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Ion Pairing

Yizhak Marcus*,† and Glenn Hefter‡

Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem 91904, Israel, and Chemistry Department, Murdoch University, Murdoch, WA 6150, Australia

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1. Introduction

1.1. Definition of Terms

Ion pairing describes the (partial) association of oppositely charged ions in electrolyte solutions to form distinct chemical species called ion pairs. Ion pair formation is invoked as the most plausible explanation either of certain types of direct experimental evidence (e.g., the appearance of a new band in the vibrational spectrum, see section 3.6) or of deviations observed at moderate concentrations from predictions of electrolyte theories that accurately describe the properties of very dilute electrolyte solutions. If the ion association is reasonably strong (the value depends on the charges on the ions and the relative permittivity of the solvent, but corresponds roughly to an association constant, K_A, of, say, ∼1000 M^{-1} in water, where $M \equiv \text{mol dm}^{-3}$), there is usually little difficulty in separating the properties of the ion pair from the long-range nonspecific ion−ion interactions that exist in all electrolyte solutions. However, when the ion association is weak, there is a strong correlation between these nonspecific ion−ion interactions (characterized in terms of activity coefficients) and ion pair formation (characterized in terms of an association constant). The often quoted saying of Onsager[1] is appropriate here: "The distinction between free ions and associated pairs depends on an arbitrary convention.... In a complete theory this does not matter; what we remove from one page of the ledger would be entered elsewhere with the same effect." From a more practical standpoint, Robinson and Stokes[2] (pp 49−50) comment: "The chief criterion for [classifying] an electrolyte [as nonassociated] is the absence of valid evidence for any form of association. Since the validity of such evidence can be a matter of personal opinion...there can be no general agreement."

To minimize such subjectivity, species are generally described as ion pairs if two oppositely charged ions in solution stay together at a separation, r, which is smaller than some specified cutoff distance, R. Ions further apart than R are considered "free". Various theories have been proposed for choosing the value of R and for describing the properties of the ion pairs and free ions that together produce the observed behavior of electrolyte solutions.

It is generally accepted that ions cannot approach each other more closely than some "distance of closest approach", a, due to the strong repulsive forces of the electron shells of the ions, even if polarizable. The distance a is understood

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† Hebrew University.
‡ Murdoch University.

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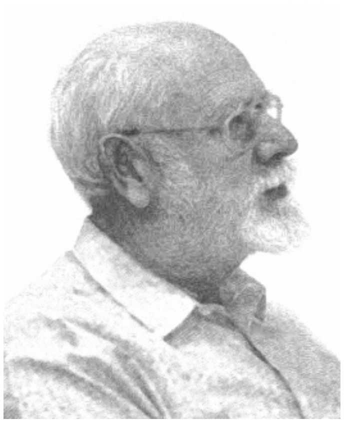
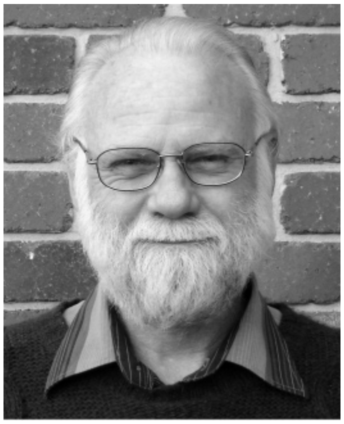


Yizhak Marcus was born in Germany and immigrated to Israel as a child. He obtained his M.Sc. degree in 1952 and his Ph.D. degree in 1956 in chemistry from the Hebrew University of Jerusalem. There he was Professor of Inorganic and Analytical Chemistry from 1965 to his retirement (to emeritus status) in 1999, and he continues to be active. Professor Marcus spent a dozen years with the Israeli Atomic Energy Commission laboratories, and he was a visiting scientist and professor in various countries: Australia, England, Germany, Japan, Turkey, and the U.S.A. His research interests concern solution chemistry, and he has published in this and neighboring fields 6 books and over 270 papers in refereed journals.



Glenn Hefter received his B.Sc. (in 1969) and his 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 areas, in which he has published over 200 papers, 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 co-edited and contributed to a book: *The Experimental Determination of Solubilities* (2003).

to bear some relation to the sum of the (crystal ionic) radii of the oppositely charged ions, generally $a \geq r_+ + r_-$. In summary, two ions of opposite sign are considered to form an ion pair if their distance apart is between a and R for a time longer than the time needed to diffuse over such a distance. Once ions are paired, they are thought to have no tendency to associate with other ions in dilute solutions, although, at higher electrolyte concentrations, ion triplets, quadruplets, or larger aggregates may form.

