]	18
KCl	20.1,[a] 18.5[c]	**19.4**
KBr	25.0,[a] *23.4*[d]	24.2
KI	36.1,[a] 34.5[c]	35.3
$KHCO_2$	[21.5][b]	22
RbCl	28.3,[a] 28.3[c]	28.3
RbBr	33.2,[a] *33.4*[d]	33.3
RbI	44.5[c]	44
CsCl	*33.4*,[a] 33.4[c]	33.4
CsBr	*38.3*,[a] *38.4*[d]	38.4
CsI	49.5[c]	49
$Ca(HCO_2)_2$	[28.0][b]	
$Ba(HCO_2)_2$	[28.1][b]	

[a] Reference 117, pyc, add, 25 °C. [b] Reference 119, method?, 30 °C. [c] Reference 120, method?, 25 °C. [d] Reference 120, add, 25 °C [e] Values in square brackets [ ] are rejected. Recommended values are shown in **bold** type. Values obtained by additivity are given in *italic* type.

Table 11. Standard Partial Molar Volumes of Ions, $V^{\circ}(\mathrm{ion})/(\mathrm{cm^3\ mol^{-1}})$,[d] in Formic Acid (HCOOH), Calculated According to Mukerjee's Method

		V°(ion)	
ion	V°(electrolyte) used	selected	reported
H^+	9 (Cl^-)	9	9[a]
Li^+	1 (HCO_2^-)		
Na^+	−3 (Cl^-), −4 (Br^-)	−4	−4,[a] −20,[d] 6[c]
K^+	0 (Cl^-), 0 (I^-)	0	1,[a] −17,[b] 9[c]
Rb^+	9 (Cl^-)	9	9,[a] 19[c]
Cs^+	14 (Cl^-)	14	14,[a] 24[c]
Ca^{2+}	−16 (HCO_2^-)		−10[b]
Ba^{2+}	−16 (HCO_2^-)		−10[b]
Cl^-	19 (K^+), 19 (Rb^+), 19 (Cs^+)	19	19,[a] 9[c]
Br^-	24 (K^+), 24 (Rb^+), 24 (Cs^+)	24	24,[a] 15[c]
I^-	35 (K^+), 35 (Rb^+), 35 (Cs^+)	35	35,[a] 25[c]
HCO_2^-	22 (Na^+), 22 (K^+)	22	38[b]

[a] Reference 117, muk [b] Reference 119, assuming $V^{\circ}(HCO_2^-) = V^{\circ}(HCOOH)$. [c] Reference 120, assuming $V^{\circ}(K^+)/V^{\circ}(Cl^-) = \lambda^{\circ}(K^+)/\lambda^{\circ}(Cl^-)$. [d] Estimated uncertainty ±4 cm^3 mol^{-1}.

The V° values reported for anhydrous formic acid (HCOOH) at 25 °C are shown in Table 10. Only one source[117] gave the experimental method, and the $^{\phi}V$ data were reported only in the Supplementary Material, which was not being made available on the Web at that time. The V°(ion) values for HCOOH were reported in the same table as those for ethylene glycol (EG) solutions.[117] It was therefore assumed that the same electrolytes (except the lithium salts) reported for EG were also used for formic acid, permitting reconstruction of the V°(electrolyte) in HCOOH data from additivity. The data for the formates[119] include the values $V^{\circ}(LiHCO_2) > V^{\circ}(KHCO_2)$, which is highly unlikely and suggests ion-pairing effects may have been present. V° values for alkali metal chlorides and iodides were determined experimentally.[120] For the bromides, only that of sodium was so obtained, with the other reported values being calculated from additivity.

Sen[117] also derived V°(ion) values using Mukerjee's method (Table 11). From the discussion in section 3.3, these estimates are probably reliable to ±4 cm^3 mol^{-1}, but they are not confirmed. The assumption[120] that $V^{\circ}(K^+)/V^{\circ}(Cl^-) = \lambda^{\circ}(K^+)/\lambda^{\circ}(Cl^-)$ leads to values of cations/anions that are higher/lower by ~10 cm^3 mol^{-1}. The assumption applied to the formates, namely that $V(HCO_2^-) = V(HCOOH)$,[119] is unreliable,

Table 12. Standard Partial Molar Volumes, V°/(cm^3 mol^{-1}), of Electrolytes in Ethylene Carbonate (EC) at 40 °C[e]

electrolyte	reported V°	electrolyte	reported V°
$LiClO_4$	43.4[a]	Pr_4NClO_4	265.3[a]
$LiPF_6$	[14.6][a,c]	Bu_4NI	323.6[b,d]
$LiCF_3SO_3$	74.2[a]	Bu_4NClO_4	332.5[a]
NaI	44.4[d]	Pe_4NI	392.6[b,d]
KI	47.4[d]	Hx_4NI	461.4[b,d]
Et_4NI	183.9[b,d]	Hx_4NClO_4	467.7[a]
Et_4NClO_4	197.4[a]	Hp_4NI	530.6[b,d]
Pr_4NI	254.5[b,d]		

[a] Reference 41, vtd. [b] Reference 121, vtd, also 50−70 °C. [c] Probably a misprint. [d] Reference 122, dil, also 50 to 80 °C. [e] All values are unconfirmed. Values in square brackets [ ] are rejected.

Table 13. Standard Partial Molar Volumes of Ions, V°(ion)/(cm^3 mol^{-1}),[b] in Ethylene Carbonate (EC) at 40 °C[a]

ion	V°(electrolyte) used	selected V°(ion)
Li^+	5 (ClO_4^-)	5[a]
Na^+	14 (I^-)	14
K^+	17 (I^-)	17
Et_4N^+	159 (ClO_4^-), 154 (I^-)	159[a]
Pr_4N^+	227 (ClO_4^-), 225 (I^-)	227[a]
Bu_4N^+	294 (ClO_4^-), 294 (I^-)	294[a]
Pe_4N^+	363 (I^-)	363
Hx_4N^+	430 (ClO_4^-), 431 (I^-)	430[a]
I^-	30 (Bu_4N^+)	30
ClO_4^-	39 (Bu_4N^+)	38[a]
$CF_3SO_3^-$	69 (Li^+)	69[a]

[a] Identical values based on the same data reported in ref 41. [b] Obtained by *N*-extrapolation, uncertainty unknown.

since it ignores the expected considerable electrostriction of the solvent due to the charge of the anion.

5.6. Salt and Ion Volumes in Ethylene Carbonate (EC)

The V° values for electrolytes in ethylene carbonate (EC) at 40 °C, from two sources only, are shown in Table 12. Unfortunately, the salts for which the data were reported differed in the two studies, so none of the volumes are confirmed. The very low value reported for $LiPF_6$, 14.6 cm^3 mol^{-1}, is probably a misprint, since in PC $V^\circ(LiPF_6) \gg V^\circ(LiClO_4)$.[41] The additivity test $V^\circ(ClO_4^-) - V^\circ(I^-)$ for the tetraalkylammonium salts, from refs 41 and 121, respectively, shows diminishing values as the alkyl chains get longer. The V°(ion) values calculated according to the *N*-extrapolation method[41] are shown in Table 13 but are not considered reliable due to the shortcomings of this method (section 3.4).

5.7. Salt and Ion Volumes in Propylene Carbonate (PC)

The numerous V° data available for electrolytes in propylene carbonate (PC) at 25 °C are shown in Table 14. Tests of the expected ionic additivities are (in cm^3 mol^{-1}) as follows: $V^\circ(ClO_4^-) - V^\circ(Cl^-) = 28.3$ (Et_4N^+), 30.9 (Pr_4N^+); $V^\circ(ClO_4^-) - V^\circ(Br^-) = 21.8$ (Li^+), 22.0 (Et_4N^+), 22.2 (Pr_4N^+); $V^\circ(ClO_4^-) - V^\circ(I^-) = 11.0$ (Na^+), 9.1 (K^+), 11.4 (Et_4N^+), 12.4 (Pr_4N^+); $V^\circ(I^-) - V^\circ(Cl^-) = 17.5$ (Na^+), 16.9 (Et_4N^+), 18.5 (Pr_4N^+); $V^\circ(Na^+) - V^\circ(Li^+) = 4.3$ (ClO_4^-), 4.2 ($CF_3SO_3^-$); $V^\circ(K^+) - V^\circ(Na^+) = 10.3$ (I^-), 7.2 (ClO_4^-), 4.7 ($CF_3SO_3^-$); V°-

Table 14. Standard Partial Molar Volumes, V°/(cm^3 mol^{-1}), of Electrolytes in Propylene Carbonate (PC) at 25 °C[o]

	V°	
electrolyte	reported	selected
LiBr	15.3,[a] 15.3[b]	**15.3**
$LiClO_4$	36.8,[a] 38.8,[c] 37.2,[b] 36.2,[d] 36.3,[j] 36.7,[k] 36.1[l]	**37.1**
$LiBF_4$	35.5[i]	35.5
$LiAsF_6$	64.4,[c] 62.8[e]	**63.6**
$LiPF_6$	62.4[d]	62.4
$LiCF_3SO_3$	74.1[d]	*71*
NaI	[45.4],[f] 27.7,[g] 31.9,[a] 32.0[j]	30.5
$NaClO_4$	41.3,[a] 41.8,[c] 41.4,[j] 41.0[l]	**41.5**
$NaCF_3SO_3$	78.3[c]	78
$NaBPh_4$	281.5,[a] 282.2,[h] 281.8,[c] 281,[g] 280[l]	**281.4**
KI	[47.4],[f] 40.3,[g] 38.8,[a] 39.5,[j] [86.7][n]	**39.5**
$KClO_4$	48.8,[a] 48.3,[j] [53.4][l]	48.6
KCF_3SO_3	83.0[c]	*87*
$KBPh_4$	[295][g]	*291*
RbI	43.2,[a] 43.6,[j] [88.8][n]	43.4
$RbClO_4$	[58.0][l]	*55*
CsI	49.8,[a] 50.0[j]	49.9
$CsClO_4$	61.7[l]	61.7
$AgClO_4$	36.3[l]	36.3
Me_4NClO_4	126.9,[a] 128.0,[d] 126.9[j]	**127.5**
Et_4NCl	159.9,[a] 159.9[j]	159.9
Et_4NBr	166.2,[a] 166.1,[h] 165.2,[j] [161.8],[i] 166.2[m]	**165.9**
Et_4NI	175.2,[f] 178.3[a]	176.8
Et_4NClO_4	188.0,[a] 188.4,[d] 188.0[j]	**188.2**
Pr_4NCl	228.2,[a] 228.0[j]	228.1
Pr_4NBr	235.6,[a] 235.6,[j] 233.3,[i] 235.7[m]	**234.8**
Pr_4NI	246.7[f]	*245*
Pr_4NClO_4	259.1[d]	*257*
Bu_4NBr	304.2,[a] 304.5,[h] 303.8,[j] [307.1],[i] 304.1,[m] [310][n]	**304.9**
Bu_4NI	316.0,[f] 316.1,[h] [323][n]	**316**
Bu_4NClO_4	[333.9][d]	*327*
Bu_4NBH_4	565.8[h]	566
Bu_4NBBu_4	588.7[h]	589
Bu_4NBPh_4	[542.1][i]	*567*
Pe_4NBr	373.5,[a] 372.0[i]	**372.8**
iPe_4NBr	372.9,[a] 373.0[j]	373.0
Pe_4NI	[383.9][f]	*388*
Hx_4NBr	450.1,[i] [442.2][m]	450
Hx_4NClO_4	468.3[d]	468
Hp_4NBr	[520.5][i]	*513*
Hp_4NI	519.1[f]	519
Ph_4PBr	311.7[a]	311.7
Ph_4AsCl	308.0[a]	308
Ph_4AsBr	308[g]	*318*
Ph_4AsI	322,[g] 327[l]	324
$Ph_4AsCF_3SO_3$	371.5[c]	*372*
$Mg(ClO_4)_2$	56.9[l]	57
$Ca(ClO_4)_2$	64.8[l]	65
$Sr(ClO_4)_2$	65.2[l]	65
$Ba(ClO_4)_2$	72.0[l]	72
$Pb(ClO_4)_2$	67.8[l]	68

[a] Reference 84, vtd. [b] Reference 123, vtd. [c] Reference 38, vtd, $^{\phi}V$ values at 0.05 mol dm^{-3}. [d] Reference 41, vtd, 40 °C. [e] Reference 107, vtd (also 10, 40 °C), V° calculated by reviewers from density data. [f] Reference 124, pyc, extrapolated from 36 to 70 °C. [g] Reference 96, vtd. [h] Reference 125, also 10−30 °C. [i] Reference 126, pyc (also data at 35 and 45 °C), V° calculated by reviewers from density data. [j] Reference 72, recalculated literature data with ion pairing according to the Bjerrum model; not taken as an independent confirmation. [k] Reference 127, vtd. [l] Reference 128, pyc. [m] Reference 42, vtd. [n] Reference 53, dil. [o] Values in square brackets [ ] are rejected. Recommended values are shown in **bold** type. Values obtained by additivity are given in *italic* type.

Table 15. Standard Partial Molar Volumes of Ions, $V°$(ion)/(cm^3 mol^{-1}),[g] in Propylene Carbonate (PC) at 25 °C, Calculated Assuming $V°(Ph_4As^+) = V°(BPh_4^-) + 8 = V°(Ph_4P^+) + 6$ cm^3 mol^{-1}

		$V°$(ion)	
ion	$V°$(electrolyte) used	selected	reported
Li^+	−11 (Br^-), −7 (ClO_4^-)	−9	−5,[a] 5,[b] −10,[d] 9[e]
Na^+	−2 (BPh_4^-)	−2	−16,[c] −2,[a] −5[d]
K^+	7 (I^-), 5 (ClO_4^-), 3 ($CF_3SO_3^-$)	7	3,[a] 8[d]
Rb^+	11 (I^-)	11	12[d]
Cs^+	17 (I^-)	17	16[d]
Ag^+	−8 (ClO_4^-)	−8	−9[d]
Me_4N^+	84 (ClO_4^-)	84	94[b]
Et_4N^+	140 (Br^-), 145 (I^-), 144 (ClO_4^-)	143	140,[c] 157,[b] 160,[e] 161[f]
Pr_4N^+	210 (Br^-), 215 (I^-), 215 (ClO_4^-)	213	228,[b] 230,[e] 230[f]
Bu_4N^+	278 (Br^-), 284 (I^-), 290 (ClO_4^-)	283	278,[c] 303,[b] 298,[e] 299[f]
Pe_4N^+	348 (Br^-), 340 (I^-)	344	368[f]
iPe_4N^+	347 (Br^-)	347	
Hx_4N^+	424 (ClO_4^-, Br^-)	424	437,[b] 436,[e] 438[f]
Hp_4N^+	487 (I^-)	487	
Ph_4P^+	286 (Ph_4PBPh_4, Br^-)	286	
Ph_4As^+	292 (Ph_4AsBPh_4, $Ph_4AsCF_3SO_3$), 293 (Ph_4AsI)	292	292[a]
Mg^{2+}	−31 (ClO_4^-)	−31	−34[d]
Ca^{2+}	−23 (ClO_4^-)	−23	−26[d]
Sr^{2+}	−23 (ClO_4^-))	−23	−26[d]
Ba^{2+}	−16 (ClO_4^-)	−16	−19[d]
Pb^{2+}	−20 (ClO_4^-)	−20	−23[d]
Cl^-	17 (Et_4N^+), 15 (Pr_4N^+)	16	
Br^-	26 (Ph_4P^+)	26	26,[c] 6[e]
I^-	33 (Na^+)	33	38,[c] 32[d]
ClO_4^-	44 (Na^+)	44	52,[a] 31,[b] 46,[d] 28[e]
PF_6^-	72 (Li^+)	72	57[b]
AsF_6^-	72 (Li^+)	72	77[a]
$CF_3SO_3^-$	80 (Ph_4As^+), 80 (Na^+)	80	88,[a] 69[b]
BBu_4^-	306 (Bu_4N^+)	306	312[c]
BPh_4^-	284 (Ph_4PBPh_4, Ph_4AsBPh_4), 285 (Ph_4AsI)	284	288,[c] 284[a]

[a] Reference 38, TA = TB. [b] Reference 41, *N*ex, at 40 °C. [c] Reference 84, uvp. [d] Reference 128, TA = TB. [e] Reference 96, *M*ex. [f] Reference 129, *M*ex. [g] Estimated uncertainty ±2 cm^3 mol^{-1}.

$(Pr_4N^+) - V°(Et_4N^+) = 68.3$ (Cl^-), 68.9 (Br^-), 69.9 (I^-), 70.9 (ClO_4^-); $V°(Bu_4N^+) - V°(Pr_4N^+) = 70.1$ (Br^-), 69.4 (I^-), 74.8 (ClO_4^-). The following paragraph contains comments on the reliability of the values in Table 14.

PC has a reasonably high permittivity ($\epsilon = 66.1$ at 25 °C), so relatively little ion pairing of electrolytes is expected. Rather more attention has been paid to lithium salts than for other solvents due to the use of PC in Li batteries. When more than a single reported value is available, the agreement between them is good. For other alkali metal salts, some strong deviations occur, as for NaI and KI,[124] whose values were obtained by a necessarily approximate extrapolation of reported data at 35 to 70 °C. The values for NaI reported by other authors are in poorer agreement than desirable, but additivity, established using other sodium and iodide salts, suggests the average value is reasonable. No confirmation exists for the RbI and CsI values (the second set of entries in Table 14 for these salts is merely a recalculation of earlier data). For the tetraalkylammonium salts, wherever there is more than one entry, the agreement is good. The data for tetraethyl- to tetraheptylammonium bromide,[126] when plotted against their relative molar masses, fall near but not on a straight line. Those from ref 72 deviate by not more than 0.7 cm^3 mol^{-1} from linearity.

There are data for several tetraphenylarsonium salts and for one tetraphenylphosphonium salt as well as concordant values for $NaBPh_4$ and the relevant sodium salts required for the TATB and TPTB assumptions to be applied. When the necessary sodium salt value was not available, it was obtained by additivity using $NaClO_4$ and the relevant lithium or tetraethylammonium salts. The $V°$(ion) values obtained from this splitting of $V°$(electrolyte) are shown in Table 15. Agreement with the values obtained by the uvp method[84] is not particularly good, and the values obtained by the *N*-extrapolation method[41] are systematically and considerably too high for the cations and too low for the anions. This cannot be ascribed to the temperature employed (40 °C),[41] as the corresponding $V°$(electrolyte) values do not differ appreciably from the 25 °C values.

5.8. Salt and Ion Volumes in Acetonitrile (MeCN)

The standard partial molar volumes of electrolytes in acetonitrile (MeCN) at 25 °C are shown in Table 16. Some tests of the expected ionic additivities are (in cm^3 mol^{-1}) as follows: $V°(ClO_4^-) - V°(Cl^-) = 29.5$ (Na^+), 31.3 (Et_4N^+); $V°(ClO_4^-) - V°(Br^-) = 25.2$ (Li^+), 26.5 (Et_4N^+), 25.4(Pr_4N^+); $V°(ClO_4^-) - V°(I^-) = 11.2$ (Na^+), 11.2 (Et_4N^+, 156.0 value); $V°(I^-) - V°(Cl^-) = 18.3$ (Na^+), 19.7 (Et_4N^+), 21.7 (Ph_4As^+); $V°(Na^+) - V°(Li^+) = 0.6$ (I^-), 0.2 (ClO_4^-); $V°(K^+) - V°(Na^+) = 11.4$ (I^-), 15.5 (BPh_4^-); $V°(Pr_4N^+) - V°(Et_4N^+) = 72.9$ (Br^-), 69.8 (I^-, 165.1 value), 71.8 (ClO_4^-); $V°(Bu_4N^+) - V°(Et_4N^+) = 139.3$ (Br^-), 140 (I^-, 165.1 value), 140.6 (ClO_4^-). The following paragraphs contain comments on the reliability of the values shown in Table 16.

Table 16. Standard Partial Molar Volumes, $V°/(cm^3\ mol^{-1})$, of Electrolytes in Acetonitrile (MeCN) at 25 °C[s]

electrolyte	$V°$ reported	$V°$ selected
LiBr	−9.9,[a] [−4.9],[b] [−24.1],[i] [−4.8],[m] −10[n]	−9.9
LiI	4.9,[c] [1.0][n]	5
$LiClO_4$	14.9,[a] 20.8,[d] 15.3,[b] 14.0[i]	**15.3**
$LiAsF_6$	44.2,[e] 49.2[d]	44.2
NaCl	−12[f,r]	*−14*
NaI	[−6.4],[g] [7.3],[c] 4.7,[a] [11],[f] 4.5,[e] 3.8,[i] 4.0,[n] 4[o]	**4.3**
NaSCN	8.8,[a] 5.9,[i] [2][o]	7.4
$NaNO_3$	0[f]	*−2*
$NaClO_4$	16.9,[a] 21.0,[d] 14.0[i]	15.5
$NaCF_3SO_3$	60.8[d]	*56*
$NaBPh_4$	255,[c] 255.6,[a] 261.0[d]	**255.5**
KI	15.7,[c] 15.6,[a] 14.8[i]	**15.7**
KSCN	19.7,[a] 19.7,[e] 16.6[i]	**18.7**
KCF_3SO_3	68.5[d]	64
$KBPh_4$	[271][c]	*264*
RbI	18.9,[a] 17.7[i]	**18.3**
CsI	26,[a] 26.8[i]	**26.4**
NH_4SCN	29.3[e]	29.3
$CuNO_3$	−15[f]	−15
$AgNO_3$	−3,[f] −6.4[h]	−4.7
$EtNH_3NO_3$	27.0,[l] 33,[o] 36.0[i]	32
Et_4NCl	136.3,[a] 135.4[i]	**135.9**
Et_4NBr	140.8,[a] 140.8,[j] 140.4,[e] 139.6,[i] 140.6[q]	**140.7**
Et_4NI	165.1,[j] 156.0,[a] 165.5,[p] 154.7[i]	*157*
Et_4NClO_4	166.7,[e] 167.7,[a] 166.5[i]	**167.2**
Pr_4NBr	214.7,[j] 212.5,[a] 213.7,[e] 211.0,[i] 212.8[q]	**213.6**
$PrNH_3Br$	51	51
Pr_4NI	234.9[j]	*231*
Pr_4NClO_4	238.7[e]	239
Bu_4NBr	[286.1],[j] 280.6,[a] 280.8,[e] 279,[o] 278.7,[i] 280.9[q]	**280.0**
Bu_4NI	[305.0][j]	*301*
Bu_4NClO_4	307.2,[e] 308.3[k]	**307.8**
Bu_4NBF_4	307.2[e]	307
Bu_4NBPh_4	549.5[k]	550
Pe_4NBr	350.7,[a] 349.5,[i] 351.0	**350.4**
iPe_4NBr	351.2[a]	351
Hx_4NBr	422.5	423
Hp_4NBr	492.2	492
Et_4PI	169.2[p]	169
Ph_4PBr	281.2[a]	281
Ph_4AsCl	285,[c] 283.6[a]	284.3
Ph_4AsBr	292,[c] 289.0[a]	290.5
Ph_4AsI	305,[c] 307[f]	306
Ph_4AsNO_3	296[f]	296
$Ph_4AsCF_3SO_3$	353.5[d]	*354*

[a] Reference 82, vtd. [b] Reference 123, vtd. [c] Reference 96, vtd. [d] Reference 38, vtd, ${}^{\phi}V$ at 0.05 M; not included in mean. [e] Reference 55, dil. [f] Reference 130, vtd. [g] Reference 134/1, dil. [h] Reference 103, vtd. [i] Reference 72, method not reported, probably vtd. [j] Reference 101, pyc. [k] Reference 131, vtd, also 20, 30 °C. [l] Reference 132, vtd. [m] Reference 127. [n] Reference 53, dil. [o] Reference 30, applying the Bjerrum association model, values read from figure. [p] Reference 64, vtd. [q] Reference 133, pyc. [r] Additive value? (NaCl not soluble in MeCN). [s] Values in square brackets [ ] are rejected. Recommended values are shown in **bold** type. Values obtained by additivity are given in *italic* type.