A major role in the association of ions in solution into pairs is thought to be played by long-range electrostatic forces between the ions, usually modeled as a Coulomb's law attraction, attenuated by the solvent permittivity. In many theories, the solvent is treated as a dielectric continuum characterized solely by its bulk permittivity, $\epsilon = 4\pi\epsilon_0\epsilon_r$, where ϵ_0 is the permittivity of free space and ϵ_r is the relative permittivity (dielectric constant) of the pure solvent. Typically, the ions are treated as hard spheres of diameter a and only pairwise interactions between them are considered. This collection of assumptions is nowadays known as the "restricted primitive model" (RPM). More sophisticated models of electrolyte solutions have, of course, been developed, but their mathematical complexity, often coupled with extensive use of adjustable parameters, puts their detailed consideration outside the scope of this review.

Very short-range interactions (hard or nearly-hard sphere repulsions) involve the mutual exclusion of ions at $r < a$. However, at distances $a < r < R$, solvation of the constituent ions must be considered. On this basis an ion pair may be classified as a (double) solvent-separated ion pair (2SIP), when the primary solvation shells of both ions remain essentially intact, as a solvent-shared ion pair (SIP), if a single solvent layer exists in the space between the ion partners of the pair, or as a contact ion pair (CIP), if no solvent exists between the partners and the ions are in direct contact (Figure 1).

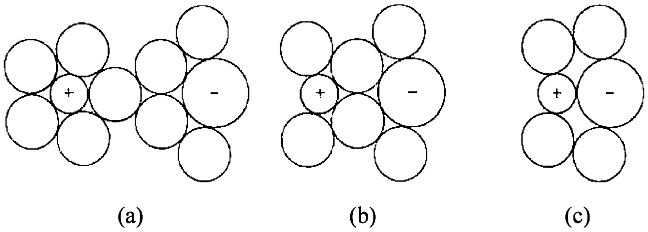


Figure 1. Schematic representation of ion-pair types: (a) solvent separated (2SIP), (b) solvent shared (SIP), and (c) contact (CIP). The complete solvation shell around the ion pair is not displayed. (Reproduced from ref 16, p 221, with permission of Wiley. Copyright 1985.)

The long-range electrostatic forces that keep the partners of an ion pair together are nondirectional. Ion pairs are, therefore, nominally distinguishable from complexes, even those involving only one cation and one anion, in which covalent coordinative bonds are formed. In the latter, electron density is transferred from the anion (the ligand) to a free orbital in the cation (the metal ion). Other Lewis base–Lewis acid interactions involving ions coupled with the transfer of electron density should be excluded from the concept of ion pairing too. However, once an ion pair is formed, electron density transfer may occur in a second stage, but the consideration of such cases is outside the scope of the present review.

It is pertinent to look a little more closely at the relationship between ion pairing and complexation. As noted above, the conventional view is that ion pairs are held together by long-range, nondirectional electrostatic forces while complexes are formed by short-range, spatially directed donor–acceptor (coordinative) covalent interactions. However, this difference is largely semantic. Once an ion pair is formed, there is no method for determining the origins of the attractive forces holding it together, although we may choose to impose particular models of such forces on it. Nor can strength of association be used as a distinguishing criterion, since electrostatic and covalent forces are broadly similar (some strong ion pairs are more stable than some species that would normally be regarded as complexes).

Similarly, a kinetic criterion is also not universally applicable: while most ion pairs are labile, their rates of formation or dissociation are not always greater than those of “complexes”. Ion triplets $A^-C^{n+}A^-$, formed by purely long-range electrostatic forces (section 5.1), look like the product of the second stage of a multistage complexation process. As will be discussed further below, it is more profitable to consider ion pairing and complexation as essentially indistinguishable or just slightly different aspects of the same phenomenon.

For ion pairs to be treated as distinct entities (chemical species) in electrolyte solutions, valid evidence for them must exist. For example, in many situations: “An ion pair must be long-lived enough to be a recognizable kinetic entity in the solution.”[2] Therefore, brief encounters of oppositely charged ions due to their thermal motions in solution are not considered per se to produce ion pairs. There is no generally valid range of lifetimes of ion pairs, but rate constants for their dissociation approaching 10^9 s^{-1}, corresponding to a lifetime of $\sim$1 ns, have been reported.[3] Regardless of their lifetimes, ion pairs can be considered to be at chemical equilibrium with the free ions, with the extent of formation quantified by the fraction α of the total number of ions remaining free and $(1 - \alpha)$ as the fraction associated, with an association constant K_A. Consider the ion-pairing equilibrium in an electrolyte solution of concentration c (usually in the units of molarity, M):