The value for $V°$(LiBr) should be more negative than -4.9 cm^3 mol^{-1}(ref 123) or -4.8 cm^3 mol^{-1} (ref 127) but certainly not as low as -24.1 cm^3 mol^{-1};[72] additivity suggests a value of -9.9 cm^3 mol^{-1}.[82] Additivity also indicates that the values of Atkins et al.[38] are systematically 5 cm^3 mol^{-1} too large. This is mostly because they are ${}^{\phi}V$ values determined at 0.05 M. In common with other solvents of relatively high compressibility, the electrostriction in MeCN is large. Correction of ${}^{\phi}V$ to infinite dilution using eq 12 predicts a decrease of 3 cm^3 mol^{-1}, accounting for most of the discrepancy. The negative value of $V°$(NaI) quoted in ref 1 is obviously wrong. Although solution densities were reported in the original paper,[134] at $c \geq 0.13$ M, extrapolation of the four lowest concentrations using Masson's expression, eq 6, yields a positive intercept of 4.7 cm^3 mol^{-1}. On the other hand, the value of 11 cm^3 mol^{-1} for $V°$(NaI)[130] is definitely too high. Agreement between the extensive list of older $V°$ values[82] and the more recent ones[72] is fair, and the mean values can be taken as recommended. It should be noted that in this recent publication,[72] improving on and correcting earlier reported values,[30] electrolyte association was taken into account in the extrapolation of ${}^{\phi}V$ to zero concentration. Unfortunately, only the final results, and not the plotted data and their extrapolation, are given.

The solubilities of alkali metal chlorides in MeCN are rather low, and so only a few $V°$ values are available. Additivity using more soluble salts yields $V°(I^-) - V°(Cl^-) = 19.6 \pm 2.0$ cm^3 mol^{-1}. This difference leads to -14 cm^3 mol^{-1} for NaCl, compatible with the reported value[130] of -12 cm^3 mol^{-1}. A decision between the two sets of values for $V°(Et_4NI)$ is difficult. The $V°(I^-) - V°(Cl^-)$ difference with the selected value for $V°(Et_4NCl)$ favors 155.5 cm^3 mol^{-1} rather than the higher values of 165.1[101] or 165.5[64] cm^3 mol^{-1}. On the other hand (all values in cm^3 mol^{-1}), the differences $V°(I^-) - V°(Br^-)$, which are 15.2 ± 0.3 for the Li^+ and Ph_4As^+ salts but 21.4 ± 0.2 for the Pr_4N^+ and Bu_4N^+ salts, do not help: with the former suggesting 155.5 and the latter 162.1 for $V°(Et_4NI)$.

The results of splitting of $V°$(electrolyte) values into their ionic contributions according to the TATB assumption are shown in Table 17. The availability of $V°$ data for five TA^+ salts, one TP^+ salt, two TB^- salts, and the corresponding alkali metal salts permits many combinations to be tested for additivity and provides a sound basis for implementation of the TATB and TPTB assumptions. Apart from the value of $V°(KBPh_4)$, which is somewhat too large, the other data produce convergent $V°$(ion) values, which are within the ±2 cm^3 mol^{-1} thought to be associated with the TATB assumption.

The estimates of $V°$(ion) obtained by the *M*-extrapolation method[101] are considerably (20−30 cm^3 mol^{-1}) larger than the values obtained using other assumptions and are considered unreliable. Other reported $V°$(ion) values are close to the present TATB-based numbers. Surprisingly, those based on $V°(TA^+) = V°(TB^-)$[38,96] are in better agreement than the expected ±4 cm^3 mol^{-1}. The ratio $V°(Bu_4N^+)/V°(BPh_4^-) = 0.992$ obtained in MeCN according to the TPTB assumption[131] is the same as that found by these authors in many other non-hydrogen-bonded solvents, so this ratio was used in MeCN too. However, the ratio arising from the TATB assumption is 1.018, so that reliance on the constancy of this ratio is not warranted.

Table 17. Standard Partial Molar Volumes of Ions, $V°$(ion)/($cm^3\ mol^{-1}$),[g] in Acetonitrile (MeCN) at 25 °C, Calculated Assuming $V°(Ph_4As^+) = V°(BPh_4^-) + 8\ cm^3\ mol^{-1}$

		$V°$(ion)	
ion	$V°$(electrolyte) used	selected	reported
Li^+	−20 (Br^-), −20 (I^-)	−20	−20,[a] −23,[b] −16[c]
Na^+	−17 (BPh_4^-), −15 (NO_3^-)	−17	−18,[a] −21,[b] −16,[c] −15[d]
K^+	−9 (I^-), −2 (BPh_4^-), −4 ($CF_3SO_3^-$)	−9	−9,[a] −11,[b] −9[c]
Rb^+	−6 (I^-)	−6	−7[b]
Cs^+	1 (I^-)	1	0[b]
Cu^+	−30 (NO_3^-)	−30	
Ag^+	−20 (NO_3^-)	−20	−18[d]
NH_4^+	0 (SCN^-)	0	
Et_4N^+	133 (Cl^-), 131 (Br^-), 133 (ClO_4^-)	132	[165],[e] 130[b]
Pr_4N^+	204 (Br^-), 210 (I^-), 205 (ClO_4^-)	206	[237],[e] 202[b]
Bu_4N^+	273 (Br^-), 280 (I^-), 274 (ClO_4^-)	276	[308],[e] 270,[b] 281[f]
Pe_4N^+	341 (Br^-)	341	340[b]
iPe_4N^+	341 (Br^-)	341	340[b]
Ph_4P^+	271 (Br^-)	271	270[b]
$Ph4As^+$	280 (Ph_4AsCl, NaCl), 282 (Ph_4AsI, NaI), 280 (Ph_4AsNO_3, $NaNO_3$), 278 ($Ph_4AsCF_3SO_3$, $NaCF_3SO_3$), 282 ($Ph_4AsCF_3SO_3$, KCF_3SO_3); all with $NaBPh_4$	281	283,[a] 277,[c] 281[d]
Cl^-	3 (Ph_4As^+)	3	6,[b] 2,[a] 3[d]
Br^-	10 (Ph_4As^+)	10	[−27],[e] 9,[a] 11[b]
I^-	25 (Ph_4As^+)	25	[3],[e] 25,[a] 26[b]
SCN^-	29 (K^+)	29	30[b]
NO_3^-	15 (Ph_4As^+)	15	15[d]
ClO_4^-	34 (Bu_4N^+), 35 (Li^+)	34	38,[b] 37,[c] 35[f]
BF_4^-	31 (Bu_4N^+)	31	
AsF_6^-	64 (Li^+)	64	65[c]
$CF_3SO_3^-$	73 (Ph_4As^+)	73	77[c]
BPh_4^-	273 (average value using the combinations listed under Ph_4As^+)	273	274,[a] 277,[b] 273,[d] 283[f]

[a] Reference 96, TA = TB. [b] Reference 82, uvp. [c] Reference 38, TA = TB. [d] Reference 103, TATB. [e] Reference 101, *M*ex. [f] Reference 131, TPTB (also values for 20, 30 °C). [g] Estimated uncertainty ±2 $cm^3\ mol^{-1}$.

It should be noted that many of the "selected" values in Table 17 are based on only one $V°$(electrolyte) determination and thus must be used with due care.

5.9. Salt and Ion Volumes in Formamide (FA)

The molar volumes of salts in formamide (FA) at 25 °C have been studied extensively. Table 18 summarizes the $V°$ values reported for a large number of electrolytes, mostly 1:1 but also 2:1 and even 3:1 (one) charge types. Many of these salts show excellent agreement among independent determinations. It is particularly noteworthy that the $V°$ values derived from density measurements generally agree well with those determined by high precision dilatometry.[55] This has enabled the $V°$ values of ~20 electrolytes (notably including a 2:1 salt, $Ba(CF_3SO_3)_2$) to be recommended. Because of its very high relative permittivity (ϵ = 111 at 25 °C), ion-pairing effects would be expected to be minimal in FA and all salts can probably be studied to relatively high concentrations without seriously prejudicing the extrapolation to infinite dilution. Nevertheless, there is no justification for making simplistic linear extrapolations from measurements of $^{\phi}V$ made *only* at very high *c*.[135,138] Surprisingly, *some* of the $V°$ values obtained in this way ($NaClO_4$, NaSCN) are in good agreement with those obtained from additivity of well-based data (Table 18). The fact that others ($Mg(ClO_4)_2$) differ wildly underlines the probability that any such agreement is fortuitous, and all values obtained in this manner are rejected. The data required for calculation of the Debye−Hückel slope, and the slope itself, eq 14, have been known for a long time;[139] it is interesting that with one exception[136] all subsequent authors have used only the empirical Masson equation (eq 6).

The abundance of data in FA permits extensive additivity testing. A nonexhaustive list follows, with deviant values given in *italic* font (all values in $cm^3\ mol^{-1}$): $V°(Br^-) - V°(Cl^-)$ = 6.9 (Na^+), 7.1 (K^+), 6.7 (Rb^+), 6.6 (Cs^+), 6.6 (NH_4^+); $V°(I^-) - V°(Br^-)$ = 11.8 (Na^+), 11.8 (K^+), 12.0 (Rb^+), 12.1 (Cs^+), *5.4 (NH_4^+)*, 12.3 (Et_4N^+), 12.0 (Pr_4N^+), 11.9 (Bu_4N^+); $V°(ClO_4^-) - V°(Cl^-)$ = 29.7 (Li^+), 28.0 (Na^+), 28.9 (K^+); $V°(NO_3^-) - V°(Br^-)$ = 5.9 (Na^+), 5.3 (K^+), 5.7 (Rb^+), 5.4(NH_4^+); $V°(CF_3SO_3^-) - V°(Cl^-)$ = *65.0 (Na^+)*, 61.0 (K^+), 60.5 ($^1/_2Ba^{2+}$); $V°(Na^+) - V°(Li^+)$ = 1.4 (Cl^-), 1.7 (ClO_4^-); $V°(K^+) - V°(Na^+)$ = 10.4 (Cl^-), 10.6 (Br^-), 10.6 (I^-), 10 (NO_3^-), 11.3 (ClO_4^-), *6.4 ($CF_3SO_3^-$)*, 10.4 (SCN^-); $V°(Cs^+) - V°(K^+)$ = *13.1 (F^-)*, 10.6 (Cl^-), 10.1 (Br^-), 10.4 (I^-), 10.5 (NO_3^-); $V°(NH_4^+) - V°(K^+)$ = 5.5 (Cl^-), 5.0 (Br^-), 5.1 (NO_3^-); $V°(Et_4N^+) - V°(K^+)$ = 134.8 (Br^-), 135.3(I^-); $V°(Pr_4N^+) - V°(Et_4N^+)$ = 68.8 (Br^-), 68.5 (I^-); $V°(Bu_4N^+) - V°(Et_4N^+)$ = 136.9 (Br^-), 136.5 (I^-).

The availability of this extensive list enables a more rigorous assessment of the data than is possible for most of the solvent systems. Thus, values for $NaCF_3SO_3$,[136] NH_4I,[141] and Pe_4NI[142] have been rejected, even though they mostly deviate from additivity or mean values by <3 $cm^3\ mol^{-1}$, a difference well below that observed for many other solvents. All of the data for the 2:1 salts reported[135] have been

Table 18. Standard Partial Molar Volumes, $V°/(cm^3\ mol^{-1})$, of Electrolytes in Formamide (FA) at 25 °C[s]

	$V°$	
electrolyte	reported	selected
HCl	28.1[a]	28
HBr	34.5[a,p]	*35*
HI	46.9[a,p]	*47*
$LiCl$	19.6,[b] [22.2],[c] 20.1[d]	**19.9**
$LiBr$	26.0[a,p]	*25*
LiI	38.4[a,p]	*37*
$LiClO_4$	49.6[d]	49.6
$NaCl$	21.1,[e] 21.5[d]	**21.3**
$NaBr$	28.0,[e] [30.3],[f] 28.34,[g] 28.1[d]	**28.2**
NaI	39.9,[e] [42.3],[f] 40.1[d]	**40.0**
$NaNO_3$	33.6,[e] [36.9],[f] 34.6[d]	**34.1**
$NaClO_4$	[51.3][f]	*51*
$NaSCN$	[46.4][f]	*45*
$NaCF_3SO_3$	[86.3][d]	*83*
$NaBPh_4$	289.0,[l] 289.1[d]	**289.1**
KF	18.9[d]	18.9
KCl	32.0,[e] 31.7,[d] 31.33,[h] 32.0[i]	**31.7**
KBr	38.9,[e] 38.6,[d] 38.9[i]	**38.8**
KI	50.8,[e,q] 50.3,[d] 50.8[i]	**50.6**
KNO_3	44.1[e]	44.1
$KClO_4$	60.6[d]	60.6
$KSCN$	54.82[g]	54.8
KCF_3SO_3	92.90,[g] 92.4[d]	**92.7**
$RbCl$	35.9[j]	35.9
$RbBr$	42.6[j]	42.6
RbI	54.6[j]	54.6
$RbNO_3$	48.2[j]	48.3
CsF	32.0[d]	32.0
$CsCl$	42.3,[j] 42.3[d]	**42.3**
$CsBr$	49.3,[j] 48.5[d]	**48.9**
CsI	61.0[j]	61.0
$CsNO_3$	54.6[j]	54.6
NH_4Cl	37.2[e]	37.2
NH_4Br	44.1,[e] 43.6[d]	**43.8**
NH_4I	[49.2][j]	*56*
NH_4NO_3	49.2[e]	49.2
Me_4NBr	114.9[d]	114.9
Et_4NBr	173.75,[g] 173.4[d]	**173.6**
Et_4NI	185.5,[b] 186.3[k]	**185.9**
Pr_4NBr	242.50,[g] 242.2[d]	**242.4**
Pr_4NI	255.5,[b] 253.3[k]	**254.4**
Bu_4NBr	310.76,[g] 310.3[d]	**310.5**
Bu_4NI	322.4,[b] 322.4[k]	**322.4**
Pe_4NBr	378.7[d]	378.7
Pe_4NI	394.0,[b] [397.5][k]	394.0
Hx_4NI	463.8[k]	463.8
Ph_4PCl	319.0[d]	319.0
Ph_4PBr	326.9[d]	326.9
Ph_4AsCl	326[m]	326
Ph_4AsI	345[m]	345
$Mg(ClO_4)_2$	[103.7][c]	*86*
$Mg(CF_3SO_3)_2$	149.3[d]	149.3
$CaCl_2$	[40.7][c]	
$CaBr_2$	[51.6][c]	
$Ca(NO_3)_2$	[65.7][c]	
$BaCl_2$	37.76[g]	37.8
$Ba(CF_3SO_3)_2$	160.6,[d] 158.65[g,n]	**158.7**
$ZnCl_2$	[42.5][c]	
$ZnBr_2$	[53.7][c]	
ZnI_2	[66.0][c]	
$[Coen_3](ClO_4)_3$[r]	285.6[g]	285.6

[a] Reference 117, pyc. [b] Reference 68, pyc, extrapolated by the reviewers from data at higher temperatures. [c] Reference 135, pyc, values obtained from density measurements at concentrations (> ca. 0.3 M) that are too high for meaningful evaluation of $V°$. [d] Reference 136, vtd. [e] Reference 137, pyc. [f] Reference 138, pyc, values obtained from density measurements at concentrations (> ca. 0.3 M) that are too high for meaningful evaluation of $V°$. [g] Reference 55, dil, vtd. [h] Reference 139, dil. [i] Reference 140, pyc. [j] Reference 141, pyc. [k] Reference 142, pyc, 35 °C. [l] Reference 143, pyc. [m] Reference 96, vtd. [n] Preferred value, see also ref 136. [o] Calculated by the present reviewers by additivity using the selected $V°$(ion) values from Table 19. [p] Reference 93, review of literature data. [q] Value given in ref 93 is a misprint. [r] en = 1,2-diaminoethane. [s] Values in square brackets [ ] are rejected. Recommended values are shown in **bold** type. Values obtained by additivity are given in *italic* type.

rejected, as they were obtained by linear extrapolation of $^{\phi}V$ against c (*not* $c^{1/2}$) data obtained at very high concentrations ($c > 0.3$ M). As discussed above, such values cannot be reliable except fortuitously.

Formamide is one of the few solvents in which the $V°$ of a fluoride salt has been determined. Measurements involving fluoride are always difficult because of the sparing solubility of most of its salts, its extreme reactivity in dry nonaqueous solvents, and the tendency of its salts to ion pair.[144] Nevertheless, the additivity tests above indicate that the reported value of $V°(CsF)$ deviates only slightly from those of related salts and is therefore realistic.

An unusually wide range of data is available for obtaining the TATB and TPTB reference electrolyte volumes. Two (semi-)independent additivity routes exist for both salts, although all depend on the value of $V°(NaBPh_4)$. Fortunately, this is well characterized, with two independent studies using different methods reporting almost identical values (Table 18). The TATB and TPTB volumes so derived are in almost exact agreement (better than ±1 $cm^3\ mol^{-1}$). The latter has been used to derive the other ionic values, as it is based on more recent and more precise data.

Table 19 lists $V°$(ion) values derived from the TPTB assumption using appropriate combinations of the selected volumes from Table 18. These estimates are similar to the earlier TATB-based $V°$(ion) values of Parker et al.,[96] based on somewhat less precise data, and those derived using Mukerjee's method. On the other hand, the values estimated from the molar-mass-based (*M*ex) extrapolation[142] differ by up to 9 $cm^3\ mol^{-1}$. The more recent values of $V°(R_4N^+)$ at 35 °C, also obtained by the *M*ex method,[129] are in even worse agreement, differing by up to 18 $cm^3\ mol^{-1}$ from the present TPTB values. This is unlikely to be due to the small difference in temperature (see section 5.11).

5.10. Salt and Ion Volumes in *N*-Methylformamide (NMF)

Volumetric data at 25 °C have been reported mostly for 1:1 electrolytes in *N*-methylformamide (NMF), but some results are also available for 2:1 and 3:1 charge types. The $V°$ values for these salts are summarized in Table 20. Most of the data originate from the dilatometric study by Bottomley and Bremers.[55] Unusually, another dilatometric investigation has also been reported.[53] Both of these studies were of very high precision and were made down to quite low concentrations. Where comparison is possible, the results are in good agreement (≤0.8 $cm^3\ mol^{-1}$).

Table 19. Standard Partial Molar Volumes of Ions, $V°(\text{ion})/(\text{cm}^3\ \text{mol}^{-1})$,[h] in Formamide (FA) at 25 °C, Calculated Assuming $V°(Ph_4P^+) = V°(BPh_4^-) + 2\ \text{cm}^3\ \text{mol}^{-1}$

ion	$V°$(electrolyte) used	$V°$(ion)	
		selected	reported
H^+	3 (Cl^-)	3	5[a]
Li^+	−8 (Br^-), −6 (I^-)	−7	−4,[a] −4,[b] −3,[c] −5[e]
Na^+	−3 (BPh_4^-)	−3	−3,[a] −3,[b] −1,[c] −4[e]
K^+	7 (Cl^-)	7	8,[a] 4,[b] 9,[c] 7[e]
Rb^+	11 (Cl^-), 11 (Br^-), 11 (I^-)	11	12,[a] 13[c]
Cs^+	18 (Cl^-), 17 (Br^-), 17 (I^-)	17	19,[a] 12,[b] 19,[c] 17[e]
NH_4^+	12 (Cl^-), 12 (Br^-)	12	15,[c] 12[e]
Me_4N^+	83 (Br^-)	83	83[e]
Et_4N^+	142 (Br^-), 142 (I^-)	142	146,[d] 142,[e] 158[g]
Pr_4N^+	211 (Br^-), 211 (I^-)	211	213,[d] 211,[e] 228[g]
Bu_4N^+	279 (Br^-), 279 (I^-)	279	282,[d] 279,[e] 297[g]
Pe_4N^+	347 (Br^-), 350 (I^-)	349	358,[d] 347,[e] 366[g]
Hx_4N^+	420 (I^-)	420	424,[d] 436[g]
Ph_4P^+	294 (Ph_4PCl, $NaBPh_4$, NaCl), 295 (Ph_4PBr, $NaBPh_4$, NaBr)	294	295[e]
Ph_4As^+	301 (Ph_4AsCl, $NaBPh_4$, NaCl), 301 (Ph_4AsI, $NaBPh_4$, NaI)	301	302[d]
Mg^{2+}	−22 ($CF_3SO_3^-$)	−22	−26[e]
Ca^{2+}	−9 (Cl^-), −12 (Br^-), −8 (NO_3^-)	[−9][f]	
Ba^{2+}	−11 (Cl^-), −13 ($CF_3SO_3^-$)	−12	−15[e]
Zn^{2+}	−7 (Cl^-), −10 (Br^-), −21 (I^-)	[−12][f]	
$[Co(en)_3]^{3+}$	124 (ClO_4^-)	124	
F^-	12 (K^+), 15 (Cs^+)	13	14[e]
Cl^-	25 (Ph_4P^+)	25	24,[a] 24,[b] 23,[c] 25[e]
Br^-	32 (Na^+), 32 (K^+), 33 (Ph_4P^+)	32	30,[a] 31,[b] 30,[c] 32[e]
I^-	44 (Na^+), 44 (K^+)	44	42,[a] 43,[b] 42,[c] 44[e]
NO_3^-	38 (Na^+), 37 (K^+)	37	38[e]
ClO_4^-	54 (K^+)	54	54[e]
SCN^-	48 (K^+)	48	
$CF_3SO_3^-$	86 (K^+)	86	87[e]
BPh_4^-	292 (Ph_4PCl, $NaBPh_4$, NaCl), 293 (Ph_4AsCl, $NaBPh_4$, (NaCl), 293 (Ph_4AsI, $NaBPh_4$, NaI)	292	293,[b] 293[e]

[a] Reference 117, muk. [b] Reference 96, TA = TB. [c] Reference 141, muk. [d] Reference 142, *M*ex. [e] Reference 136, TPTB. [f] Value rejected because the data on which it is based are rejected; see Table 18. [g] Reference 129, *M*ex, at 35 °C. [h] Estimated uncertainty ±2 $\text{cm}^3\ \text{mol}^{-1}$.