$$C^{c+} + A^{a-} \leftrightarrows CA^{(c-a)+} \tag{1}$$

where C^{c+} is the cation, A^{a-}, is the anion and $CA^{(c-a)+}$ is the ion pair, with all species being solvated to an extent determined by the interaction of each species with the surrounding solvent. The net charge of the ion pair $(c - a)$ may be zero (for a symmetrical electrolyte) but need not be so. The fractions α and $(1 - \alpha)$ are those that are obtained experimentally by various methods. Using the usual relationship between activities and concentrations on the molarity concentration scale ($a_i = c_i y_i$), the formation of the ion pair can be quantified in terms of the equilibrium concentration quotient, K_A, or in terms of the standard (infinite dilution) association constant $K_A°$ and a ratio of activity coefficients:

$$K_A = (1 - \alpha)c/(\alpha c)^2 = (1 - \alpha)/\alpha^2 c = K_A°(y_\pm'^2/y_{IP}) \tag{2a}$$

where $y_\pm'$ is the mean ionic activity coefficient of the *free* ions and y_{IP} is the activity coefficient of the ion pair. As mentioned above, the values of $K_A°$ and of $y_\pm'^2/y_{IP}$ become strongly correlated when the former is small. However, theoretically derived values of $K_A°$ and of $y_\pm'$ (and also y_{IP} if it has not been arbitrarily set to unity as is often done) have been calculated in attempts to break this correlation. These values can then be used to predict α values; agreement with experimental α values was considered accordingly to validate the theory.

1.2. Scope

The purpose of this review is to expound the present (mid-2005) status of the ion-pairing concept and illustrate it with examples of well characterized ion pairs formed in electrolyte solutions in various solvents. As in previous publications by the present authors,[4−7] the solvents considered have been restricted to the common molecular substances that are liquid at near-ambient temperatures and that serve as reasonable solvents for electrolytes. The focus of the present review has again been on electrolytes composed of simple, monatomic, and mainly symmetrical polyatomic ions. The consideration of ion pairs involving charged organic molecules that play an important role in organic chemistry[8,9] is substantially outside the scope of this review. No attempt is made to be comprehensive when discussing various cases of ion pair formation. The main theories proposed for dealing with ion pairing are presented, again without attempting to be exhaustive. Although some of these theories are quite old, they continue to be employed in recent studies.

The experimental methods used for studying ion pairing are necessarily the key to a valid description of this phenomenon. Historically, the conductivity of electrolyte solutions has been the major tool employed, followed by potentiometry and, less directly, by measurements of electrolyte solution thermodynamic properties, mainly activity and osmotic coefficients. The consequences of ion pairing for thermodynamic properties, such as density (partial molar volumes) and enthalpy changes, are also considered. Spectroscopic measurements (mostly UV−vis, IR, Raman, and NMR) on electrolyte solutions have played a significant role in the elucidation of ion-pairing phenomena, and their premises are reviewed accordingly. Relaxation methods, mainly dielectric relaxation spectroscopy, although much less widely employed, have provided invaluable insights into the nature and kinetics of ion pairs and are also considered.

Ion-pairing studies have mostly been of single electrolytes in dilute solutions, although more concentrated solutions (where further association to triple ions, quadruple ions, and higher aggregates may occur) have also received attention. Polyelectrolytes are a special case of ion pair aggregates and are only briefly reviewed here, since their behavior merits a comprehensive separate review. The formation of ion pairs is strongly influenced by the solvation of the ions; hence, the transfer of ion pairs between solvents of different solvation abilities is discussed. This is an example of the useful methodology of ion pair distribution, which is widely employed for separation and synthetic purposes (section 6.3).

Because of its importance, ion pairing has been the subject of chapters in the classic treatises on electrolyte solutions: *The Physical Chemistry of Electrolytic Solutions* by Harned and Owen[10] and *Electrolyte Solutions* by Robinson and Stokes.[2] The monographs *Electrolytic Dissociation* by Monk[11] and *Ion Association* by Davies,[12] described the then (early 1960s) “state of the art”, including the methods used and the results obtained, along with their interpretation and consequences. Subsequent books such as *Interactions in Electrolyte Solutions* by Nancollas[13] and *Ions and Ion Pairs in Organic Reactions* edited by Szwarc[9] also contain useful accounts of various aspects of ion pairing, as do several other books, including some by one of the present authors.[14−16] The most recent comprehensive coverage of the subject is found in various sections of the book *Physical Chemistry of Electrolyte Solutions: Modern Aspects*, by Barthel, Krienke, and Kunz.[17] Surprisingly few readily accessible review articles on ion pairing are available; those of Kraus[18] and Szwarc[8] published long ago are noteworthy.