Given that NMF is not a particularly difficult solvent to work with and its exceptionally high relative permittivity ($\epsilon = 182$) reduces complications from ion pairing, this level of agreement emphasizes just how difficult it is to obtain reliable $V°$ values for electrolytes in nonaqueous solvents even when reliable workers use the most accurate procedures available. Four salts have also been investigated by Pang[23] using vibrating tube densimetry. With the exception of the case of KBr, these results are also in excellent agreement with those of the dilatometric studies.

A number of additivity tests are possible: $V°(Br^-) - V°(Cl^-) =$ *1.4 (Li^+)*, 4.4 (Na^+), 3.8 (K^+), 5.3 (NH_4^+); $V°(I^-) - V°(Br^-) = 13.8$ (Li^+), 10.2 (Na^+), 11.0 (K^+); $V°(ClO_4^-) - V°(NO_3^-) = 13.3$ (Na^+), 13.2 (K^+); $V°(CF_3SO_3^-) - V°(SCN^-) = 39.6$ (Na^+), 40.1 (K^+); $V°(Na^+) - V°(Li^+) = 5.4$ (Cl^-), 8.4 (Br^-), 4.8 (I^-); $V°(K^+) - V°(Na^+) = 8.0$ (Cl^-), 7.4 (Br^-), 8.2 (I^-), 7.9 (NO_3^-), 7.8 (ClO_4^-), 7.7(SCN^-), 8.2 ($CF_3SO_3^-$); $V°(NH_4^+) - V°(K^+) = 5.4$ (Cl^-), 5.7 (NO_3^-), 4.0 (SCN^-) [where all values are in $\text{cm}^3\ \text{mol}^{-1}$ and those given in *italic* type are outliers]. Detailed examination of these differences suggests that the reported values of $V°(LiBr)$[53,55] might be a little too low. All other values are very consistent, with deviations of about ±0.5 $\text{cm}^3\ \text{mol}^{-1}$.

Application of the TPTB assumption to the data in Table 20 produces the $V°$(ion) values shown in Table 21. The only other estimate of $V°$(ion) values is due to Pang,[23] but as they were based on essentially the same data and assumption, they do not differ from the present estimates.

5.11. Salt and Ion Volumes in *N*,*N*-Dimethylformamide (DMF)

Standard partial molar volumes at 25 °C have been reported for a large number of salts in *N*,*N*-dimethylformamide (DMF) (Table 22), including 1:1, 2:1, and 3:1 charge types, making it one of the more thoroughly studied solvent systems. Data for many of the salts have been independently replicated to better than ±1 $\text{cm}^3\ \text{mol}^{-1}$, enabling the mean $V°$ values for several salts to be recommended.

Numerous additivity tests can be applied, for example: $V°(I^-) - V°(Br^-) = 17.6$ (Li^+), 14.9 (Na^+), 16.4 (K^+), 14.5 (Cs^+), 14.5 (Et_4N^+), 18 (Pr_4N^+), 13.1 (Bu_4N^+), 17 (Pe_4N^+), 18 (Hx_4N^+), 15 (Hp_4N^+), 18 (Ph_4As^+); $V°(I^-) - V°(NO_3^-) =$ *10.9 (Li^+)*, 5.0 (Na^+), 7.0 (K^+), 6.3 (Rb^+), 4.6 (NH_4^+); $V°(Na^+) - V°(Li^+) = 7.1$ (Br^-), 4.4 (I^-), *10.3 (NO_3^-)*; $V°(K^+) - V°(Na^+) = 7.6$ (Br^-), 9.1 (I^-), 7.1 (NO_3^-); $V°(NH_4^+) - V°(K^+) = 3.6$ (I^-), 6.0 (NO_3^-); $V°(Et_4N^+) - V°(K^+) = 135.6$ (Br^-), 133.7 (I^-); $V°(Pr_4N^+) - V°(Et_4N^+) = 69.5$ (Br^-), 73 (I^-); $V°(Bu_4N^+) - V°(Et_4N^+) = 139.9$ (Br^-), 138.5 (I^-); $V°(Ph_4As^+) - V°(Bu_4N^+) = 9.6$ (Br^-), *14.5 (I^-)*, [where all values are in $\text{cm}^3\ \text{mol}^{-1}$ and outliers are indicated in *italic* type].

Detailed comparisons of these additivities indicate that the reported value for $V°(LiNO_3)$ is too low by

Table 20. Standard Partial Molar Volumes, $V°/(\mathrm{cm^3\ mol^{-1}})$, of Electrolytes in *N*-Methylformamide (NMF) at 25 °C

electrolyte	$V°/(\mathrm{cm^3\ mol^{-1}})$	selected $V°$
LiCl	16.9,[a] 17.7[b]	**17.3**
LiBr	19.8,[a] 17.6[c]	**18.7**
LiI	32.5[a]	32.5
NaCl	22.7,[b] 22.7,[c] 22[d]	**22.7**
NaBr	27.6,[b] 26.6[d]	**27.1**
NaI	37.5,[a] 38.3,[b] 36.2[c]	**37.3**
$NaNO_3$	33.5[b]	33.5
$NaClO_4$	46.8[b]	46.8
NaSCN	42.8[b]	42.8
$NaCF_3SO_3$	82.4[b]	82.4
$NaBPh_4$	281.0[c]	281.0
KCl	30.7,[b] 29[d]	30.7
KBr	36.3,[b] 32.2,[c] 35.1[d]	34.5
KI	46.2,[a] 45.6,[b] 44.6[c]	**45.5**
KNO_3	41.4[a]	41.4
$KClO_4$	54.6[a]	54.6
KSCN	50.5[a]	50.5
KCF_3SO_3	90.6[a]	90.6
CsCl	40.5[b]	40.5
NH_4Cl	36.1[a]	36.1
NH_4Br	41.4[a]	41.4
NH_4NO_3	47.1[a]	47.1
NH_4SCN	54.5[a]	54.5
Et_4NBr	170.5[a]	170.5
Pr_4NBr	241.4[a]	241.4
Bu_4NBr	310.5[a]	310.5
Ph_4PCl	312.5[c]	312.5
$Mg(CF_3SO_3)_2$	143.1[b]	143.1
$BaCl_2$	36.5[b]	36.5
$Ba(CF_3SO_3)_2$	156.1[b]	156.1
$[Co(en)_3](ClO_4)_3$[e]	266.2[b]	266.2

[a] Reference 53, dil. [b] Reference 55, dil, vtd. [c] Reference 123, vtd. [d] Reference 54, pyc. [e] en = 1,2-diaminoethane

Table 21. Standard Partial Molar Volumes of Ions, $V°(\mathrm{ion})/(\mathrm{cm^3\ mol^{-1}})$,[b] in *N*-Methylformamide (NMF) at 25 °C, Calculated Assuming $V°(Ph_4P^+) = V°(BPh_4^-) + 2$ cm³ mol⁻¹

ion	$V°$(electrolyte) used	selected $V°$(ion)[a]
Li^+	−9 (Cl^-), −11 (Br^-), −9 (I^-)	−10
Na^+	−3 (BPh_4^-)	−3
K^+	5 (Cl^-)	5
Cs^+	14 (Cl^-)	14
NH_4^+	10 (Cl^-), 11 (Br^-), 10 (NO_3^-)	10
Et_4N^+	140 (Br^-)	140
Pr_4N^+	211 (Br^-)	211
Bu_4N^+	280 (Br^-)	280
Ph_4P^+	286 (Ph_4PCl, $NaBPh_4$, NaCl)	286
Mg^{2+}	−29 ($CF_3SO_3^-$)	−29
Ba^{2+}	−16 ($CF_3SO_3^-$), −16 (Cl^-)	−16
$[Coen_3]^{3+}$	116 (ClO_4^-)	116
Cl^-	26 (Ph_4P^+)	26
Br^-	31 (Na^+), 30 (K^+)	30
I^-	41 (Na^+), 41 (K^+)	41
NO_3^-	37 (Na^+), 37 (K^+)	37
ClO_4^-	50 (Na^+), 50 (K^+)	50
SCN^-	46 (Na^+), 46 (K^+)	46
$CF_3SO_3^-$	86 (Na^+), 86 (K^+)	86
BPh_4^-	284 (Ph_4PCl, $NaBPh_4$, NaCl)	284

[a] Similar results obtained by Pang[23] based on essentially the same data. [b] Estimated uncertainty ±2 cm³ mol⁻¹.

~5 cm³ mol⁻¹. Most of the other salt data are consistent to better than ±2 cm³ mol⁻¹, which is satisfactory but not as good as might be expected. Values of $V°$ for some electrolytes show disappointing levels of agreement between independent determinations. The means of such data are classified as tentative. Most of the values reported by Kalugin et al.[145] have been rejected, either because they differ from other determinations for well-characterized salts or because they are in serious disagreement with the additivity-derived values of the present review. For some well-characterized salts, the good quality of the available data has allowed a number of outliers to be rejected. As in all solvents, the values reported for the higher valent electrolytes must be considered with caution. Although the data refer to perchlorate salts and the relative permittivity of DMF is reasonably high ($\epsilon = 36.7$ at 25 °C), the difficulties of obtaining $V°$ values that are not influenced by ion pairing must not be underestimated.

Unusually, the solubilities of both TATB and TPTB are sufficiently high in DMF to enable direct determination of their $V°$ values by density measurements.[96,148] Unfortunately, however, the directly determined values have large uncertainties, so the much more precise $V°$ values obtained by additivity of the appropriate salts were preferred. The TATB and TPTB values obtained in this way are consistent to ±1 cm³ mol⁻¹. As the TPTB data are more recent and more precise, they were preferred for the purposes of obtaining $V°$(ion).

The values of $V°$(ion) so obtained via the TPTB assumption are given in Table 23. These values are in good agreement, as would be expected, with earlier[96] and more recent[128] estimates of $V°$(ion) based on the TATB assumption. On the other hand, the $V°$(ion) values obtained by both the uvp[80] and Mukerjee[95,111,149] methods sometimes differ markedly from the present TPTB values (by up to 24 cm³ mol⁻¹ (Table 23), with cations too low and anions too high). The last two assumptions are also in only modest agreement with each other (Table 23), differing by up to 12 cm³ mol⁻¹. For a few ions, the Mukerjee values are actually closer to the present TPTB values than they are to the uvp numbers. Given that the TATB and TPTB values are well based experimentally (alternative additivity routes, a number of independently determined $V°$(electrolyte) values, Table 22), these differences appear to be real. Understanding them may well shed light on the limitations of the current assumptions (see also section 3). The $V°(R_4N^+)$ values obtained by the *M*ex method[42,129] deviate wildly from all other estimates, differing by as much as 36 cm³ mol⁻¹ from the uvp estimates and by up to 21 cm³ mol⁻¹ from the present TPTB values (Table 23). The *M*ex values for anions that have been (or can be) derived are far too small (or even negative) to be realistic, again emphasizing the unsatisfactory nature of this assumption. It is noteworthy that the $V°(R_4N^+)$ values obtained by the *M*ex method are almost identical at 25 °C[42] and 35 °C.[129] This has implications for a number of other solvents.

It is interesting to compare the values of $V°(Bu_4N^+) = 281$ cm³ mol⁻¹ and $V°(BBu_4^-) = 310$ cm³ mol⁻¹ obtained via the TPTB assumption. These values are clearly very different, which indicates that the TATB/TPTB assumption is incompatible with assuming $V°(Bu_4N^+)/V°(BBu_4^-) = V°_{\mathrm{vdW}}(Bu_4N^+)/V°_{\mathrm{vdW}}(BBu_4^-) = 0.995$, as has been done by Sacco et al.[148]

Table 22. Standard Partial Molar Volumes, $V°/(cm^3\ mol^{-1})$, of Electrolytes in *N*,*N*-Dimethylformamide (DMF) at 25 °C[u]

electrolyte	$V°$	
	reported	selected
LiCl	−4.4,[a] −3.1,[b] [*−8.5*][q]	**−3.8**
LiBr	0.5,[b] [*2*, *−3.5*],[q] −0.9	**0.2**
LiI	19.5,[c] 16.1[b]	17.8
$LiNO_3$	[6.9][a]	*12*[m]
$LiClO_4$	26.0[s]	26.0
NaCl	[*5.9*],[a,r] [*−6.5*][q]	*1*[m]
NaBr	6.6,[a] 7.9,[b] [4][d,n]	**7.3**
NaIt	21.3,[e] 23.1,[a] 21.5,[c] 22.6,[b] 22.4,[f] [20][d]	**22.2**
$NaNO_3$	[24.5],[e] 17.2[a]	17.2
$NaClO_4$	33.3[p]	33.3
$NaBPh_4$	280,[c] 281.7,[g] 279.7[h]	**280.5**
KCl	[*13.0*],[a] [*4.5*][q]	*9*[m]
KBr	14.1,[a,r] 15.6[b,r]	**14.9**
KIt	[35.8],[e] 30.5,[a] 32.8,[c] 30.5[b]	**31.3**
KNO_3	24.3[a]	24.3
RbCl	[*17.0*],[a] [*8*][q]	*13*[m]
RbBr	[*18.5*, *17.9*][q]	*19*[m]
RbI	34.0,[a] 35.1,[b] [*30.0*, *36.5*][q]	**34.6**
$RbNO_3$	28.3[a]	28.3
CsCl	[*12.5*, *23.5*][q]	*20*[m]
CsBr	26.2,[b] [*23*, *24.4*][q]	26.2
CsIt	40.4,[a] 41.0[b]	**40.7**
$CsNO_3$	[*34.8*][a]	*36*[m]
$AgClO_4$	24.1	24.1
NH_4Cl	[*18.9*][a]	*14*[m]
NH_4Br	[23],[d] [32.2][e]	*20*[m]
NH_4I	[38.4],[e,r] 34.9[a]	34.9
NH_4NO_3	[41.7],[e] 30.3	30.3
Et_4NCl	[*147.5*][q]	*145*[m]
Et_4NBr	151.2,[b] 150.0,[g] [148.4],[q] 150.3[s]	**150.5**
Et_4NI	165[e,r]	165
Pr_4NCl	[*220*, *221*][q]	*216*[m]
Pr_4NBr	222.2,[b] 219.6,[o] 219.5[s]	220
Pr_4NI	238[e,r]	238
Bu_4NCl	[*288.4*][q]	*284*[m]
Bu_4NBr	290.44,[i] 290.4,[b] [294.2],[j] 290.5,[g] [289.4],[o] [288.5],[d] [288.1][s]	**290.4**
Bu_4NI	[306],[e,r] 303.4,[g] 303.6,[d] [*305.4*][q]	**303.5**
Bu_4NBH_4	564.8[g]	564.8
Bu_4NBBu_4	594.0,[j] 587.9[g],	591
Bu_4NBPh_4	[531][d]	*563*[m]
Pe_4NBr	360.1	360
Pe_4NI	377[e,r]	377
Hx_4NBr	430.9,[o] 427.2[s]	429
Hx_4NI	447[e]	447
Hp_4NBr	497.5[o]	498
Hp_4NI	513[e]	513
Ph_4PBr	[285.0],[j] 292.7[h]	292.7
Ph_4PBPh_4	569.4[j]	*566*[m]
Ph_4AsBr	300[c]	300
Ph_4AsI	318[c]	318
Ph_4AsBPh_4	570,[c] *577*[c]	*574*[m]
$Be(ClO_4)_2$	22.4[k]	22
$Mg(ClO_4)_2$	43.1[p]	43
$Ca(ClO_4)_2$	45.8[p]	46
$Sr(ClO_4)_2$	47.6[p]	48
$Ba(ClO_4)_2$	48.1[p]	48
$Pb(ClO_4)_2$	40.0[p]	40
$Mn(ClO_4)_2$	32.9[l]	33
$Co(ClO_4)_2$	28.5[l]	29
$Ni(ClO_4)_2$	26.1[l]	26
$Cu(ClO_4)_2$	29.3[l]	29
$Zn(ClO_4)_2$	28.3[l]	28
$Al(ClO_4)_3$	20.2[k]	20
$In(ClO_4)_3$	30.8[k]	31

[a] Reference 111, vtd. [b] Reference 95, vtd. [c] Reference 96, vtd. [d] Reference 145, vtd; these values are mostly rejected, as they differ significantly from those of other studies for well characterized salts. [e] Cited in ref 1; most values are broadly consistent with data at 35−75 °C in ref 143, pyc. [f] Reference 146, vtd. [g] Reference 125, vtd. [h] Reference 23, vtd. [i] Reference 147, vtd. [j] Reference 148, vtd. [k] Reference 149, pyc [l] Reference 150, pyc. [m] Calculated by the present reviewers by additivity using the selected $V°$(ion) values from Table 23. [n] Note the value given for the "*B*" coefficient by the authors of ref 145 is a misprint; it should be 0.116. [o] Calculated by the present reviewers from density data (vtd) in ref 151. [p] Reference 128, pyc. [q] Reference 93, review of literature data, original data not accessible. [r] Slightly different value given in ref 93 although taken from the same source. [s] Reference 115, vtd. [t] Graphical data also available in ref 152, method?, in very poor agreement with other values. [u] Values in square brackets [ ] are rejected. Recommended values are shown in **bold** type. Values obtained by additivity are given in *italic* type.

5.12. Salt and Ion Volumes in *N*-Methylacetamide (NMA)

Values of $V°$(electrolyte) in *N*-methylacetamide (NMA) at 35 °C are shown in Table 24. Data for several different salts are available, but all originate from the Lucknow group and therefore cannot be considered to have been confirmed independently. The additivity tests [$V°(K^+) - V°(Na^+) = 7.6$ (Br^-), 3.9 (I^-), 7.8 (NO_3^-); $V°(NH_4^+) - V°(Na^+) = 9.5$ (Cl^-), 12.1 (Br^-), 9.7 (I^-), 12.2 (NO_3); $V°(Br^-) - V°(Cl^-) =$ 6.6 (Na^+), 9.2 (NH_4^+); $V°(I^-) - V°(Br^-) = 9.4$ (Na^+), 5.7 (K^+), 7.0 (NH_4^+); $V°(I^-) - V°(NO_3^-) = 7.0$ (Na^+), 3.1 (K^+), 4.5 (NH_4^+) (all values in $cm^3\ mol^{-1}$)] are not particularly consistent, and so the uncertainties of the reported values are considerable. A plot of $V°(R_4NI)$ versus the number of carbon atoms in R_4N^+ (i.e., *N*-extrapolation, section 3.4) yields $V°(I^-) = 37 \pm 4\ cm^3\ mol^{-1}$, but the standard deviation points to inaccuracies in the data.

Data required for application of the TATB/TPTB assumption were unavailable, so $V°$(ion) values (Table 25) were obtained by Mukerjee's method (section 3.3). The resulting value of $V°(I^-) = 39\ cm^3\ mol^{-1}$ is in good agreement with that estimated from the *N*-extrapolation.

5.13. Salt and Ion Volumes in *N*,*N*-Dimethylacetamide (DMA)

The $V°$ values for electrolytes in *N*,*N*-dimethylacetamide (DMA) at 25 °C are shown in Table 26. Most of the data are from the group in Gdansk[131,157−159] and have not been confirmed independently; neither have those of Das et al.[160] For two salts, the same group reported different values in two papers. The additivity test [$V°(ClO_4^-) - V°(Br^-) = 51.7$ (Pr_4N^+), 50.2 (Bu_4N^+) $cm^3\ mol^{-1}$] is in fair agreement but could be applied only to two sets of salts. However, this difference is much larger than is observed for these two ions in other solvents, and so, in view of the abnormally low $V°$ values of the tetraphenylborate salts,[160] the $V°$(electrolyte) values from this source are rejected.

The volume increment per methylene group in the tetraalkylammonium salts varies somewhat along the chains: $V°(-CH_2-) = [V°((C_nH_{2n+1})_4N^+) -$

Table 23. Standard Partial Molar Volumes of Ions, $V°(\text{ion})/(\text{cm}^3\ \text{mol}^{-1})$,[o] in *N*,*N*-Dimethylformamide (DMF) at 25 °C, Calculated Assuming $V°(Ph_4P^+) = V°(BPh_4^-) + 2\ \text{cm}^3\ \text{mol}^{-1}$

		$V°$(ion)	
ion	$V°$(electrolyte) used	selected	reported
Li^+	−9 (Br^-), −6 (I^-)	−8	−24,[a] −26,[b] −19,[c] −5,[d] −19,[e] −15,[f] −6,[l] 10[m]
Na^+	−2 (BPh_4^-)	−2	−22,[a] −16,[b] −9,[c] −3,[d] −12,[e] −8,[f] −4[l]
K^+	5 (Br^-), 7 (I^-), 5 (NO_3^-)	6	−11,[a] −9,[b] −2,[c] 8,[d] −5,[e] −1,[f] 8[l]
Rb^+	11 (I^-), 9 (NO_3^-)	10	−10,[a] −5,[b] 2,[c] 0,[e] 4,[f] 9[l]
Cs^+	17 (Br^-), 17 (I^-)	17	2,[a] 2,[b] 9,[c] 16,[d] 6,[e] 10,[f] 15[l]
Ag^+	−11 (ClO_4^-)	−11	−13[l]
NH_4^+	11 (I^-), 11 (NO_3^-)	11	−2,[a] −3,[b] 4[c]
Et_4N^+	142 (Br^-), 141 (I^-)	142	126,[b] 131,[e] 135,[f] 127,[g] 161,[m] 161[n]
Pr_4N^+	211 (Br^-), 214 (I^-)	213	198,[b] 202,[e] 206,[f] 230,[m] 233[n]
Bu_4N^+	281 (Br^-), 279 (I^-)	281	266,[b] 270,[e] 274,[f] 296,[h] 266,[g] 299,[m] 302[n]
Pe_4N^+	351 (Br^-), 353 (I^-)	352	337,[b] 373[n]
Hx_4N^+	420 (Br^-), 423 (I^-)	422	438,[m] 444[n]
Hp_4N^+	489 (Br^-), 489 (I^-)	489	
Ph_4P^+	284 (Ph_4PBr, $NaBPh_4$, NaBr)	284	289[h]
Ph_4As^+	291 (Ph_4AsBr, $NaBPh_4$, NaBr)	291	293,[d] 293[l]
Be^{2+}	−48 (ClO_4^-)	−48	−54[j]
Mg^{2+}	−27 (ClO_4^-)	−27	−31[l]
Ca^{2+}	−24 (ClO_4^-)	−24	−28[l]
Sr^{2+}	−22 (ClO_4^-)	−22	−26[l]
Ba^{2+}	−22 (ClO_4^-)	−22	−26[l]
Pb^{2+}	−30 (ClO_4^-)	−30	−34[l]
Mn^{2+}	−37 (ClO_4^-)	−37	−45[j]
Co^{2+}	−42 (ClO_4^-)	−42	−49[j]
Ni^{2+}	−44 (ClO_4^-)	−44	−51[j]
Cu^{2+}	−41 (ClO_4^-)	−41	−48[j]
Zn^{2+}	−42 (ClO_4^-)	−42	−49[j]
Al^{3+}	−85 (ClO_4^-)	−85	−94[j]
In^{3+}	−74 (ClO_4^-)	−74	−84[j]
Cl^-	4 (Li^+)	3	25,[a] 22,[b] 15,[c] 17,[e] 13,[f] 10[l]
Br^-	9 (Ph_4P^+)	9	33,[a] 23,[b] 16,[c] 7,[d] 20,[e] 16,[f] −3,[h,i] 10,[l] −11[m]
I^-	24 (Na^+)	24	44,[a] 39,[b] 32,[c] 25,[d] 35,[e] 31,[f] 10[l]
NO_3^-	19 (Na^+)	19	33,[a] 33,[b] 27[c]
ClO_4^-	35 (Na^+)	35[k,l]	38,[j] 40,[l] 28,[k] 16[m]
BH_4^-	284 (Bu_4N^+)	284	
BBu_4^-	310 (Bu_4N^+)	310	298,[h] 322[g]
BPh_4^-	282 (Ph_4PBr, $NaBPh_4$, NaBr), 283 (Ph_4AsBr, $NaBPh_4$, NaBr)	282	284,[d] 281,[h] 298,[g] 284[l]

[a] Reference 111, uvp, averaged values. [b] Reference 111, uvp, based on $V°(NO_3^-) = 33.3\ \text{cm}^3\ \text{mol}^{-1}$. [c] Reference 111, muk. [d] Reference 96, TA = TB. [e] Reference 95, cor. [f] Reference 95, muk. [g] Reference 125, uvp, derived from ref 111. [h] Reference 148, vdW. [i] Average value of similar methods. [j] References 149 and 150, cor + muk. [k] Value of refs 149 and 150, adjusted to the TPTB scale by the present reviewers. [l] Reference 128, TATB. [m] Reference 43, *M*ex. [n] Reference 129, *M*ex, at 35 °C. [o] Estimated uncertainty ±2 $\text{cm}^3\ \text{mol}^{-1}$.

Table 24. Standard Partial Molar Volumes, $V°/(\text{cm}^3\ \text{mol}^{-1})$, of Electrolytes in *N*-Methylacetamide (NMA) at 35 °C[e]

	$V°$			$V°$	
electrolyte	reported	selected	electrolyte	reported	selected
LiCl	20.5[a,b]	20	NH_4I	51.7[b,c]	54
NaCl	26.0[b,c]	25	NH_4NO_3	47.2[b,c]	47
NaBr	32.6[b,c]	31	Et_4NI	175.4[a]	176
NaI	42.0[b,c]	42	Pr_4NI	247.5[a]	248
$NaNO_3$	35.0[b,c]	35	Bu_4NI	322.9[a]	323
KBr	40.2[b,c]	37	Pe_4NI	391.1[a]	392
KI	45.9[a−c]	48	Hx_4NI	461.2[a]	462
KNO_3	42.8[b,c]	41	Hp_4NI	527.3[a]	527
NH_4Cl	35.5[b,c]	37	$Sr(NO_3)_2$	54.6[d]	
NH_4Br	44.7[b,c]	43	$Ba(NO_3)_2$	57.8[d]	

[a] Reference 68, dil, also 40−80 °C. [b] Reference 153, dil. [c] Reference 154,155, dil. [d] Reference 156/1. [e] All values are unconfirmed. Values in *italics* are calculated by the present reviewers by additivity using the $V°$(ion) values in Table 25.

$V°((C_{n-1}H_{2n-1})_4N^+)]/(4\ \text{cm}^3\ \text{mol}^{-1}) = 17.2$ ($n = 1$), 15.9 ($n = 2$), 17.4 ($n = 3$), and 17.0 ($n = 4$) for perchlorates and 17.4 ($n = 4$), 15.2 ($n = 5$), 21.0 ($n = 6$), 17.0 ($n = 7$), and 15.7 ($n = 8$) for bromides. A systematic study of the divalent first-row transition metal perchlorates was made,[158] taking care not to introduce water into the DMA solutions, as was the case in some studies with other solvents, where hydrated salts were employed.

Neither the TATB/TPTB nor the Mukerjee methods could be used for obtaining the $V°$(ion) values, due to the lack of the necessary $V°$(electrolyte) data. However, the ratio $V°(Bu_4N^+)/V°(BPh_4^-) = 0.992$ was established in several aprotic solvents (based on the TPTB assumption) and was used to split the value of $V°(Bu_4NBPh_4)$ into the ionic contributions.[158] On this basis a value of $V°(ClO_4^-) = 39\ \text{cm}^3\ \text{mol}^{-1}$ was derived and, hence, those of the other cations shown in Table 27. Somewhat different values were reported later by this group,[159] but they were within the claimed limits of error.

5.14. Salt and Ion Volumes in *N*-Methylpropanamide (NMP)

The standard partial molar volumes of electrolytes, $V°$, in *N*-methylpropanamide (NMP) at 25 °C are

Table 25. Standard Partial Molar Volumes of Ions, V°(ion)/(cm^3 mol^{-1}),[d] in *N*-Methylacetamide (NMA) at 35 °C, Using Mukerjee's Method

		V°(ion)	
ion	V°(electrolyte) used	selected	reported
Li^+	−2 (Cl^-)	−2	
Na^+	3 (Cl^-), 3 (I^-)	3	3[a,b]
K^+	11 (NO_3^-), 6 (I^-), 12 (Br^-)	9	9,[a] 10[b]
NH_4^+	15 (NO_3^-)	15	15,[a] 16[b]
Et_4N^+	137 (Et_4N^+)	137	161[c]
Pr_4N^+	209 (Pr_4N^+)	209	233[c]
Bu_4N^+	284 (Bu_4N^+)	284	309[c]
Pe_4N^+	353 (Pe_4N^+)	353	377[c]
Hx_4N^+	423 (Hx_4N^+)	423	447[c]
Hp_4N^+	488 (Hp_4N^+)	488	
Sr^{2+}	−9 (NO_3^-)	−9	
Ba^{2+}	−6 (NO_3^-)	−6	
Cl^-	23 (Na^+), 21 (NH_4^+)	22	22,[a] 23[b]
Br^-	30 (Na^+), 30 (K^+), 29 (NH_4^+)	28	28[a,b]
I^-	39 (Na^+), 37 (K^+), 38 (NH_4^+), 39 (Bu_4N^+)	39	39[a,b]
NO_3^-	32 (Na^+), 33 (K^+), 32 (NH_4^+)	32	32[a,b]

[a] Reference 153, muk. [b] Reference 155, muk. [c] Reference 129, *M*ex. [d] Estimated uncertainty ±4 cm^3 mol^{-1}.

Table 26. Standard Partial Molar Volumes, V°/(cm^3 mol^{-1}), of Electrolytes in *N*,*N*-Dimethylacetamide (DMA) at 25 °C[g]

	V°	
electrolyte	reported	selected
LiCl	7.8[f]	7.8
LiBr	16.6[f]	16.6
LiI	23.0[f]	23.0
$LiClO_4$	23.5[f]	23.5
$LiBF_4$	22.4[f]	22.4
$NaBPh_4$	[220.2][e]	
$KBPh_4$	[222.5][e]	
NH_4ClO_4	47.1[d]	47.1
Me_4NClO_4	115.9[d]	115.9
Et_4NClO_4	179.3[d]	179.3
Pr_4NBr	[197.4][e]	*243*
Pr_4NClO_4	249.1[d]	249.1
Bu_4NBr	[266.8][e]	*311*
Bu_4NClO_4	315.8,[b] 317.0[c,d]	**316.4**
Bu_4NBPh_4	[556.2],[b] 563.8,[c] [553.0][e]	*564*
Pe_4NBr	[327.6][e]	
Hx_4NBr	[411.7][e]	
Hp_4NBr	[479.6][e]	
Oc_4NBr	[542.4][e]	
$Be(ClO_4)_2$	26.1[a]	26
$Mn(ClO_4)_2$	47.6[b]	48
$Co(ClO_4)_2$	41.2[b]	41
$Ni(ClO_4)_2$	35.4[b]	35
$Cu(ClO_4)_2$	27.1,[a] 36.3[b]	
$Zn(ClO_4)_2$	55.6[b]	56
$Al(ClO_4)_{32}$	−37.9[a]	−38

[a] Reference 149, vtd. [b] Reference 158, vtd. [c] Reference 131, vtd, also 20 and 30 °C. [d] Reference 159, vtd. [e] Reference 160, pyc, V° calculated by the compilers from the density data. [f] Reference 161, pyc. [g] Values in square brackets [ ] are rejected. Recommended values are shown in **bold** type. Values obtained by additivity are given in *italic* type.

shown in Table 28. The data for several salts are available from two sources, but none has been confirmed independently. The difference $V^\circ(Br^-) - V^\circ(Cl^-)$ is 5.1 for Na^+ and 5.4 for K^+ (cm^3 mol^{-1}). For splitting the salt data into V°(ion) values, Mukerjee's method was used,[162] with results shown in Table 29.

Table 27. Standard Partial Molar Volumes of Ions, V°(ion)/(cm^3 mol^{-1}),[f] in *N*,*N*-Dimethylacetamide (DMA) at 25 °C[a]

		V°(ion)	
ion	V°(electrolyte) used	selected	reported
Li^+	−16 (ClO_4^-)		26[e]
Na^+			
K^+			
NH_4^+	8 (ClO_4^-)	8	8[a,d]
Me_4N^+	77 (ClO_4^-)	77	78[a,d]
Et_4N^+	141 (ClO_4^-)	141	
Pr_4N^+	210 (ClO_4^-)	210	
Bu_4N^+	278 (ClO_4^-)	278	279,[a,b] 281[a,c]
Mn^{2+}	−30 (ClO_4^-)		−30[a,b]
Co^{2+}	−37 (ClO_4^-)		−36[a,b]
Ni^{2+}	−43 (ClO_4^-)		−42[a,b]
Cu^{2+}			−41[a,b]
Zn^{2+}	−22 (ClO_4^-)		−22[a,b]
Cl^-	24 (Li^+)	24	−19[e]
Br^-	33 (Li^+)	33	−10[e]
I^-	39 (Li^+)	39	−3[e]
ClO_4^-	39[a]	39	39,[a,b] 36,[a,c] −3[e]
BF_4^-	38 (Li^+)	38	−4[e]
BPh_4^-	286 (Bu_4N^+)	286	279,[a,b] 283[a,c]

[a] Using the ratio $V^\circ(Bu_4N^+)/V^\circ(BPh_4^-)$ traceable to the TPTB assumption, refs 131 and 158. [b] Reference 158. [c] Reference 131. [d] Reference 159. [e] Reference 161, *M*ex. [f] Estimated uncertainty ±2 cm^3 mol^{-1}.

Table 28. Standard Partial Molar Volumes, V°/(cm^3 mol^{-1}), of Electrolytes in *N*-Methylpropanamide (NMP) at 25 °C[e]

electrolyte	reported V°	electrolyte	reported V°
HOBz[d]	100.2[a]	KBr	40.9[a]
NaCl	30.7[a]	Pr_4NI	210.0[b]
NaBr	35.8[a]	Bu_4NI	316.9[b]
$NaNO_3$	39.6[a,c]	Pe_4NI	389.0[b]
NaOBz[d]	103.6[a]	Hp_4NI	522.5[b]
KCl	35.5[a]		

[a] Reference 162, mfl, 25 °C. [b] Reference 121, dil, extrapolated by the compilers from data at 35−70 °C. [c] Data also at 15−40 °C. [d] OBz^- = benzoate. [e] All values are unconfirmed.

Table 29. Standard Partial Molar Volumes of Ions, V°(ion)/(cm^3 mol^{-1}),[b] in *N*-Methylpropanamide (NMP) at 25 °C, Using Mukerjee's Method

ion	reported V°(ion)[a]	ion	reported V°(ion)[a]
H^+	3.4	Br^-	29.8
Na^+	6.0	NO_3^-	33.6
K^+	11.1	OBz^-	97.7
Cl^-	24.7		

[a] Identical results based on the same data reported in ref 162, muk. [b] Estimated uncertainty ±4 cm^3 mol^{-1}.

5.15. Salt and Ion Volumes in Hexamethylphosphoric Triamide (HMPT)

Standard partial molar volumes at 25 °C have been reported for only a few 1:1 electrolytes in hexamethylphosphoric triamide (HMPT; Table 30). Replicate data from independent sources are available for only three salts: NaI, Ph_4AsBr, and Ph_4AsBPh_4 (TATB). However, the values obtained either are not in very good agreement (NaI, Ph_4AsBr) or are stated by the original authors to have large uncertainties (TATB), and thus, none has been recommended. No additivity tests were possible, but it is noted that the value of V°(TATB) obtained by additivity differs markedly (by

Table 30. Standard Partial Molar Volumes, $V°/(\mathrm{cm^3\ mol^{-1}})$, of Electrolytes in Hexamethylphosphoric Triamide (HMPT) at 25 °C[h]

electrolyte	reported $V°$
LiCl	*−7*[f]
LiBr	*3*[f]
LiI	20.7[a]
NaCl	*2*[f]
NaBr	*12*[f]
NaI	29.8,[a] 27.4,[d] **29**[g]
$NaBPh_4$	283[a]
KCl	*14*[f]
KBr	*24*[f]
KI	41.6[a]
RbCl	*19*[f]
RbBr	*29*[f]
RbI	*47*[f]
CsCl	*25.5*[f]
CsBr	*34.5*[f]
CsI	*53.5*[f]
Pr_4NBr	212[e]
Bu_4NBr	296[b]
Bu_4NBBu_4	573[b]
Pe_4NBr	343[e]
Hx_4NBr	421[e]
Hp_4NBr	503[e]
Ph_4AsBr	281,[a] 289,[b,c] **285**[g]
Ph_4AsI	301[a]
Ph_4AsBPh_4	564,[a,c] *555*,[a] 565,[b,c] **561**[g]

[a] Reference 96, vtd. [b] Reference 163, vtd. [c] Cited by authors as having a large uncertainty. [d] Reference 164, bou. [e] Reference 165, vtd, calculated by the present reviewers from density data in the original paper. [f] Reference 93, review of literature data; original data not accessible. [g] Value selected by present reviewers. [h] Recommended values are shown in **bold** type. Values obtained by additivity are given in *italic* type.

~10 cm^3 mol^{-1}) from the directly measured values.[96,163]

Although in other solvents the values of $V°$(TATB) obtained by additivity have been preferred over those obtained by direct measurement, the uncertainties noted above make it more prudent to take the mean of all the reported values as the best available estimate at the present time. Application of the selected result for $V°$(TATB) to the other data in Table 30 gives the $V°$(ion) values listed in Table 31. Little can be said about these data, but it is interesting to note that, as for other typical dipolar aprotic solvents such as DMF and DMSO, the values of $V°(Bu_4N^+)$ and $V°(BBu_4^-)$ obtained via the TATB assumption differ by ~20 cm^3 mol^{-1}. However, in HMPT the effect is opposite that in DMF and DMSO; that is, $V°(BBu_4^-) < V°(Bu_4N^+)$. The source of this remarkable difference is unknown.

Table 31. Standard Partial Molar Volumes of Ions, $V°(\mathrm{ion})/(\mathrm{cm^3\ mol^{-1}})$,[d] in Hexamethylphosphoric Triamide (HMPT) at 25 °C, Calculated Assuming $V°(Ph_4As^+) = V°(BPh_4^-) + 8\ \mathrm{cm^3\ mol^{-1}}$

		$V°$(ion)	
ion	$V°$(electrolyte) used	selected	reported[a]
Li^+	1 (I^-)	1	2
Na^+	6 (BPh_4^-)	6	11
K^+	22 (I^-)	22	23
Pr_4N^+	212 (Br^-)	212	
Bu_4N^+	296 (Br^-)	296	
Pe_4N^+	343 (Br^-)	343	
Hx_4N^+	421 (Br^-)	421	
Hp_4N^+	503 (Br^-)	503	
Ph_4As^+	282 (Ph_4AsI, $NaBPh_4$, NaI), 286[b]	285[c]	282
Br^-	0 (Ph_4As^+)	0	1
I^-	16 (Ph_4As^+), 23 (Na^+)	20	19
BBu_4^-	277 (Bu_4N^+)	277	
BPh_4^-	274 (Ph_4AsI, $NaBPh_4$, NaI), 278[b]	277[c]	273

[a] Reference 96, TA = TB, based on almost the same values presented in Table 30; similar values are also reported in ref 23. [b] Derived from averaged TATB values obtained by direct measurement (refs 96 and 163). [c] Derived from averaged TATB values allowing for round-off errors. [d] Estimated uncertainty ±2 cm^3 mol^{-1}.

5.16. Salt and Ion Volumes in Nitromethane (NM, $MeNO_2$)

Table 32. Standard Partial Molar Volumes, $V°/(\mathrm{cm^3\ mol^{-1}})$,[b] of Electrolytes in Nitromethane (NM) at 25 °C

electrolyte	reported $V°$	electrolyte	reported $V°$
$LiCF_3SO_3$	59.7[a]	Ph_4PF	297.9[a]
$NaCF_3SO_3$	64.7[a]	Ph_4PCl	298.7[a]
$NaBPh_4$	270.3[a]	Ph_4PBr	306.1[a]
KCF_3SO_3	69.0[a]	Ph_4PI	319.0[a]
$CsCF_3SO_3$	79.3[a]	$Ph_4PCF_3SO_3$	362.2[a]

[a] Reference 23, vtd. [b] Values are unconfirmed.

Table 33. Standard Partial Molar Volumes of Ions, $V°(\mathrm{ion})/(\mathrm{cm^3\ mol^{-1}})$,[b] in Nitromethane (NM) at 25 °C, Calculated Assuming $V°(Ph_4P^+) = V°(BPh_4^-) + 2\ \mathrm{cm^3\ mol^{-1}}$

ion	$V°$(electrolyte) used[a]
Li^+	−18 ($CF_3SO_3^-$)
Na^+	−13 (BPh_4^-)
K^+	−8 ($CF_3SO_3^-$)
Cs^+	3 ($CF_3SO_3^-$)
Ph_4P^+	285 ($Ph_4PCF_3SO_3$, $NaBPh_4$, $NaCF_3SO_3$)
F^-	13 (Ph_4P^+)
Cl^-	14 (Ph_4P^+)
Br^-	21 (Ph_4P^+)
I^-	34 (Ph_4P^+)
$CF_3SO_3^-$	79 (Ph_4P^+)
BPh_4^-	283 ($Ph_4PCF_3SO_3$, $NaBPh_4$, $NaCF_3SO_3$)

[a] Values identical to those given in ref 23, using the same TPTB split as that in the present review. [b] Estimated uncertainty ±3 cm^3 mol^{-1}.

The only values available for the standard partial molar volumes of electrolytes in nitromethane (NM) are those given in the unpublished thesis of Pang[23] at 25 °C. His findings are summarized in Table 32. The $V°$ values were determined from Masson plots of $^{\phi}V$ (eq 6), obtained by vibrating tube densimetry, against $c^{1/2}$ at $c < 0.1$ M. However, given that the relative permittivity for NM is not very high ($\epsilon = 35.8$ at 25 °C) and that for many salts the $^{\phi}V$ values showed no significant dependence on c,[23] the uncertainty in the $V°$ values is probably higher than usual. No additivity tests are possible, so no assessment of the self-consistency of the data can be made.

The $V°$(ion) values obtained by application of the TPTB assumption to the data in Table 32 are summarized in Table 33. A Mukerjee plot for these data (not shown) gives $V°$(ion) values that agree with the TPTB assumption to within ±4 cm^3 mol^{-1}. Examination of the plot suggests that $V°(F^-)$ might be too large, but little else can be said at this stage, pending further studies.

Table 34. Standard Partial Molar Volumes, $V°/(\mathrm{cm^3\ mol^{-1}})$, of Electrolytes in Dimethylsufoxide (DMSO) at 25 °C

electrolyte	$V°/(\mathrm{cm^3\ mol^{-1}})$	selected $V°$
LiCl	4.2,^{a} 4.7,^{b} [10.4],^{c} 4.7^{d}	**4.5**
LiBr	[*9.1*],^{b,t} 14.0,^{e} [19.6],^{c} 11.8,^{d} 12.3,^{j} 13.5^{x}	**12.9**
LiI	28.4,^{a} *23.7*^{b}	28.4
$LiNO_3$	[*18.1*]^{b}	*21*^{q}
$LiClO_4$	[92.1]^{f}	*41*^{q}
NaCl	11.6,^{a} [*15.0*],^{b} 12.9,^{s} 12.3,^{c} 13.1,^{e} [14.6^{x}]	**12.5**
NaBr	[20],^{g} 19.4,^{b} 19.9, 19.1,^{d} 19.4^{s}	**19.5**
NaI	[36],^{g} 32.8,^{a} *34.0*,^{b} 33.4,^{c} 33.5,^{h} 34.2,^{d} 34.8^{s,u}	**33.7**
$NaNO_3$	28,^{g} 28.4^{b}	**28.2**
$NaClO_4$	45.7^{c}	45.7
$NaBPh_4$	290,^{a} 290.0,^{c} 289,^{f} 291.8,^{k} 290.0,^{s} [284.1^{x}]	**290.2**
KOH	19^{w}	19
KCl	20.0,^{a} [*23.8*]^{b}	20.0
KBr	[23],^{g} 28.1,^{b} 27.7,^{c} 29.4,^{d} 28.1^{s}	**28.4**
KI	40.5,^{a} 42.8,^{b} 43.1,^{s} 41.9,^{c} 42.7^{h}	**42.2**
KNO_3	[34],^{g} 37.3^{b}	37.3
RbCl	[*29.9*],^{b} [*22.2*, *32.5*]^{s}	*26*^{q}
RbBr	[36.0],^{b} 33.7,^{s} 32.7,^{c} 32.5,^{f} 32.8^{x}	**33.0**
RbI	48.9,^{b} 47.5,^{h} [*43.2*, *49.5*]^{s}	**48.2**
$RbNO_3$	41.6^{b}	41.6
CsCl	*31.5*,^{b} [*25*, *39.4*]^{s}	*32*^{q}
CsBr	39.9,^{b,t} 39.8,^{s} 39.5^{x}	**39.8**
CsI	[46],^{g,t} 53.5,^{b} 54.9,^{h} [49.7]^{d}	**54.2**
$CsNO_3$	47.5^{b}	47.5
$AgNO_3$	19.1^{l}	19.1
NH_4ClO_4	58.9^{m}	58.9
Me_4NCl	94.6^{i}	94.6
Me_4NBr	99.5,^{i} 102.8^{s}	101
Me_4NClO_4	129.2^{m}	129.2
Et_4NBr	161.4^{s}	161.4
Et_4NI	171^{g}	171
Et_4NNO_3	168.6^{l}	168.6
Et_4NClO_4	187.8^{l,m}	187.8
Pr_4NBr	232.0^{s,v}	232
Pr_4NI	240^{g}	240
Pr_4NClO_4	258.7^{m}	258.7
Bu_4NBr	298.7,^{e} 300.2^{s}	**299.5**
Bu_4NI	[305]^{g}	*313*^{q}
Bu_4NClO_4	326.9^{m,n}	326.9
Bu_4NBBu_4	589.3^{e}	589.3
Bu_4NBPh_4	571.7^{n}	571.7
Pe_4NI	373^{g}	373
Pe_3BuNBr	404^{x}	404
Hp_4NI	517^{g}	517
Bu_4PBr	316.3^{s}	316.3
Ph_4PF	287.6^{d}	287.6
Ph_4PBr	304.1,^{c} 308.0^{e}	306
Ph_4PBPh_4	[549.0]^{e}	*577*^{q}
Ph_4AsCl	304,^{a} 303.3^{k}	**303.7**
Ph_4AsI	321^{a}	321
Ph_4AsBPh_4	[588],^{a} [*579*]^{a}	*582*^{q}
$Be(ClO_4)_2$	79.4^{l}	79
$Mg(ClO_4)_2$	62.7^{l}	63
$Mn(ClO_4)_2$	[71.8],^{o} 62.4^{p}	62
$Co(ClO_4)_2$	[69.5],^{o} 58.2^{p}	58
$NiCl_2$	[−5.8]^{p,r}	*−16*^{q}
$Ni(ClO_4)_2$	[66.4],^{o} 55.0^{p}	55
$Cu(ClO_4)_2$	[68.4],^{o} 57.0^{p}	57
$ZnCl_2$	[40.3]^{p,r}	*−11*^{q}
$Zn(ClO_4)_2$	[73.1],^{o} 59.8^{p}	60
$Al(ClO_4)_3$	78.8^{l}	79
$Fe(ClO_4)_3$	84.9^{l}	85

[a] Reference 96, vtd. [b] Reference 81, vtd. [c] Reference 166, vtd. [d] Reference 23, vtd. [e] Calculated in ref 166 using density data (vtd) from ref 178. [f] Reference 167, method not stated. [g] Reference 143, pyc, extrapolated by the reviewers from data at 35−70 °C. [h] Reference 169, method not stated but probably bou [ref 168]. [i] Reference 170, vtd; data also available for unsymmetrical alkylammonium salts. [j] Reference 171, vtd. [k] Reference 172, vtd. [l] Reference 173, vtd. [m] Reference 159, vtd. [n] Reference 131, vtd. [o] Reference 174, vtd. [p] Reference 175, vtd. [q] Calculated by the present reviewers by additivity using the selected $V°$(ion) values from Table 35. [r] Values rejected due to poor additivity, possibly as a result of complex formation. [s] Reference 176, vtd? [t] Slightly different value given in ref 93 although taken from the same source. [u] Another, obviously incorrect, value of 96.1 $\mathrm{cm^3\ mol^{-1}}$ is also cited in ref 93. [v] Incorrectly cited as Pr_4NCl in ref 93. [w] Estimated by the present reviewers by extrapolation of data for DMSO + W mixtures in ref 176; unknown uncertainty. [x] Reference 177, pyc, calculated by compilers from densities; data also at 35 and 45 °C.

5.17. Salt and Ion Volumes in Dimethylsulfoxide (DMSO)

The standard partial molar volumes of salts in dimethyl sulfoxide (DMSO) have been studied extensively at 25 °C (Table 34), with values mainly for 1:1 electrolytes but with a few for 2:1 and 3:1 salts also being available. Relatively few of these values have been independently replicated, and only some of the 1:1 electrolytes are sufficiently well characterized to permit their means to be recommended.

Extensive additivity tests are possible with typical results as follows (all values in $\mathrm{cm^3\ mol^{-1}}$): $V°(Br^-) - V°(Cl^-) = 8.4\ (Li^+)$, 7.0 ($Na^+$), 8.4 ($K^+$), 4.9 ($Me_4N^+$); $V°(I^-) - V°(Br^-) = 15.5\ (Li^+)$, 14.2 ($Na^+$), 13.8 ($K^+$), 15.2 ($Rb^+$), 14.3 ($Cs^+$), *6.3 ($Bu_4N^+$)*; $V°(I^-) - V°(Cl^-) = 21.2\ (Na^+)$, 22.2 ($K^+$), *17.3 ($Ph_4As^+$)*; $V°(ClO_4^-) - V°(I^-) =$ *63.7 (Li^+)*, 12.2 (Na^+), 16.8 (Et_4N^+), *21.9 (Bu_4N^+)*; $V°(NO_3^-) - V°(Br^-) = 8.7\ (Na^+)$, 8.9 ($K^+$), 8.6 ($Rb^+$), 7.7 ($Cs^+$); $V°(Na^+) - V°(Li^+) = 8.0\ (Cl^-)$, 6.6 ($Br^-$), 5.3 ($I^-$); $V°(K^+) - V°(Na^+) = 7.5\ (Cl^-)$, 8.9 ($B^-$), 8.5 ($I^-$), 9.1 ($NO_3^-$); $V°(Rb^+) - V°(K^+) = 4.6\ (Br^-)$, 6.0 ($I^-$), 4.3 ($NO_3^-$); $V°(Cs^+) - V°(K^+) = 11.4\ (Br^-)$, 12.0 ($I^-$), 10.2 ($NO_3^-$); $V°(Me_4N^+) - V°(K^+) = 74.6\ (Cl^-)$, 72.6 ($Br^-$); $V°(Et_4N^+) - V°(K^+) = 128.8\ (I^-)$, 131.3 ($NO_3^-$); $V°(Pr_4N^+) - V°(Et_4N^+) = 69\ (I^-)$, 70.9 ($ClO_4^-$); $V°(Bu_4N^+) - V°(Et_4N^+) =$ *134 (I^-)*, 139.1 (ClO_4^-). Values in *italic* font are outliers.

These additivities indicate that the reported $V°$ values for $LiClO_4$, Bu_4NI, (directly measured) TPTB,[166] $NiCl_2$,[175] and $ZnCl_2$[175] are incorrect. For the latter two salts, this is directly ascribable to ion pairing not having been properly taken into account. The errors for $LiClO_4$ and $ZnCl_2$ are particularly spectacular (∼50 $\mathrm{cm^3\ mol^{-1}}$). The additivities are also useful for distinguishing between alternative values of $V°$ for various salts and have facilitated rejection of a number of outliers (Table 34).

As for DMF, the solubilities of both TATB and TPTB are sufficient to enable their $V°$ values to be determined from direct density measurements of their solutions, but again as for DMF, the uncertainties in the values so determined[96,148] are high. Thus, the $V°$(TATB,TPTB) values obtained by additivity, which are mutually consistent to better than 1 $\mathrm{cm^3\ mol^{-1}}$, are preferred. The $V°$(ion) values based on the TPTB assumption are given in Table 35. The present values are consistent, as would be expected, with the

Table 35. Standard Partial Molar Volumes of Ions, $V°$(ion)/(cm^3 mol^{-1}),[k] in Dimethylsulfoxide (DMSO) at 25 °C, Calculated Assuming $V°(Ph_4P^+) = V°(BPh_4^-) + 2$ cm^3 mol^{-1}

ion	$V°$(electrolyte) used	$V°$(ion)	
		selected	reported
Li^+	−5 (Cl^-), −4 (Br^-), −2 (I^-)	−4	0,[a] −20[b]
Na^+	3 (BPh_4^-)	3	6,[a] −10[b]
K^+	11 (Cl^-), 12 (Br^-), 11 (I^-)	11	14,[a] −1[b]
Rb^+	16 (I^-), 18 (I^-)	17	5[b]
Cs^+	23 (Br^-), 24 (I^-)	23	19,[a] 10[b]
Ag_+	−6 (NO_3^-)	−6	−5[c]
NH_4^+	14 (ClO_4^-)	14	
Me_4N^+	85 (Cl^-), 84 (Br^-)	85	
Et_4N^+	144 (Br^-), 140 (I^-), 144 (NO_3^-)	143	161[j]
Pr_4N^+	209 (I^-), 214 (ClO_4^-)	212	231[j]
Bu_4N^+	283 (Br^-), 282 (ClO_4^-)	282	294,[d] 283,[e] 298[j]
Pe_4N^+	342 (I^-)	342	367[j]
Hp_4N^+	486 (I^-)	486	
Ph_4P^+	289 (Ph_4PBr, $NaBPh_4$, NaBr)	289	279[d]
Ph_4As^+	295 (Ph_4AsCl, $NaBPh_4$, NaCl)	295	294[a]
Be^{2+}	−10 (ClO_4^-)	−10	−8[c]
Mg^{2+}	−27 (ClO_4^-)	−27	−24[c]
Mn^{2+}	−27 (ClO_4^-)	−27	−25[f]
Co^{2+}	−31 (ClO_4^-)	−31	−29[f]
Ni^{2+}	−34 (ClO_4^-)	−34	−32[f]
Cu^{2+}	−32 (ClO_4^-)	−32	−30[f]
Zn^{2+}	−29 (ClO_4^-)	−29	−27[f]
Al^{3+}	−55 (ClO_4^-)	−55	−52[c]
Fe^{3+}	−49 (ClO_4^-)	−49	−46[c]
OH^-	8 (K^+)	8[i]	
F^-	−2 (Ph_4P^+)	−2	
Cl^-	10 (Na^+), 9 (Ph_4As^+)	9	6,[a] 25[b]
Br^-	17 (Na^+), 17 (Ph_4P^+)	17	14,[a] 30,[b] 5,[d] 30[d]
I^-	31 (Na^+) [26 (Ph_4As^+)]	31	27,[a] 27,[g] 43[b]
NO_3^-	25 (Na^+), 26 (K^+), 25 (Rb^+), 24 (Cs^+)	25	39[b]
ClO_4^-	43 (Na^+), 45 (Me_4N^+), 45 (Et_4N^+)	44	43.5[h]
BBu_4^-	307 (Bu_4N^+)	307	295[d]
BPh_4^-	287 (Ph_4PBr, $NaBPh_4$, NaBr), 287 (Ph_4AsCl, $NaBPh_4$, NaCl)	287	285,[a] 271,[d] 288[e]

[a] Reference 96, TA = TB. [b] Reference 81, uvp, based on $V°(Br^-) = 29.7$ cm^3 mol^{-1}. [c] Reference 173, based on TPTB-traceable $V°(ClO_4^-) = 43.5$ cm^3 mol^{-1}. [d] Reference 178, vdW. [e] Reference 131, based on TPTB-traceable $V°(ClO_4^-) = 43.5$ cm^3 mol^{-1}. [f] Reference 175, based on TPTB-traceable $V°(ClO_4^-) = 43.5$ cm^3 mol^{-1}. [g] Reference 81, *M*ex based on R_4NI data of ref 143. [h] References 131, 159, 173, and 175, preferred TPTB-traceable value; other values were derived by different methods discussed in ref 159. [i] Unknown uncertainty; see footnote *w* in Table 34. [j] Reference 129, *M*ex, at 35 °C. [k] Estimated uncertainty ±2 cm^3 mol^{-1}.

Table 36. Standard Partial Molar Volumes, $V°$/(cm^3 mol^{-1}), of Electrolytes in Dichloromethane (CH_2Cl_2) at 25 °C[a]

electrolyte	reported $V°$	electrolyte	reported $V°$
Et_4NClO_4	167	Hx_4NClO_4	442
Pr_4NClO_4	235.5	Oc_4NClO_4	581
Bu_4NBr	283	Dc_4NBr	692
Bu_4NI	295	Dc_4NClO_4	716
Bu_4NSCN	297	Ph_4AsCl	271
Bu_4NClO_4	304.5	Ph_4AsBr	277
Bu_4NBBu_4	538	Ph_4AsI	292
Bu_4NBPh_4	532	Ph_4AsSCN	294
Hx_4NI	432	Ph_4AsClO_4	303

[a] Reference 179, vtd. Values are unconfirmed.

earlier estimates by Parker et al.[96] based on their approximate results for TATB. However, they differ markedly (by up to 16 cm^3 mol^{-1}) from those obtained by the uvp assumption[81] but only by ∼4 cm^3 mol^{-1} from the application of Mukerjee's method using current ionic radii (section 3). As in most other solvents, the $V°(R_4N^+)$ values derived from the *M*ex method[96] differ greatly (by up to 25 cm^3 mol^{-1}) from the TATB/TPTB-derived values. The slight temperature difference should not have much effect on these values (see section 5.11). The values of $V°(Bu_4N^+) \approx V°(BBu_4^-) + 20$ cm^3 mol^{-1} again differ substantially on the TATB/TPTB scale, as is found for DMF (section 5.11).

5.18. Salt and Ion Volumes in Dichloromethane (CH_2Cl_2)

A single paper[179] has reported apparent molar volumes at 25 °C, obtained by the vtd method, of tetraalkylammonium and tetraphenylarsonium salts in dichloromethane. It was recognized that due to the low relative permittivity of the solvent, $\epsilon = 8.93$ at 25 °C, a considerable fraction of the salts would be associated, so that eq 18 [${}^{\phi}V = \alpha{}^{\phi}V_i + (1 - \alpha){}^{\phi}V_{ip}$] was invoked. However, since plots of ${}^{\phi}V$ against $c^{1/2}$ in the range $0.03 \le c^{1/2}/(\text{mol}^{1/2}\ \text{dm}^{-3/2}) \le 0.45$ were linear, it was concluded that ${}^{\phi}V_{ip} \approx {}^{\phi}V_i$, so that extrapolation of such plots to $c^{1/2} = 0$ yielded valid $V°$ values (Table 36). Exceptions were the plots for the tetraphenylarsonium and substituted borate salts, which were curved, as would be expected when ${}^{\phi}V_{ip} > {}^{\phi}V_i$ and the fraction associated, $(1 - \alpha)$, increases with increasing *c*. For these salts it was assumed that $V°$ was 5 cm^3 mol^{-1} lower than the value obtained by extrapolation of the linear portion of the curves (at $c^{1/2} > 0.1$ mol$^{1/2}$ dm$^{-3/2}$). Ionic additivity could be demonstrated for the following: $V°(Bu_4N^+) - V°(Ph_4As^+) = 6$ (Br^-), 3 (I^-), 3 (SCN^-), and 1.5 (ClO_4^-) and $V°(ClO_4^-) - V°(I^-) = 9.5$ (Bu_4N^+), 10 (Hx_4N^+), and 11 (Ph_4As^+) cm^3 mol^{-1}. The approach taken[179] was reasonable, and the authors suggested a maximal uncertainty, mainly associated with the likely (unresolved) effects of ion pairing, of 2 cm^3 mol^{-1} for the tetraalkylammonium salts and 5 cm^3 mol^{-1} for the tetraphenylarsonium salts. However, without further studies and more sophisticated data processing, the real errors are unknown.

Application of the TATB method for splitting the $V°$ values into the ionic contributions results in the values shown in Table 37. Somewhat different (lower cation, higher anion) values were obtained by the authors[179] by application of the Criss and Cobble correspondence method,[180] according to which, for a set of ions in two solvents A and B, $V°(\text{ion,A}) = aV°(\text{ion,B}) + b$. Application of this to CH_2Cl_2 and MeCN gave $V°(Bu_4N^+) = 269.1$ cm^3 mol^{-1} and to CH_2Cl_2 and PC gave 269.4 cm^3 mol^{-1}. The value 269 cm^3 mol^{-1} for this ion was therefore reported, and hence, the values for the other ions shown in Table 37 were obtained.[179] The authors[179] also reported that the *M*ex method produced the unreasonably low value $V°(ClO_4^-) = 6$ cm^3 mol^{-1} whereas the *N*ex method yielded $V°(ClO_4^-) = 29$ cm^3 mol^{-1}, which is still slightly on the low side of the value selected.

5.19. Miscellaneous Solvents

Over the years many authors have reported desultory density data for electrolytes in various solvents,

Table 37. Standard Partial Molar Volumes of Ions, $V°$(ion)/(cm^3 mol^{-1})[b] in Dichloromethane (CH_2Cl_2) at 25 °C, Calculated Assuming $V°(Ph_4As^+) = V°(BPh_4^-) + 8$ cm^3 mol^{-1}

ion	$V°$(electrolyte) used	$V°$(ion) selected	$V°$(ion) reported
Et_4N^+	134 (ClO_4^-)	134	130
Pr_4N^+	202.5 (ClO_4^-)	203	199
Bu_4N^+	271 (BPh_4^-), 271.5 (ClO_4^-)	271	269
Hx_4N^+	409 (ClO_4^-), 408 (I^-)	409	405
Oc_4N^+	548 (ClO_4^-)	548	544
Dc_4N^+	683 (ClO_4^-), 680 (Br^-)	682	680
Ph_4As^+	269 (I^-, ClO_4^-)	269	266
Cl^-	2 (Ph_4As^+)	2	6
Br^-	12 (Bu_4N^+)	12	12
I^-	24 (Bu_4N^+)	24	26
SCN^-	26 (Bu_4N^+), 25 (Ph_4As^+)	26	28
ClO_4^-	32 (Ph_4As^+), 33.5 (Bu_4N^+)	33	37
BBu_4^-	267 (Bu_4N^+)	267	269
BPh_4^-	261 (Bu_4N^+)	261	264

[a] Reference 179, correspondence method (see text). [b] Estimated uncertainty ±3 cm^3 mol^{-1}.

often along with calculation of apparent and/or standard partial molar volumes. In the absence of additional data that might have allowed a critical assessment, these reports were not sufficient to be included into separate tables. As a service to future researchers, the available information is compiled in Table 38. Included are solvents of medium or low relative permittivity, where ion pairing undoubtedly takes place. Almost certainly, the reported "$V°$(electrolyte)" values, invariably obtained by the Masson expression (eq 6), do not represent the true standard partial molar volumes of the dissociated electrolyte.

Only in few cases did the authors attempt to calculate $V°$(ion) values. The reported values for glycerol[185] have been split by the present reviewers using Mukerjee's method (but with plots against r^2; see section 3.3), with the results listed in Table 39. Wadi and Kathuria[194] applied the Mukerjee method (using the usual plots against r^3) to their data in 2-aminoethanol (MEA) with the resulting $V°$(ion) values shown in Table 39. They added values for Rb^+ and Cs^+ for which no $V°$(electrolyte) data were reported, obtained from the "correspondence principle":[80] $V°(\text{ion,MEA}) = a + bV°(\text{ion,water})$. The accuracy of these $V°$(ion) data[194] may be questioned on the basis of the unlikely undulating course of their plots against the composition of mixtures of water with MEA. For 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF) the reported values[38] were for $^{\phi}V$ at 0.05 M and were taken to be approximations for $V°$(electrolyte). These were then split into the ionic contributions on the assumption that TA = TB (i.e., that $^{\phi}V(Ph_4As^+) = {}^{\phi}V(BPh_4^-)$; Table 39). This would underestimate cation values and overestimate anion ones by ~4 cm^3 mol^{-1} compared to the preferred TATB split (section 3.5). Extrapolations of plots of $V°(R_4NX)$ against the molar mass of R_4N^+ (*M*ex, section 3.4) were employed for 2-methoxyethanol (MeOEtOH) for X = Br^- and ClO_4^- (refs 96 and 197) and for sulfolane (TMS) for X = I^- to yield the $V°$(ion) values shown in Table 39. The $V°(X^-)$ values are seen to be considerably and unreasonably too low (hence, the $V°(R_4N^+)$ values are too high), as is usual for the unreliable *M*ex method.

6. Discussion

6.1. Effects of Ion–Solvent Interactions on Ionic Volumes

A commonly used approach to understanding ion–solvent interactions considers the process of ion solvation as the transfer of the ion from the ideal gas phase to the solution. Although this process can be invoked at any concentration, to ensure that only ion–solvent interactions are occurring (without the effects of ion–ion interactions), only the transfer at infinite dilution of the ion in the solvent will be considered. The ion then transfers from a situation where it is devoid of interactions to a situation where it interacts (mutually) with the surrounding solvent alone. It is convenient to regard this process as proceeding in several stages, as often invoked when discussing standard molar Gibbs energies of solvation of ions: (1) The ion is discharged in the ideal gas phase. (2) A cavity of the size of the ion is created in the solvent. (3) The (discharged) ion is transferred from the ideal gas phase into the cavity. (4) The ion is re-charged in the solution. (5) The ion interacts with the solvent by (a) long-range electrostatic interactions and (b) short-range covalent interactions (donor–acceptor and hydrogen bonding). (6) The solvent is rearranged around the ion due to the interactions and to the inherent structure of the solvent. Each of these stages is accompanied by changes in the thermodynamic properties, such as the Gibbs energy, enthalpy, and so forth, and the volume. These changes are ultimately expressed in the standard partial molar volume of the ion, $V°$(ion).

To simplify discussion and to avoid the large changes in the molar volume associated with the transfer of an ion from the gas phase to the solution, it is more instructive to limit consideration to just the following contributions to $V°$(ion).

(1) The ion has a definite *intrinsic* size, V_{int}, for which a cavity in the solvent must be provided.

(2) The ion has a large electric field that exerts a strong compressive effect on the surrounding solvent, referred to as *electrostriction*, V_{el}.

(3) Short-range interactions take place, in particular where multivalent cations (donor–acceptor interactions) and anions (hydrogen bonding) are concerned, that are manifested by a volume effect V_{cov}.

(4) The volume of the solvent, V_{str}, changes due to its rearrangement around the ion as a result of the size, shape, electric field (beyond the effects of electrostriction), and short-range interactions of the ion and the size, shape, and structure of the solvent molecules.

If these volume effects are chosen as to be independent of each other (orthogonal), then the partial molar volume of the ion can be considered as their sum:

$$V°(\text{ion}) = V_{\text{int}} + V_{\text{el}} + V_{\text{cov}} + V_{\text{str}} \qquad (30)$$

Table 38. Reported Standard Partial Molar Volumes, $V°$/(cm^3 mol^{-1}), of Electrolytes in Various Solvents at 25 °C

solvent	electrolyte	reported $V°$
n-PrOH	HCl	6[a]
	LiCl	0,[b] −11[c]
	$LiNO_3$	12,[d] 17[gg]
	Et_4NI	162[e]
	Et_4NPi[nn]	167[e]
	$Ca(NO_3)_2$	43[f]
i-PrOH	$LiNO_3$	14[gg]
	Bu_4NBr	296[g]
n-BuOH	LiCl	3,[b] −12[c]
	$LiNO_3$	19[gg]
	NaI	−10[h]
	$NaBPh_4$	?[h]
	Et_4NCl	127[h]
	Et_4NI	169[e]
	Et_4NPi[nn]	172[e]
	Bu_4NCl	?[h]
	Bu_4NBr	240[h]
	Bu_4NI	319[h]
i-BuOH	LiCl	1,[b] −13[c]
	$LiNO_3$	17[gg]
n-HxOH	LiCl	−11[c]
2-EtHxOH	LiCl	−16[c]
2-MeOEtOH	Me_4NClO_4	105[kk]
	Et_4NBr	150[jj]
	Et_4NClO_4	171[kk]
	Pr_4NBr	217[jj]
	Pr_4NClO_4	239[kk]
	Bu_4NBr	288[jj]
	Bu_4NClO_4	308[kk]
	Pe_4NBr	354[jj]
	Pe_4NClO_4	376[kk]
	Hx_4NBr	424[jj]
	Hx_4NClO_4	445[kk]
	Hp_4NBr	488[jj]
furfurol	Et_4NI	173[j]
propylene glycol	HCl	10[i]
glycerol	NaCl	14[k]
	KCl	24[k]
	KBr	33[k]
	KI	45[k]
THF	LiBr	14[o]
	$LiClO_4$	22,[o] 23[n]
	$LiAsF_6$	42[n]
	$NaClO_4$	28[n]
	$NaCF_3SO_3$	74[n]
	$NaBPh_4$	247,[n] 252[ii]
	KCF_3SO_3	81[n]
	$Ph_4AsCF_3SO_3$	345[n]
1,2-dimethoxyethane	LiBr	1,[l] 14[m]
	$LiClO_4$	13,[l] 37,[m] 15[n]
	$LiAsF_6$	16[n]
	$NaClO_4$	18[n]
	$NaCF_3SO_3$	64[n]
	$NaBPh_4$	234[n]
	KCF_3SO_3	69[n]
	Bu_4NBr	296[mm]
	Pe_4NBr	365[mm]
	Hx_4NBr	435[mm]
	Hp_4NBr	504[mm]
	$Ph_4AsCF_3SO_3$	337[n]
1,3-dioxolane	$LiClO_4$	28[l]
salicylaldehyde	Et_4NI	176[j]
4-methyl-2-pentanone	CsBr	−34[hh]
	Bu_4NBr	226[hh]
	Bu_4NI	240[hh]
	Bu_4NClO_4	314[hh]
sulfuric acid	$LiHSO_4$	47[z]
	$NaHSO_4$	46[z]
	$KHSO_4$	53[z]
	$RbHSO_4$	59[z]
	$CsHSO_4$	68[z]
	$AgHSO_4$	53[z]
	$TlHSO_4$	62[z]
	NH_4HSO_4	59[z]
sulfuric acid	$H_3O^+ + HSO_4^-$	61[z]
	$Ca(HSO_4)_2$	84[z]
	$Sr(HSO_4)_2$	87[z]
	$Ba(HSO4)_2$	96[z]
selenic acid	$NaHSeO_4$	58[aa]
	$KHSeO_4$	62[aa]
	NH_4HSeO_4	68[aa]
phosphoric acid	$HClO_4$	54[y]
	$LiClO_4$	52[y]
	LiH_2PO_4	49[y]
	NaH_2PO_4	51[y]
	$KHSO_4$	59[y]
	KH_2PO_4	58[y]
	$Mg(H_2PO_4)_2$	87[y]
methyl formate	LiBr	2[o]
	$LiClO_4$	19[o]
dimethyl carbonate	$LiClO_4$	26[p]
	$LiCF_3SO_3$	72[p]
	Bu_4NClO_4	329[p]
	Hx_4NClO_4	470[p]
γ-butyrolactone	LiBr	11[l]
	$LiClO_4$	35[l]
triethyl phosphate	NH_4ClO_4	48[q]
	Et_4ClO_4	166[q]
	Pr_4ClO_4	238[q]
	Bu_4ClO_4	309,[q] 310[r]
	Bu_4NBPh_4	553[r]
ammonia	Na (Na^+e^-)	59[s]
	NaCl	−38[t]
	NaI	−15[t]
	KI	−6[t]
methylamine	LiCl	−19[x]
	$LiNO_3$	12[x]
ethylenediamine	LiCl	14[bb]
	NaBr	33[u]
	$NaNO_3$	36[bb]
	AgCl	67[u]
	$AgNO_3$	30,[u] 20[bb]
	Bu_4NI	325[bb]
	HgI_2	69,[u] 112[bb]
	$Hg(CN)_2$	61[u]
2-aminoethanol	NaCl	17.8[dd]
	NaBr	21.8[dd]
	NaI	33.0[dd]
	KI	41.1[dd]
propanonitrile	Et_4NI	156[j]
nitrobenzene	Pr_4NClO_4	250[ee]
	Bu_4NClO_4	318[ee]
	Bu_4NPinn	407[ff]
	Ph_4PClO_4	327[ee]
sulfur dioxide	Me_4NBr	29[v]
	Et_4NBr	92[v]
	Pr_4NBr	164[v]
	BuNBr	235[v]
	Me_4NI	36[v]
	Et_4NI	104[v]
	Pr_4NI	173[v]
	Bu_4NI	246[v]
tetramethylene sulfone	NaI	29l[l]
	KI	39,[hh] 32[ll]
	RbNI	45,[hh] 35[ll]
	CsNI	54,[hh] 37[ll]
	Et_4NI	176[w]
	Pr_4NI	243[w]
	Bu_4NBr	302[hh]
	Bu_4NI	310,[w] 335,[hh] 277[ll]
	Pe_4NI	378,[w] 358[ll]
	Hx_4NI	445,[w] 425[ll]
	Hp_4NI	484[ll]
methyl thiocyanate	Et_4NI	167[j]
epichlorohydrin	Pr_4NI	234[j]
chlorobenzene	Bu_4NPi[nn]	402[cc]
o-dichlorobenzene	Bu_4NI	302[cc]

[a] Reference 97. [b] Reference 8. [c] Reference 71. [d] Reference 181. [e] Reference 64. [f] Reference 182. [g] Reference 183. [h] Reference 184, calculated by compilers from the densities, but the value 68 obtained for $NaBPh_4$ is unlikely to be correct. [i] Reference 116. [j] Reference 5. [k] Reference 185. [l] Reference 127. [m] Reference 40. [n] Reference 38. [o] Reference 123. [p] Reference 41. [q] Reference 159. [r] Reference 131. [s] Reference 186. [t] Reference 187. [u] Reference 14. [v] Reference 101. [w] Reference 188, 30 °C (also 40, 50 °C). [x] Reference 189/1. [y] Reference 200/1. [z] Reference 190/1. [aa] Reference 191/1. [bb] Reference 192/1. [cc] Reference 193/1. [dd] Reference 194. [ee] Reference 105. [ff] Reference 193. [gg] Reference 195, for *n*-PrOH data extrapolated to $m = 0$ and for other alcohols at $m = 0.6$ mol kg^{-1}. [hh] Reference 53, 40 °C. [ii] Reference 196. [jj] Reference 197. [kk] Reference 129. [ll] Reference 198. [mm] Reference 199. [nn] Pi = picrate.

Table 39. Reported Values of Standard Partial Molar Volumes of Ions, $V°(\text{ion})/(\text{cm}^3\ \text{mol}^{-1})$, for Miscellaneous Nonaqueous Solvents at 25 °C

	$V°(\text{ion})/(\text{cm}^3\ \text{mol}^{-1})$					
ion	glycerol[a]	MEA[b]	MeOEtOH[c]	DME[d]	THF[e]	TMS[f]
Li^+				−23	−17	
Na^+	−5	−4		−20	−13	
K^+	5	4		−15	−5	
Rb^+		9[g]				
Cs^+		15[g]				
Et_4N^+			157			157
Pr_4N^+			225			224
Bu_4N^+			294	299[i]		290
Pe_4N^+			362	369[i]		358
Hx_4N^+			431	438[i]		426
Hp_4N^+				507[i]		
Ph_4As^+				254	259	
Cl^-	19	22				
Br^-	28	26	−7[h]	−3[i]		
I^-	40	37				19
ClO_4^-			14	37	41	
AsF_6^-				39	57	
$CF_3SO_3^-$				84	86	
BPh_4^-				254	259	

[a] Reference 185, calculated by present reviewers, muk. [b] Monoethanolamine (2-aminoethanol), ref 194, muk. [c] 2-Methoxyethanol, ref 129, *M*ex. [d] 1,2-Dimethoxyethane, $^{\phi}V$ at $c = 0.05$ mol dm^{-3}, ref 38, TA = TB. [e] Tetrahydrofuran, $^{\phi}V$ at $c = 0.05$ mol dm^{-3}, ref 38, TA = TB. [f] Tetramethylene sulfone (sulfolane) at 30 °C, ref 188, *M*ex. [g] From correspondence method 180. [h] Reference 197, same values for R_4N^+, except Bu_4N^+, 295. [i] Reference 199, ex.

A somewhat different expression was presented by Millero[106] on the basis of the Frank and Wen model for aqueous ions:[201]

$$V°(\text{ion}) = V_{\text{int}} + V_{\text{el}} + V_{\text{dis}} + V_{\text{cag}} \qquad (31)$$

Here, V_{dis} describes the volume effect of the broken (disordered) water structure around structure-breaking ions and V_{cag} describes the volume effect of "caged" water around hydrophobic ions with alkyl or phenyl substituents. As some of these effects are applicable exclusively for water, eq 30 was preferred for the following discussion.

The relative magnitudes of these effects depend on the ions and the solvents. Marcus et al.[202] reported a comprehensive statistical treatment of the dependence of $V°(\text{ion})$ on properties of both ions and solvents. A computer program was employed to identify those properties that were statistically significant among a range of likely properties. It was found that different sets of properties are important for large ions (with alkyl or phenyl substituents) and small ions. The final result for the former was

$$V°(\text{large ion}) = 0.146 r_2^{\,3}[V_1^* - 7.1\alpha_1 + 0.44\delta_1] - 0.14\alpha_2[V_1^* - 8.6\alpha_1] \qquad (32)$$

where the subscripts 1 and 2 denote the solvent and ion, α is the polarizability (in 10^{-30} m^3), V_1^* is the molar volume of the pure solvent, and δ is the Hildebrand solubility parameter (in J$^{1/2}$ cm$^{-3/2}$).

For the small ions the corresponding expression was

$$V°(\text{small ion}) = 0.08 r_2^{\,3}[0.20 V_1^* + 1.00\delta_1] - 0.88 HB_2[\kappa_{T1} - 0.9 g_1] \qquad (33)$$

where HB denotes the hydrogen bonding ability of the ion,[203] κ_T is the solvent compressibility (in 10^{-10} Pa^{-1}), and g is its Kirkwood angular correlation parameter (a measure of solvent structuredness). The numerical coefficients are valid for the volumes in cubic cemtimeters per mole. These expressions cannot be disentangled in terms of the contributions in eq 30, but certain effects can be discerned. The intrinsic volume V_{int} depends on $r_2^{\,3}$ but also on V_1, due to voids in the packing. The electrostriction, important mainly for the small ions, should depend on κ_{T1} with a negative sign. Solvent structural effects, V_{str}, would be expected to depend on δ_1 and g_1 with a positive sign.

With reference to eq 30, small cations have a small V_{int} but a large (negative) V_{el}. If they are monatomic with complete electron shells, their short-range interactions (solvation by solvents having molecules with electron density donation abilities) do not have a strong requirement for specific spatial orientations. In nonaqueous solvents, the structure of which can generally be ascribed to dipole−dipole interactions (except for protic solvents), the sum $V_{\text{cov}} + V_{\text{str}}$ can be neglected or incorporated in V_{int} (that is then solvent dependent).

Anions with $r \geq 0.18$ nm (i.e., all anions except for F^- and OH^-) have relatively large V_{int} values but small (negative) V_{el} values. In protic solvents V_{cov} may be significant, due to the hydrogen bonding, although the resulting volume effects cannot readily be quantified and the same may be true for V_{str}.

For large ions (with $r \geq 0.25$ nm) V_{el} is negligible and V_{int}, estimated from the van der Waals volumes, is about 30−40% of $V°(\text{ion})$. Hence, $V_{\text{cov}} + V_{\text{str}}$, representing mainly V_{cag} of eq 31, is of prime importance.

The following subsections discuss in detail V_{int} (6.1.1), V_{el} (6.1.2), and $V_{\text{cov}} + V_{\text{str}} \approx V_{\text{cag}}$ (6.1.3).

6.1.1. Intrinsic Ion Volumes

The intrinsic molar volume of an ion, $V_{\text{int}}(\text{ion})$, represents the physical volume occupied by a mole of ions dissolved in an infinite amount of solution, disregarding all other effects. It is, therefore, in principle independent of the solvent and is generally thought to be only slightly dependent on temperature and pressure.[1,204] Still, the estimation of V_{int} is not as straightforward as it first appears.

The volume occupied by a single (essentially isolated) spherical ion is generally assumed to be its geometric value, $(4\pi/3)r_i^{\,3}$, using the crystallographic value for r_i.[87] Nevertheless, multiplying this quantity by Avogadro's number, N_A, to put it onto a molar basis, does not yield the macroscopic V_{int}. That is

$$V_{\text{int}} \neq (4\pi N_A/3) r_i^{\,3} = A r_i^{\,3} \qquad (34)$$

with $A = 2522$ when r_i is in nanometers and V_{int} is in cubic centimeters per mole. This is because the packing of the ions among the solvent molecules must be taken into account: regardless of the shape of the ions or the solvent molecules, a certain amount of void space will exist. The fraction of void space was considered by Stokes and Robinson to equal that in randomly packed spheres of unequal size. They found a value of 0.42 empirically, using steel balls. Hence, A should be multiplied by $1/(1 - 0.42)$ to yield $A = 4350$.[205]

Some authors regard V_{int}(ion) as depending on the solvent, in the sense that in aqueous solutions they specifically considered the packing of ions into the hydrogen bonded water structure. Thus, for fitting $V°$(ion,aq) values to eq 25,

$$V°(\text{ion}) = Ar^3 - Bz^2/r \qquad (25)$$

Hepler[27] proposed $A = 5300$ for cations and 4600 for anions. Again, from a consideration of spherical ions in structured water, Glueckauf[206] concluded that the void space was proportional to the surface area of the ion. The result was equivalent to adding an increment to the crystallographic ionic radius:

$$V_{int} = N_A(4\pi/3)(r_i + a)^3 = 2522[r_i/\text{nm} + 0.055]^3 \text{ cm}^3 \text{ mol}^{-1} \qquad (35)$$

For nonspherical ions in water, more elaborate expressions were suggested.[206] Rather than using an increment to r_i, making A dependent on the radius, Mukerjee[28] suggested a common factor for cations and anions of 1.213 to multiply the radius for fitting $V°$(ion,aq) values. This is equivalent to assigning $A = 4500$. The small difference in the A values of Hepler[27] and Mukerjee[28] essentially arises from their different splitting of the $V°$(electrolyte) values into $V°$(ion) values. Suggestions by other authors concerning V_{int}(ion) have been summarized by Millero.[1]

An alternative to the estimation of A via the V_{int}(ion) term needed to fit $V°$(ion) data is estimation of V_{int}(ion) from the packing of ions in condensed phases. It has been argued that although the nature of the interactions of ions with their surroundings in crystals and in solution are not the same (ion–ion vs ion–dipole), the compressive action of the respective electric fields on the ions does not differ greatly.[207] That is, when compared with their sizes in free space, ions are compressed to a similar extent in both crystals and solutions. Hence, the volumes of ions in crystals, from which ionic radii may be derived, as used in eq 34, are relevant for the estimation of V_{int}.

Values of V_{int}(ion) in the solid state have recently been obtained by Marcus et al. by consideration of ion packing in crystals,[208] where packing voids are also manifested. Such values can be employed to represent realistically V_{int}(ion) in solution. No universal packing coefficient was found, however, and although V_{int}(ion) was correlated with r_i^3, many ions were outliers and the correlations differed between cations and anions.[208]

Table 40. Radii, r_i/nm, and Intrinsic Volumes, V_{int}/(cm^3 mol^{-1}), of Ions for Which $V°$(ion,s) Values Have Commonly Been Determined

cation	r_i	V_{int}[a]	anion	r_i	V_{int}[b]
Li^+	0.069	1.1	F^-	0.133	7.8
Na^+	0.102	3.5	Cl^-	0.181	25.5
K^+	0.138	8.7	Br^-	0.196	32.1
Rb^+	0.149	10.9	I^-	0.220	43.4
Cs^+	0.170	16.2	SCN^-	0.213	42.8
Ag^+	0.115	5.0	NO_3^-	0.200	36.3
NH_4^+	0.148	10.7	ClO_4^-	0.240	44.4
Mg^{2+}	0.072	1.2	AsF_6^-	0.243	68.3[c]
Ca^{2+}	0.100	3.3	$CF_3SO_3^-$	0.230	81.3[c]
Sr^{2+}	0.113	4.8			
Ba^{2+}	0.136	8.3			

[a] $V_{int} = 3300r_i^3$ (see text); r_i from ref 87. [b] Values within the limits of error of the data ($N_A v_J$) in ref 208 that fit best the $V°$(ion,aq) values. [c] References 224 and 225.

Consider, according to Jenkins et al.,[209] a binary crystalline salt M_pX_q, where M^{q+} is the cation and X^{p-} is the anion. The close-packed volume of a formula unit of the ions in the crystal, V_c, is usually obtained from the unit cell parameters derived from X-ray diffraction:

$$V_c = (abc/Z)[1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma]^{1/2} \qquad (36)$$

where a, b, and c are the unit cell edges, α, β, and γ are the unit cell angles, and Z is the number of formula units per unit cell. This close-packing volume is made up from volumes ascribable to the cations, $V_c(M^{q+})$, and to the anions, $V_c(X^{p-})$:

$$V_c = pV_c(M^{q+}) + qV_c(X^{p-}) \qquad (37)$$

If the volume of one ion is known, others can be calculated from the presumed constancy and additivity of the close-packed ionic volumes. Since, in general, the volumes of the anions are considerably larger than those of the cations, the latter can be considered to occupy interstices among the former. The remaining (noninterstitial) volume in the crystal is then attributed to the anions. Goldschmidt radii, r_G, were ascribed to the alkali metal and alkaline earth metal cations,[209] so that for them $V_c(M^{q+}) = (4\pi/3)r_G^3$. Hence, $V_c(X^{p-})$ for the anions was obtained from eqs 36 and 37 by difference.

The values of V_{int}, taken to be the same in solids and solutions, are listed in Table 40[208,209] for those anions commonly found in electrolyte volume studies in nonaqueous solvents. Unfortunately, the values obtained in this manner are beset by large limits of error. Except for the cases of Rb^+ and Cs^+, the intrinsic volumes of the monatomic cations are small compared with those of the anions. It makes little difference if, for fitting $V°$(cation) values (section 5), the V_{int} values calculated according to eq 25 with $A = 2522$ or those calculated with A up to 4500 are used. Accordingly, an average of these extremes ($A = 3300$) is adopted for the monatomic cations together with the Shannon and Prewitt radii,[87] since the negative electrostrictive volumes are as large as or even appreciably larger than V_{int}(ion). For the anions (except F^-), however, the negative electrostrictive volumes are considerably smaller than V_{int}, so that the latter ought to be known much more accurately.

6.1.2. Solvent Electrostriction

More than a century ago, Drude and Nernst[210] recognized that the large electric field around an ion must have a strong compressive effect on the surrounding solvent. This compression is called electrostriction and contributes significantly to the standard partial molar volume of an ion. The field also causes dielectric saturation of the permittivity of a solvent in the vicinity of an ion, since the (dipolar) solvent molecules are highly oriented by the force lines of the field and are therefore no longer free to reorient in an imposed external field. At the surface of a Na^+ ion with $r_i = 0.102$ nm, the saturated permittivity is $\epsilon \approx 4\pi\epsilon_0 n_D{}^2 = 4\pi(8.854 \times 10^{-12})1.3325^2 = 1.98 \times 10^{-10}$ $C^2\ J^{-1}\ m^{-1}$ (using the refractive index n_D of water and ignoring its field dependence) and the electric field is then $E = e/\epsilon r_i{}^2 = (1.602 \times 10^{-19})/[(1.98 \times 10^{-10})(1.02 \times 10^{-10})^2] = 7.8 \times 10^{10}$ V m^{-1}. The pressure P exerted by such a large field is ~40 GPa (400 kbar).[211] For smaller or more highly charged ions, the field and pressure are correspondingly larger. The effects of such large fields on solvent properties have not in general been measured accurately till recently because of the difficulties of producing them experimentally; most earlier studies have employed fields smaller by ≥4 orders of magnitude.[60]

Most quantitative theoretical descriptions of electrostriction have modeled the ion as a conducting charged sphere imbedded in a dielectric continuum representing the solvent. The expression derived by Drude and Nernst[210] for the (negative) volume change per mole of ions due to electrostriction is in modern terms

$$V_{el} = (N_A e^2/8\pi\epsilon_0)\epsilon^{-1} z^2 r_i{}^{-1} (\partial \ln \epsilon/\partial P)_T = -B(\epsilon) z^2/r_i \tag{38}$$

where, for water at 25 °C, $B = 0.4175$ $cm^3\ mol^{-1}$ nm. The same expression was derived by Benson and Copeland[207] from the pressure derivative of the Gibbs energy change associated with charging an ion in a solvent according to the Born model.[212] As this expression ignores the dielectric saturation near the ion, it cannot yield a realistic estimate of the electrostriction.

It has been suggested[213,214] that for multivalent cations (in water) the solvent is not a continuum starting at the surface of the bare ion of radius r_i but rather a continuum only beyond its first solvation sphere, that is, at a distance $d = r_i + \Delta r$, that should replace r_i in the denominator of eq 38. The value $\Delta r = 0.276$ nm (the "hard sphere" diameter of a water molecule in liquid water) was suggested by Akitt,[213] but $\Delta r = 0.2387$ nm was obtained by Swaddle and Mak[214] by fitting experimental data, allowing for a closer approach of the water molecules to the octahedrally hydrated cations. However, this estimate of the electrostriction amounts to only ~ -5 $cm^3\ mol^{-1}$ for a typical divalent cation with $r_i \sim 0.08$ nm. This contraction is much smaller than most $V°(M^{2+}, aq)$ values, which are typically ~ -30 $cm^3\ mol^{-1}$. The rest of the negative volume is ascribed to "captured" solvent, that is $-n_i V_w$, where n_i is the primary coordination number and V_w is the molar volume of water, irrespective of the charge z_i of the cation, for $z_i > 1$.[213,214] This, however, is tantamount to assuming that the hard sphere volume of the captured water, $n_i \times 6.5$ $cm^3\ mol^{-1}$, just disappears from the solution! A compensation for this large negative contribution (~ -108 $cm^3\ mol^{-1}$ for a coordination number of $n_i = 6$) is the larger intrinsic volume of the ion, $(4\pi N_A/3)(r_i + \Delta r)^3$, so that the net effect represents the $V°$(ion) values ($\Delta r = 0.2387$ nm was obtained from such data fitting[214]).

Such severe electrostriction is likely to apply only to highly charged ions. Since in nonaqueous solvents there are few well-characterized $V°$ values for multivalent cations and none for multivalent anions (see section 5), eq 38 should provide a reasonable estimate of the electrostriction for the bulk of the available data (for univalent ions). However, it must be recognized in the application of eq 38 that dielectric saturation must be taken into account for the smaller ions and that a key quantity required is the (relative) pressure derivative of the permittivity, $\partial \ln \epsilon/\partial P$. Up to the time of Millero's review,[1] which discussed the electrostrictive volume of ions, the only solvents for which $\partial \ln \epsilon/\partial P$ data were available were water and methanol. Thus, little use could be made of the Drude–Nernst expression, and empirical values of B were mainly employed.[28,207]

Alternative expressions for electrostriction, recognizing the dielectric saturation of the solvent near the ion, have been suggested for aqueous[211,215] and methanolic[113] solutions and more recently by Marcus[216] for nonaqueous solvents in general. Padova's expression,[215] following the electrostatic–thermodynamic considerations of Frank,[217] was

$$V^{-1}(\partial V/\partial E)_{\mu,T} = -\epsilon_0 E\,(\partial\epsilon/\partial P)_{E,T} \tag{39}$$

which involves the double integral

$$V_{el} = (4\pi\epsilon_0 N_A/2)\int_{r_i}^{\infty}\int_0^{E_r}(\partial\epsilon/\partial P)_{E,T}\,d(E^2)\,r^2\,dr \tag{40}$$

where E_r is the electric field strength at a distance r from the center of the ion. Padova employed Grahame's expression[218] for the field dependent relative permittivity:

$$\epsilon = n^2 + [\epsilon(E{=}0) - n^2]/(1 + bE^2) \tag{41}$$

where n is the refractive index of the solvent, itself pressure (field) dependent, and b is a field independent constant, depending on the solvent and temperature. Using the values of the solvent properties b, n, and $(\partial n/\partial P)_T$ for water[215] and methanol,[113] Padova evaluated the integrals numerically. He showed that for univalent ions only values of r in the ranges $0.180 \le r/\text{nm} \le 0.80$ in water and $0.197 \le r/\text{nm} \le 2.30$ in methanol needed to be used in the calculations, since below and above these limits ϵ is field independent.

Desnoyers et al.[211] also started from eq 39 but applied it to consecutive shells around the ion rather than calculating integrals from the surface of the ion to infinity, as in eq 40. The thickness of the shells corresponded to the diameter of the solvent (water) molecules. The field and resulting pressure were calculated, invoking Grahame's expression (eq 41). The calculations culminated in an expression for ΔV_{elW}, the electrostriction per mole of water:

$$\log(1 + \Delta V_{\mathrm{elW}}/V_{\mathrm{W}}) = -0.1469 \log[1 + (1.225 \times 10^{-20})(E/(\mathrm{V\ m^{-1}}))^2] \quad (42)$$

The field strength that needs to be employed in calculations according to eq 42 is that at the distance from the center of the ion to the middle of the hydration layer: $d = r_{\mathrm{i}} + r_{\mathrm{W}}$, where r_{W} is the radius of a water molecule.[211] To calculate the electrostriction per mole of ions, it is necessary to invoke a coordination number, that is, the number of water molecules in the first coordination shell (and further shells for multivalent ions). Using the Shannon and Prewitt[87] radius for $\mathrm{Na^+}$, the relevant distance is $d = r_{\mathrm{i}} + r_{\mathrm{W}} = 0.240$ nm, where the field strength is 1.4×10^{10} V m^{-1} and the value of $\Delta V_{\mathrm{elW}} = -3.0$ cm^3 (mol water)$^{-1}$ results. With a coordination number of 4 assumed by Desnoyers et al.,[211] this yields $V_{\mathrm{el}} = -12.0$ cm^3 mol^{-1}. This value is in reasonable agreement with the "experimental" quantities. With $V°(\mathrm{Na^+,aq}) = -6.7$ cm^3 mol^{-1} and $V_{\mathrm{int}} = 3.5$ cm^3 mol^{-1} (Table 40), $V_{\mathrm{el}} = (-6.7 + -3.5) = -10.2$ cm^3 mol^{-1}. The difference between the calculated and "observed" values of V_{el} is hardly significant and may well reflect the choice of the value of r_{i} or the distance d, packing effects (which influence V_{int}), solvent structural effects, and, of course, $V°$ (which has an unknown uncertainty that, see section 3, might be as large as ±2 cm^3 mol^{-1}).

With more information available on the electric field and pressure dependences of the permittivity of nonaqueous solvents,[60] it became feasible to extend the calculation of electrostriction volumes. The approach taken[216,226] involves calculation of the field strength in consecutive shells around an ion but does not confine itself to discrete shell thicknesses that depend on solvent molecular sizes. Instead, the solvent around the ion is considered to be a continuum, the permittivity of which is pressure and electric field dependent. It employs a shell-by-shell evaluation of the electrostriction for ion i and solvent s from the expression

$$V_{\mathrm{el}}(\mathrm{i,s}) = -(8\pi^2 N_{\mathrm{A}}\epsilon_0)\sum[r(j)^3 - r(j-1)^3]\{\epsilon(j)[(\partial \ln \epsilon/\partial P)_T - \kappa_{\mathrm{T}}] + \kappa_{\mathrm{T}}\}E(j)^2 \quad (43)$$

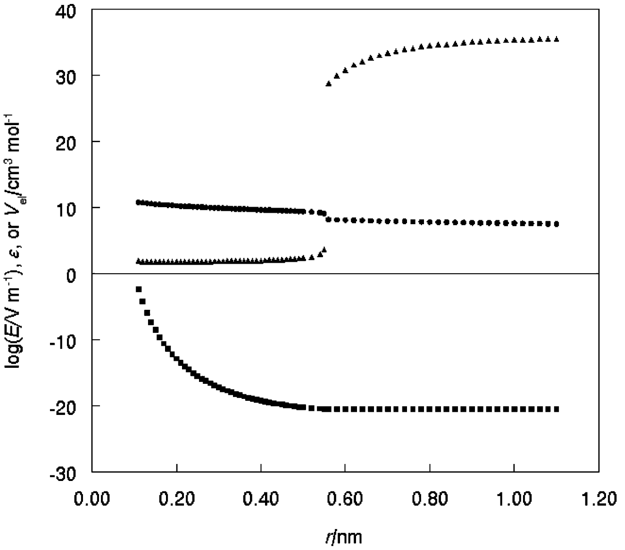


Figure 6. Electric field strength, expressed as log(E/V) (●), the relative permittivity, ϵ (▲), and the electrostriction, V_{el}/(cm^3 mol^{-1}) (■), around a $\mathrm{Na^+}$ ion in MeCN as functions of the distance r/nm from the center of the ion. Similar plots for $\mathrm{Na^+}$ in EtOH[60] and $\mathrm{K^+}$ in DMSO and $\mathrm{Li^+}$ in DME[216] have been reported.

where κ_{T}(s) is the isothermal compressibility of the solvent. The index j is the shell number starting from 1, with $r(0) = r_{\mathrm{i}}$, and a constant small radius increment $\Delta r = r(j) - r(j-1)$ is used. The sum is evaluated for successive j values until the electric field strength $E(j)$ is sufficiently small for $\epsilon(j)$ to equal the bulk value ϵ(s). Equation 43 can be modified for polar solvents, by noting that $n^2 \ll \epsilon$(s), so that the exact value of n^2 and its field and pressure dependences are immaterial. The nonlinear dielectric effect is obtained on expansion, rearrangement, and truncation of eq 41 as

$$\epsilon(E) - \epsilon(0) = \beta(\mathrm{s})E^2 \quad (44)$$

with the coefficient $\beta(\mathrm{s}) \approx -b[\epsilon(0) - n^2]$ being known to be only slightly field dependent. The electric field strength, in turn, depends on the permittivity:

$$E(j,\epsilon,r) = z_{\mathrm{i}}e/4\pi\epsilon_0[\epsilon(0) + \beta(\mathrm{s})\ E(j,\epsilon,r)^2]r(j)^2 \quad (45)$$

Therefore, an iterative calculation of both $E(j,\epsilon,r)$ and $\epsilon(j,E,r)$ must be made. Figure 6 shows the dependence of E, ϵ, and V_{el} for $\mathrm{Na^+}$ ions in acetonitrile as a functions of the distance r from the center of the ion. Note that, due to the mutual dependence of E and ϵ, E is essentially a step function. This has the consequence of a sharp increase in ϵ at a certain distance although most of the electrostriction has already taken place at this distance.

Values of $V°(\mathrm{ion}) = V_{\mathrm{int}} + V_{\mathrm{el}}$ for many univalent ions in several protic and aprotic dipolar solvents have been calculated[216] using the V_{int} values in Table 40 and V_{el} from eqs 43–45. They are in good accord with the selected "experimental" values in section 5.

6.1.3. Structural Effects

For the small univalent cations and anions, that is, those with $r_{\mathrm{i}} \leq 0.25$ nm, the sum of the electrostrictive volume, V_{el}, and the intrinsic volume, V_{int}, adequately accounts for the standard partial molar volume of the ions, even if V_{int} is taken to be solvent independent. For these ions the terms $V_{\mathrm{cov}} + V_{\mathrm{str}}$ in eq 30 are therefore negligible. This is not the case for the larger ions that are represented in the database by the tetraalkylammonium and the tetraphenyl ions with $r_{\mathrm{i}} > 0.25$ nm, for which V_{el} and, of course, V_{cov} are negligible, so that $V° \approx V_{\mathrm{int}} + V_{\mathrm{str}}$.

The V_{int} values of the R_4N^+ ions are taken to be the molar van der Waals volumes, V_{vdw}, as calculated by King[219] from the group contributions reported by Bondi:[220]

$$V_{\mathrm{vdw}}(R_4N^+)/(\mathrm{cm}^3\ \mathrm{mol}^{-1}) = V_{\mathrm{vdw}}(Me_4N^+) + 10.23n_{\mathrm{CH}_2} = 55.3 + 10.23n_{\mathrm{CH}_2} \quad (46)$$

The increment of V_{vdw} per $-CH_2-$ group is 10.23 cm^3 mol^{-1} whereas for $V°(\mathrm{aq})$ this increment is about 50% larger: 15.6 cm^3 mol^{-1}. For nonaqueous solvents, the $-CH_2-$ group increment in $V°$ is even larger, ranging from 16.3 (EG) to 18.3 (AC) cm^3 mol^{-1}, as estimated from $V°(R_4N^+)$ for successive R_4N^+ ions in the relevant tables in section 5. Clearly, for such ions a considerable structural effect needs to be taken into account.

The van der Waals volumes of Ph_4As^+ and BPh_4^- were reported by several authors,[94,221,222] with average values of 195.7 ± 2.6 and 187.7 ± 1.0 cm^3 mol^{-1}, respectively.[3] No van der Waals volume of Ph_4P^+ has been reported previously, but if the difference[220] $V_{\mathrm{vdw}}(AsH_3) - V_{\mathrm{vdw}}(PH_3) = 1.6$ cm^3 mol^{-1} is taken to apply also to the tetraphenyl ions, then $V_{\mathrm{vdw}}(Ph_4P^+) = 194$ cm^3 mol^{-1}. As for the R_4N^+ ions, the van der Waals volumes of $Ph_4X^{\pm}$, which are assumed to represent their intrinsic volumes, are much smaller than their $V°(\mathrm{ion})$ values. Hence, also for these ions, a considerable structural effect has to be applied.

The values of $V_{\mathrm{str}}(-CH_2-) = V° - V_{\mathrm{int}}$ are obtained from $^1/_4$ of the slope of the $\{V°(R_4N^+) - 40.9n_{\mathrm{CH}_2}\}$ versus n_{CH_2} plot. The $V_{\mathrm{str}}(-CH_3)$ per methyl group at the ends of the chains is obtained from $^1/_4$ of the intercept of the slope at $n_{\mathrm{CH}_2} = 1$ less 55.3; see eq 46. It was shown[216] that $V_{\mathrm{str}}(-CH_3)$ differs from and is smaller than the average $V_{\mathrm{str}}(-CH_2-)$ group value for the R_4N^+ ions for most of the solvents considered in the present review. The $V_{\mathrm{str}}(-CH_3)$ and $V_{\mathrm{str}}(-CH_2-)$ values are shown in Table 41. The values of $V_{\mathrm{str}}(-C_6H_5)$ per phenyl group are obtained as $^1/_4$ of the average differences $V°(Ph_4X^{\pm}) - V_{\mathrm{vdw}}(Ph_4X^{\pm})$, with values shown in Table 41.

It is interesting to note that, apart from the low value for water, the structural volume increment per methylene group is fairly independent of the solvent, with an average value of 7.0 ± 0.4 cm^3 mol^{-1}, for alkyl chains extending up to heptyl. This means that independently of the molecular size of the solvent, there is an exclusion volume around the ion into which the (center of the) solvent molecule cannot penetrate, as is the case for nonelectrolyte solutes too.[223] The $V°(Me_4N^+)/(\mathrm{cm}^3\ \mathrm{mol}^{-1})$ values can, therefore, be predicted (all ±2 cm^3 mol^{-1}) for the solvents for which no values have been reported: AC, 52; EC, 94; MeCN, 65; NMF, 69; DMF, 70; NMA, 69; and HMPT, 72.

However, the slight nonlinearity of the plots of $V°(R_4NX)$ or $V°(R_4N^+)$ against the alkyl chain size down to $V°(Me_4NX)$ or $V°(Me_4N^+)$ that has been noted[3] may affect these predictions. The fact that $\Delta_t V°(Me_4N^+, w\rightarrow s) = \Delta_t V°(Et_4N^+, w\rightarrow s)$ to within 1 cm^3 mol^{-1} for six solvents (section 6.2) and the accurately known values of $V°(Et_4N^+)$ leads to values of $V°(Me_4N^+)$ that are on the average 9 ± 2 cm^3 mol^{-1} larger than the above predictions. Nevertheless, missing values for intermediate tetraalkylammonium ions can be reliably predicted.

Table 41. Group Increments for Obtaining V_{str} for Tetraalkyl and -aryl Ions in Various Solvents, at 298.15 K, in cm^3 mol^{-1}

solvent	$-CH_3$	$-CH_2-$	$-C_6H_5$
water (w)	7.5	5.4	23.9
methanol (MeOH)	0.0	7.4	17.9
ethanol (EtOH)	3.9	6.7	18.0
1,2-ethanediol (EG)	5.9	6.0	23.5
2-methoxyethanol (MeOEtOH)	*a*	6.9	*c*
1,2-dimethoxyethane (DME)	*a*	7.1	15.5
acetone (AC)	*b*	8.1	15.8
ethylene carbonate (EC)	9.6	6.7	*c*
propylene carbonate (PC)	6.4	6.4	23.9
acetonitrile (MeCN)	2.4	7.2	21.0
formamide (FA)	3.5	6.7	25.8
N-methylformamide (NMF)	3.5	7.3	23.9
N,*N*-dimethylformamide (DMF)	3.6	7.2	23.3
N-methylacetamide (NMA)	3.5	7.4	*c*
N,*N*-dimethylacetamide (DMA)	5.1	6.6	24.5
hexamethylphosphoric triamide (HMPT)	4.2	8.0	22.3
dimethylsulfoxide (DMSO)	6.9	6.2	24.4
tetramethylene sulfone (TMS)	*a*	6.6	*c*
dichloromethane (CH_2Cl_2)	2.5	6.8	18.3

[a] $V_{\mathrm{str}}(-CH_3)$ cannot be calculated, since the $V°(\mathrm{ion})$ values were obtained by the *N*ex method that permits differences between successive members of the tetraalkylammonium ions to be obtained but not the reliable absolute values required to obtain $V_{\mathrm{str}}(-CH_3)$. [b] An unlikely negative value results from the data in Table 9, reflecting their possible incorrectness.[c] No $V°$ data for tetraphenyl ions.

The solvent dependence of the end groups (methyl) and phenyl groups is difficult to understand, since it does not correlate with the obvious properties of the solvents. This fact precludes the prediction of $V°$ values for the tetraalkyl or -aryl ions in solvents where the methyl and phenyl structural incremental data are not available.

Some solvent structural effects are discussed from a slightly different perspective in section 6.2, which deals with the volumes of transfer of the ions from water to the nonaqueous solvents. Such effects could be related to relatively smaller nonaqueous solvents, of which none shows any tendency for "hydrophobic" solvation, being able to penetrate somewhat between the alkyl chains or phenyl rings.

6.2. Ionic Transfer Volumes between Solvents

The volume of transfer of an ion from one solvent (A) to another (B), $\Delta_t V°(\mathrm{ion}, A\rightarrow B)$, is the difference between the standard partial molar volumes of the ion in the two solvents:

$$\Delta_t V°(\mathrm{ion}, A\rightarrow B) = V°(\mathrm{ion}, B) - V°(\mathrm{ion}, A) \quad (47)$$

As the transfer is carried out under standard state (infinite dilution) conditions, $\Delta_t V°(\mathrm{ion}, A\rightarrow B)$ reflects only differences between the mutual ion−solvent interactions in the two solvents. The choice of reference solvent (A) is arbitrary. However, as $V°$ values are best-characterized in aqueous solution and as one reason for studying nonaqueous solvents is to gain insights into the nature of liquid H_2O as a solvent, water (w) is usually adopted as the reference solvent

Table 42. Ionic Volumes of Transfer, $\Delta_t V°(\text{ion,w}\rightarrow\text{s})/(\text{cm}^3\ \text{mol}^{-1})$, between Water (w) and the Nonaqueous Solvent (s) Based on the TATB/TPTB Assumptions[d]

	$\Delta_t V°(\text{ion,w}\rightarrow\text{s})/(\text{cm}^3\ \text{mol}^{-1})$												
ion	H_2O[a]	MeOH	EtOH	EG	AC	PC	MeCN	FA	NMF	DMF	HMPT	NM	DMSO
H^+	−5.5	−12	−4	−6				9					
Li^+	−6.4	−13	−12	−2	[−56]	−3	−14	−1	−4	−1	7	−12	2
Na^+	−6.7	−12	1	4	−11	5	−10	4	4	5	13	−6	10
K^+	3.5	−12	−1	3		4	−13	4	2	3	19	−12	8
Rb^+	8.6	−13	0	3		2	−15	2		1			8
Cs^+	15.8	−13	1	5		1	−15	1	−2	1		−13	7
Ag^+	−6.2	−2				−2	−14			−5			0
NH_4^+	12.4	−10	0			−12	−12	0	−2	−1			2
Me_4N^+	84.1	−19	−8	−5		0		−1					1
Et_4N^+	143.6	−19	−7	−6	−19	−1	−12	−2	−4	−2			−1
Pr_4N^+	208.9	−10	−2	−3	−11	4	−3	2	2	4	3		3
Bu_4N^+	270.2	−7	6	5	1	13	6	9	10	11	[26]		12
Pe_4N^+	333.7	2	7			10	7	15		18	9		8
Hx_4N^+	395.9[b]					28		24		27	25		
Hp_4N^+	458.6[b]	14				28				30	44		27
Ph_4P^+	286.8	−25	−24		−32	−1	−16	7	−1	−3		−2	2
Ph_4As^+	295.2	−27		−3		−3	−14	6		−4	−10		0
F^-	4.3	−5	−21	1				9				9	−6
Cl^-	23.3	−8	−11	1	−31	−7	−20	2	3	−20		−9	−14
Br^-	30.2	−7	−15	1	−5	−4	−20	2	0	−21	−30	−9	−13
I^-	41.7	−12	−19	−1	−11	−10	−17	2	−1	−18	−22	−8	−11
NO_3^-	34.5		−13		−8		−20	3	3	−16			−10
ClO_4^-	49.6	−9			−30	−6	−16	4	0	−15			−6
SCN^-	41.2	−5					−12	7	5				
$CF_3SO_3^-$	80.2[c]		−15			0	−7	6	6			−1	
BPh_4^-	283.1	−23	−22	1	−30	1	−10	9	1	27	−6	0	4

[a] $V°(\text{ion,aq})$ based on the assumption $V°(H^+,\text{aq}) = -5.5\ \text{cm}^3\ \text{mol}^{-1}$,[2,75] which is broadly consistent with the TATB/TPTB assumption.[3] [b] Common salts insoluble in water;[230] value obtained by extrapolation of $V°(R_4N^+,\text{aq})$ vs $M(R_4N^+)$. [c] From ref 229. [d] Values in square brackets [ ] are to be rejected.

A. The advantage of employing $\Delta_t V°(\text{ion})$ rather than $V°$ values is that it removes the often rather large effects of the intrinsic volume of the ion (section 6.1.1), particularly for the anions and the larger cations. This choice is analogous to the use of $\Delta_t G°(\text{ion})$, rather than the much larger $\Delta_{\text{solvation}}G°(\text{ion})$ values, to better understand the energetics of ion solvation.[29]

Table 42 lists $\Delta_t V°(\text{ion,w}\rightarrow\text{s})$ values, with s being the target solvent B, based wherever possible on the TATB/TPTB assumption, for a broad cross section of ions for all of the solvents for which reasonable amounts of data exist. Only monovalent ions are included because of the uncertainties surrounding the values of $V°(\text{ion})$ for the multivalent cations (section 2.4) and the absence of data for multivalent anions. Also given in Table 42, column 2, are the values of $V°(\text{ion,w})$ which were mostly taken from the compilation of Marcus[228] and are based on the assumption that $V°(H^+,\text{aq}) = -5.5\ \text{cm}^3\ \text{mol}^{-1}$. This figure is derived from the detailed considerations of Conway[2,75] but is in good agreement with the TATB/TPTB assumption.[3] The values of $\Delta_t V°(\text{ion,w}\rightarrow\text{s})$ were obtained by application of eq 47 to these data and the "selected" values of $V°(\text{ion,s})$ from the relevant tables of section 5. Unless otherwise stated, all the following discussion will be based on the data in Table 42.

6.2.1. Effects of Solvent Properties

The removal of the dominating effect of intrinsic size by consideration of $\Delta_t V°(\text{ion,w}\rightarrow\text{s})$ rather than $V°(\text{ion})$ values enables insights to be gained on the effects of solvent properties. Given the importance of electrostriction (see section 6.1.2 above), it might be expected from simple physical considerations that there would be a strong correlation between $\Delta_t V°(\text{ion,w}\rightarrow\text{s})$ and both the relative permittivity (ϵ) and the isothermal compressibility (κ_T) of the solvent. Taking Na^+ and Cl^- as representative ions, plots of $\Delta_t V°(\text{ion,w}\rightarrow\text{s})$ show no correlation with permittivity. On the other hand, modest correlations ($R^2 \approx 0.5$ for a linear fit) exist against κ_T with the appropriate slope: $\Delta_t V°$ becomes more negative with increasing solvent compressibility. Surprisingly, $\Delta_t V°(Ph_4X^\pm,\text{w}\rightarrow\text{s})$ values, where $Ph_4X^\pm$ represents the "tetraphenyl" ions (Ph_4As^+, Ph_4P^+, and BPh_4^-), show definite correlations both with the solvent permittivity (Figure 7) and especially with the solvent compressibility (Figure 8). Why these effects should evidence themselves with the large relatively open-structured tetraphenyl ions is not clear.

Other solvent characteristics that were shown from a statistical analysis to be important in determining $V°(\text{ion,s})$[202] included donor/acceptor properties, molecular size (expressed as the molar volume), polarizability, and the Hildebrand solubility parameter, which is a measure of the cohesive energy density of the solvent. Each of these will now be considered, ignoring any (incidental) correlations between the solvent parameters themselves and again focusing on Na^+ and Cl^- as representative ions and the tetraphenyl ions because of their central importance in the TATB/TPTB assumptions.

As might be anticipated, there is a reasonable correlation between $\Delta_t V°(Cl^-,\text{w}\rightarrow\text{s})$ and solvent ac-

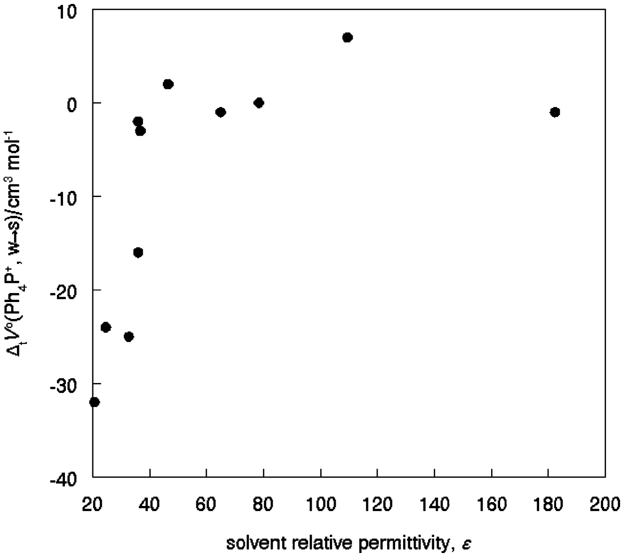


Figure 7. Standard partial molar volumes of transfer of the tetraphenyl ions between water and nonaqueous solvents as a function of solvent relative permittivity.

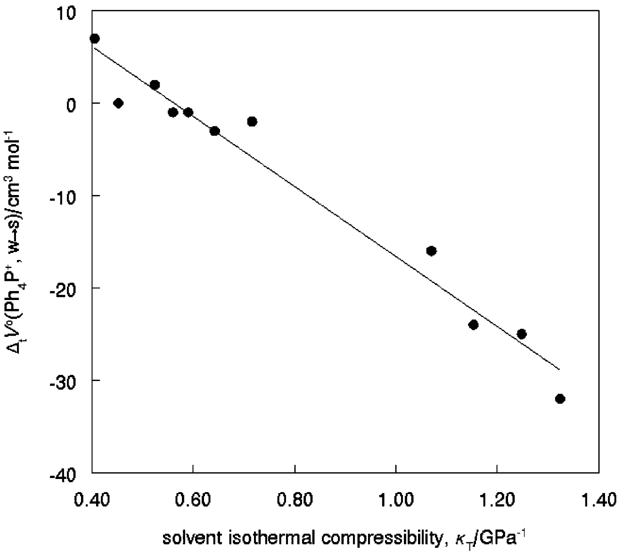


Figure 8. Standard partial molar volumes of transfer of the tetraphenyl ions between water and nonaqueous solvents as a function of solvent compressibility. The square of the correlation coefficient for the straight line (R^2) is 0.966.

ceptor strength, expressed as the Dimroth–Reichardt solvatochromic E_T parameter,[43] with $R^2 = 0.66$ for an imposed linear fit, although the dependency is somewhat curved (Figure 9). No correlation exists between $\Delta_t V°(BPh_4^-, w \rightarrow s)$ and E_T, which is consistent with the notion of such ions having minimal interactions with the solvent. In contrast, the correlation between $\Delta_t V°(Na^+, w \rightarrow s)$ and solvent donor strength, expressed as the Gutmann donor number (DN), is weak ($R^2 = 0.24$ for an assumed linear fit) and only marginally larger than the unexpected (and presumably coincidental) value of $R^2 = 0.22$ for a plot of $\Delta_t V°(Cl^-, w \rightarrow s)$ versus DN. Again, consistent with its expected solvation characteristics, there is no correlation between $\Delta_t V°(Ph_4X^{\pm}, w \rightarrow s)$ and DN.

Correlations between $\Delta_t V°(ion, w \rightarrow s)$ and the Hildebrand solubility parameter of the solvent range from modest for Cl^- ($R^2 = 0.47$ for an assumed linear fit) to weak for $Ph_4X^{\pm}$ ($R^2 = 0.18$) to nonexistent for Na^+. For the solvent molar volumes, no correlation exists with $\Delta_t V°(ion, w \rightarrow s)$ for Na^+ and $Ph_4X^{\pm}$ and only a weak one ($R^2 = 0.27$ for a linear fit) for Cl^-. Since solvent polarizabilities are highly correlated with their molar volumes ($R^2 = 0.97$ for a linear fit of the solvents in Table 42), similar (but not identical) results are found between $\Delta_t V°(ion, w \rightarrow s)$ and α_s.

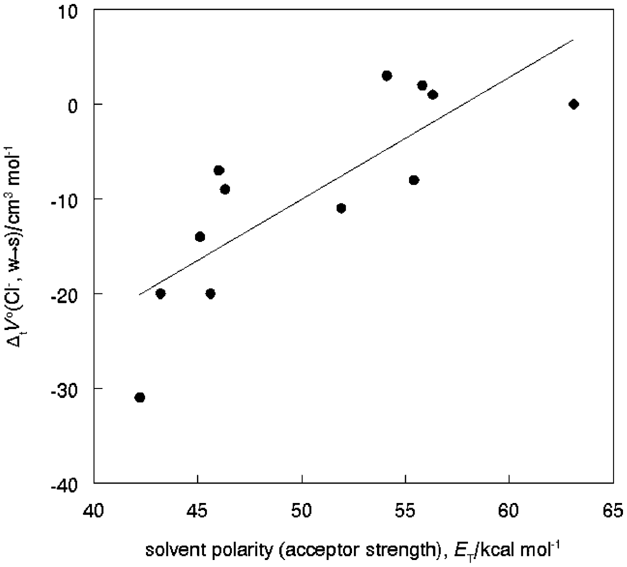


Figure 9. Standard partial molar volumes of transfer of the chloride ion between water and nonaqueous solvents as a function of solvent acceptor strength. The square of the correlation coefficient for the straight line (R^2) is 0.664.

Thus, in general, it appears that many of the factors that play important roles in determining $V°(ion,s)$ have smaller or even nonexistent effects on $\Delta_t V°(ion, w \rightarrow s)$. This is unexpected and may be due to the inadequacies of the existing database. It may also be a reflection of the composite nature of the volumes of ions in solution and the subtlety and complexity of the effects involved. The remaining discussion in this subsection is centered on the effects on representative groups of ions or on ions of particular importance and a consideration of the effects of charge.

6.2.2. Alkali Metal Ions

Figure 10 plots the values of $\Delta_t V°(M^+, w \rightarrow s)$ for the transfer of the alkali metal ions from water to a reasonable cross section of the solvents in Table 42. Note that in Figure 10 (and in Figures 11 and 12) lines connecting the data points have been added solely as a visual aid. Some of the scatter among the points is almost certainly associated with uncertainties in the $\Delta_t V°$ values. Despite the deficiencies of the database, the pattern is remarkably similar for virtually all solvents: an increase of ~(6 ± 2) cm^3 mol^{-1} going from Li^+ to Na^+ followed by a smaller decrease of ~(3 ± 1) cm^3 mol^{-1} going from Na^+ to Cs^+. Given that $\Delta_t V°(M^+, w \rightarrow s)$ values may differ by more than 20 cm^3 mol^{-1} according to the nature of the solvent (Figure 10), the preservation of this pattern is remarkable. The increase from Li^+ to Na^+ may be a reflection of packing effects: with the smaller and probably 4-coordinate Li^+ showing con-

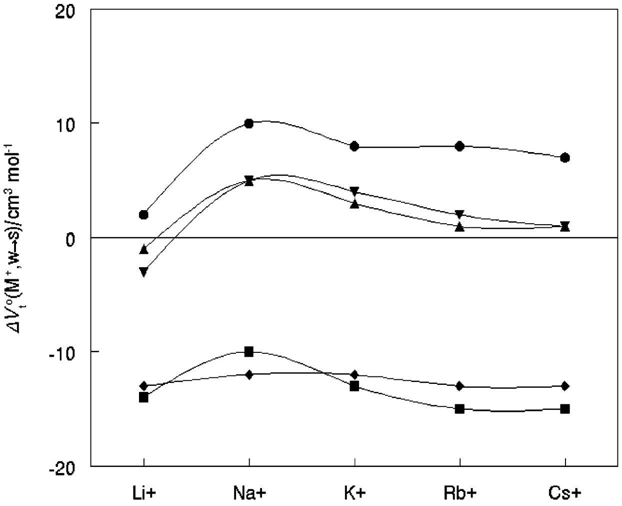


Figure 10. Standard partial molar volumes of transfer of the alkali metal ions between water and various nonaqueous solvents. Solvents: (◆) MeOH; (▼) PC; (■) MeCN; (▲) DMF; (●) DMSO.

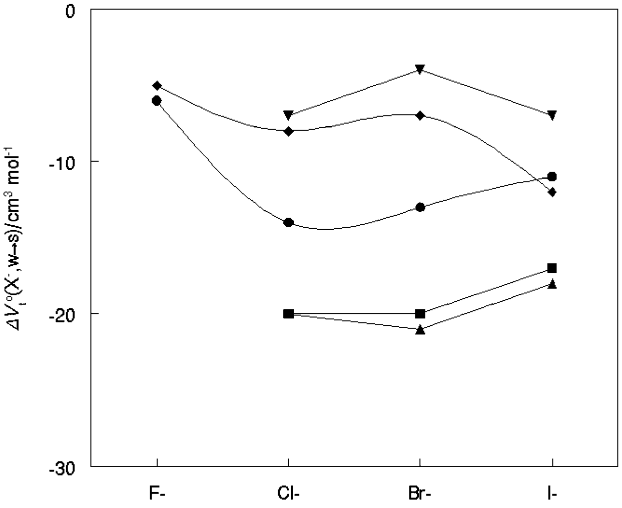


Figure 11. Standard partial molar volumes of transfer of the halide ions between water and various nonaqueous solvents. Solvents: (◆) MeOH; (▼) PC; (■) MeCN; (▲) DMF; (●) DMSO.

siderably smaller changes in $\Delta_{\mathrm{t}}V^\circ$ than the larger and typically 6-coordinate, heavier M^+ ions. It is also consistent with a greater electrostriction effect for Li^+, but if so, it seems surprising that there is so little variation from Na^+ to Cs^+. Although the pattern for transfer of M^+ between water and protic solvents (s = EtOH, FA, and EG) is similar to that for the aprotic solvents, the uniformity of the trend from Na^+ to Cs^+ is less for the alcoholic solvents. Values for $\Delta_{\mathrm{t}}V^\circ(M^+,w\rightarrow MeOH)$ are exceptional in that they are essentially invariant within the likely uncertainty.

6.2.3. Halide Ions

Values of $\Delta_{\mathrm{t}}V^\circ(X^-,w\rightarrow s)$ for the halide ions also show a definite but somewhat less clear-cut pattern (Figure 11). Thus, for the few solvents for which $\Delta_{\mathrm{t}}V^\circ(F^-,w\rightarrow s)$ is known, there is a decrease of ~8 $cm^3\ mol^{-1}$ going from F^- to Cl^-. The order from Cl^- to I^- is mixed, with transfers to some solvents (DMSO, MeCN) increasing but most showing irregular patterns. More importantly, as for the alkali metal ions,

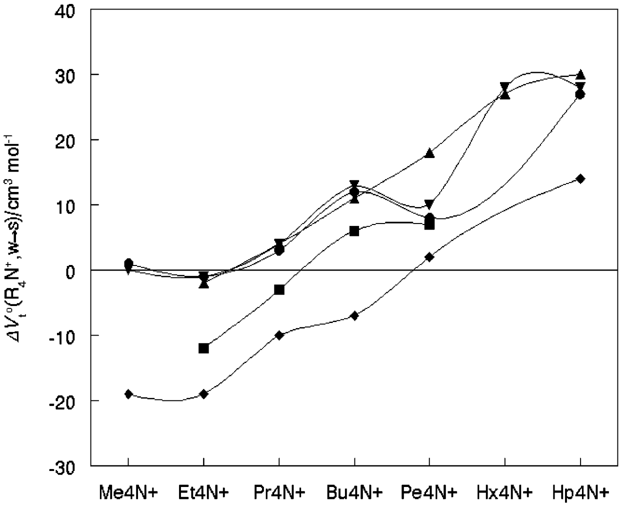


Figure 12. Standard partial molar volumes of transfer of the symmetrical tetraalkylammonium ions between water and various nonaqueous solvents. Solvents: (◆) MeOH; (▼) PC; (■) MeCN; (▲) DMF; (●) DMSO.

the differences from Cl^- to I^- are very small. The significant difference in the transfer volumes of F^- and Cl^- is probably a reflection of the very much stronger H-bonding of F^- in water. The exceptionally small value of $\Delta_{\mathrm{t}}V^\circ(F^-,w\rightarrow EG)$, even though EG is a weaker H-bond donor than water, might be related to an unusually compact structure of the solvated ion in this solvent, since EG is thought to chelate to F^-.[227]

6.2.4. Tetraalkylammonium Ions

The linearity of the volumes of the symmetrical tetraalkylammonium ions (or their salts) when plotted against molar mass or number of carbon atoms is well established and indeed forms the basis of the *M*ex and *N*ex extrapolation methods for deriving V°(ion) values (section 3.4). However, it is still revealing to look at their transfer volumes, where the differences between solvents are central.

The values of $\Delta_{\mathrm{t}}V^\circ(R_4N^+,w\rightarrow s)$ show an even more regular pattern (Figure 12) than those for the alkali metal ions. Thus, for all solvents for which reliable data are available (Table 42), $\Delta_{\mathrm{t}}V^\circ(Me_4N^+) = \Delta_{\mathrm{t}}V^\circ(Et_4N^+) \pm 1\ cm^3\ mol^{-1}$. Thereafter, $\Delta_{\mathrm{t}}V^\circ(R_4N^+,w\rightarrow s)$ increases more-or-less linearly and with much the same slope in *all* solvents. The global nature of this effect is undoubtedly related to the loss of hydrophobic hydration when R_4N^+ is transferred from water: the larger the ion (both in terms of volume and of surface area), the greater the change in volume as the hydrocarbon chains unfold into the nonaqueous solvent. This effect seems to persist up to at least Hp_4N^+, which is commonly the largest of the tetraalkylammonium ions studied to date, and is almost the same both in "water-like" solvents such as MeOH and FA and in dipolar aprotic solvents such as DMF and DMSO. This suggests that even nominally water-like solvents show no tendency for "hydro"-phobic solvation. This is consistent with the definition of hydrophobic hydration proposed by Tanford and Nozaki and based on the change of the Gibbs energy of transfer from water to ethanol (ref 31, p 113). The near equivalence of $\Delta_{\mathrm{t}}V^\circ$ values for Me_4N^+ and Et_4N^+

suggests that hydrophobic hydration of Me_4N^+ is insignificant. That is, in volumetric terms, Me_4N^+ behaves essentially like a typical inorganic ion; similar behavior has been observed for this ion with respect to other thermodynamic properties.[19,29] For a number of solvents (MeCN, PC, DMSO, and EtOH), $\Delta_t V°(Pe_4N^+,w\rightarrow s)$ is somewhat less positive than would be expected from the overall trend of the other R_4N^+ data. Whether this is a real effect or just a reflection of errors in the data cannot be determined from the data currently available.

The regularity of the trends in Figure 12 enables the values of $\Delta_t V°(R_4N^+,w\rightarrow s)$ and hence of $V°(R_4N^+,s)$ to be predicted to within a few cubic centimeters per mole, even if only one or two values of either quantity are known for that particular solvent.

6.2.5. Hydrogen Ion

In contrast to the cases of other thermodynamic properties such as Gibbs energies,[29] enthalpies,[19] and entropies,[19] very few values of $\Delta_t V°(H^+,w\rightarrow s)$ are known, which is a little surprising given the importance of the hydrogen ion. Of the values available, few can be considered reliable because the $V°(HX)$ data from which they have been derived are unconfirmed. With the exception of the case of FA, all values of $\Delta_t V°(H^+,w\rightarrow s)$ are mildly negative, probably reflecting greater electrostriction in solvents with larger compressibilities.

6.2.6. "Tetraphenyl" Ions

The volumes of the "tetraphenyl" ions, $Ph_4X^\pm$, are of course directly defined by the TATB/TPTB assumptions. Of the eleven solvents for which $\Delta_t V°(Ph_4X^\pm,w\rightarrow s)$ values are available, transfers to five (PC, NMF, DMF, NM, and DMSO) are approximately zero, to FA it is mildly positive, and to the remainder (MeOH, EtOH, AC, and MeCN) they are negative. The tetraphenyl ions are rather less hydrophobic than the longer chain R_4N^+ ions, but even so, a significant presence of water molecules between the rather open structures formed by the phenyl rings around the central atom would be unlikely. Thus, the negative values of $\Delta_t V°(Ph_4X^\pm,w\rightarrow s)$ might reflect the penetration of the more lipophilic nonaqueous solvents into these spaces. If so, it would be expected that smaller solvent molecules would show the most negative effects, and this does seem to be reflected in the data, although there is no correlation between $\Delta_t V°(Ph_4X^\pm,w\rightarrow s)$ and solvent molar volumes (this is partly because molar volumes reflect void space in the solvent as well as molecular size).

6.2.7. Perchlorate

Values of $\Delta_t V°(ClO_4^-,w\rightarrow s)$ are taken as representative of the polyatomic monovalent anions. Although the database is rather limited, the transfer volumes show a definite dependence on relative permittivity when $\epsilon_s < \epsilon_w$, similar to that shown in Figure 7, indicating that differences in electrostriction are only important at lower ϵ_s.

6.2.8. Effect of Ionic Charge

No transfer volumes for more highly charged ions have been included in Table 42 because of the uncertainties with regard to the "true" values of $V°(M^{n+},s)$ and the absence of data for multivalent anions (section 5). However, as discussed in section 6.1.2 and consistent with the Drude–Nernst equation,[210] the effects of ionic charge on $V°(ion,s)$ are large. It is therefore somewhat surprising that ionic charge appears to play a much smaller role in determining $\Delta_t V°(M^{n+},w\rightarrow s)$. Using the data available (section 5) from the better characterized solvents of reasonably high permittivity (to minimize ion pairing), with $V°(M^{n+},w)$ from the literature,[228] the transfer volumes for ions of similar size but differing charge do not differ dramatically (Table 43).

Table 43. Effect of Charge on $\Delta_t V°(M^{n+},w\rightarrow s)$ for the Transfer of Ions of Similar Crystallographic Size

	$\Delta_t V°(M^{n+},w\rightarrow s)$			
solvent	Li^+ r_i/pm = 69	Mg^{2+} r_i/pm = 72	K^+ r_i/pm = 138	Ba^{2+} r_i/pm = 136
PC	−3	1	4	8
FA	−1	10	4	12
NMF	−4	3	2	8
DMF	−2	5	3	2
DMSO	2	5	8	

Although the database is extremely limited and doubts exist about the reliability of the values for the divalent ions, the data in Table 43 suggest that the effects of ionic charge on $\Delta_t V°(M^{n+},w\rightarrow s)$ are *opposite* to their electrostriction tendencies. That is, the higher the ionic charge, the more positive is the value of $\Delta_t V°(M^{n+},w\rightarrow s)$. This suggests that the electrostriction effect is "loosened" in nonaqueous solvents compared with water. This may be related to packing effects of the solvent molecules around the cations, since all of the solvents for which data are available are rather larger than water. In this context, it may be noteworthy that this effect is largest for the two solvents (FA and NMF) with high permittivities, in which electrostriction effects will be smallest.

7. Conclusions

As is evident from the data presented in this review, a great deal has been achieved in the determination of the molar volumes of electrolytes and ions in nonaqueous solvents, but much remains to be done. In particular, it is desirable to have values for the molar volumes of a much wider range of "simple" salts in common solvents such as EtOH, EG, AC, NMF, and so forth and for a wider range of solvents, especially those with systematically varying properties. More data for the various salts used for splitting electrolyte volumes into their component ionic values (such as $NaBPh_4$, Ph_4PBr, and Ph_4AsI) would be useful. Despite the difficulties, careful measurements on salts containing higher valent ions and series of ions with systematically varying properties are especially required. Ideally, all such values would be based on measurements of apparent volumes down to solute concentrations that are as low as practicable and in which allowance is made (if appropriate) for ion-pairing effects. Reliable data on solvent properties of relevance to molar volumes, such as their isothermal compressibility and the effects of pressure and electric field strength on their dielectric constants, are also highly desirable.

With regard to theoretical aspects, the principles for calculating the volumes of ions in solvents appear to be reasonably well understood; what is required are more realistic models of solvent molecules that are more closely aligned with their actual properties such as their size, shape, charge distributions, polarizability, and so on. The increasing sophistication of modeling programs and the ongoing improvements in computer power should be very useful for such calculations.

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