1.3. History of the Ion-Pairing Concept

The electrolytic dissociation theory of Arrhenius developed in the 1880s,[19] which became widely accepted soon after its publication, recognized that electrolytes are extensively dissociated in solution but that dissociation was not necessarily complete at finite electrolyte concentrations. Indeed, Arrhenius used the (rather poor quality) experimental evidence then available, mostly electrical conductivity and freezing point data, to derive degrees of association for various electrolytes in water. However, the notion that some “strong” electrolyte solutions, exemplified by sodium chloride in water, were best considered as completely dissociated into free cations and anions was developed by Sutherland,[20] Bjerrum,[21] and others.[12]

The tremendous successes of the Debye−Hückel[22] and Onsager[23] theories (of electrolyte activities and conductivities, respectively) in the 1920s, in which dilute electrolyte solutions were modeled as consisting of completely dissociated ions perturbed by long-range Coulombic interactions, led to the almost total eclipse of the ion association model. This situation was re-enforced by the recognition that the apparent agreements obtained by Arrhenius regarding the degrees of association for most “near-strong” electrolytes, using various types of experimental data, were largely fortuitous. Davies[12] has commented: “[the idea of complete dissociation] was not advanced as a rule of universal validity. Yet...complete dissociation was so attractively simple and it harmonized so happily with [other] knowledge that [it passed as such] into popular science.....fostered, no doubt, by the suspicion that deviations from the Debye−Onsager theories would find a physical explanation [not involving association]”. This “suspicion” was aided by the almost total focus at that time and subsequently on aqueous solutions where, because of their high permittivity (see below), ion pairing is often *relatively* unimportant and hard to detect. Such views persist to the present. For example, some experienced researchers[24] have recently stated: “there is no clear evidence that [aqueous solutions of divalent metal sulfates] associate”, despite a plethora of experimental data to the contrary (reviewed in several recent papers[25,26]). Nevertheless, the failure to develop satisfactory theories that explain experimental data at even modest concentrations without resort to empirical parameters, coupled with the steady accretion of direct evidence for the existence of ion pairs, has resulted in ongoing support for the concept of ion pairing.

Brönsted’s theory of specific ionic interactions[27] postulates that ions of like charge (sign) influence each other uniformly whereas ions of opposite charge influence each other electrostatically to an extent that is specific to the nature of the ions. Based on this idea, Bjerrum[28] introduced the concept of ion pairing of strong electrolytes. The electrostatic work required to separate two ions, i and j, with charges $z_i e$ and $z_j e$, where e is the unit charge, from a distance r apart to infinity is $W_{ij}(r) = -z_i z_j e^2/\epsilon r$. Bjerrum then calculated the probability of the ion i to be at a given distance r from the ion j. If the signs of z_i and z_j are the same, then the probability increases monotonically with r, but if the signs are opposite, then the probability has a minimum at a certain distance

$$q = z_i z_j e^2/2\epsilon k_B T \tag{3}$$

where k_B is the Boltzmann constant and T is the thermodynamic (Kelvin) temperature and the effect of the solvent is expressed only through its bulk electrical permittivity ϵ (i.e., the solvent is taken as a dielectric continuum). Bjerrum suggested that all oppositely charged pairs of ions at distances $r \leq q$ apart should be considered as associated ion pairs whereas those at larger distances should be regarded as free. That is, Bjerrum set the cutoff distance for ion pairing at $R = q$. He argued that although this cutoff distance q is arbitrary, it is reasonable, since the work required to separate such ion pairs is at least twice the thermal energy. Bjerrum further considered that the ion pairs and free ions thus defined are in thermodynamic equilibrium, so that the mass action law and an association constant, K_A, can be applied to the ion-pairing process, as in eqs 1 and 2.

Free ions, being subject to the nonspecific electrostatic ion−ion interaction effects, will have a mean activity coefficient of $y_\pm'$. This can be calculated by the extended Debye−Hückel theory but with the distance of closest approach set as q (instead of the a of that theory) and the ionic strength given by αc (for 1:1 electrolytes). In this way, Bjerrum arrived at an expression for K_A (see section 2.1). This model and its expression for K_A continue to be widely applied as the “Bjerrum treatment of ion pairing”, which has been used to account for deviations of the mean ionic activity coefficients of many supposedly strong electrolytes from the extended Debye−Hückel expression. However, Bjerrum’s theory requires that a given electrolyte in all solvents (or mixtures) with the same permittivity should have the same value of K_A. Many instances where this was not the case have been reported.

Fuoss[29] initially adopted Bjerrum’s approach, presenting expressions for the ion distribution functions from which it emerged that “short-range pairs” were to be considered as distinct dipolar particles. He furthermore stated that for typical separation distances $b > 2$, where

$$b = q/a = (e^2/2\epsilon)ak_B T \tag{4}$$

contact ion pairs would not be the predominant form.

Fuoss[30] subsequently altered this view, partly on the basis of the work of Denison and Ramsey.[31] These authors considered only ions in contact to be ion pairs; those at all other distances were regarded as free. A Born cycle was then used to calculate the Gibbs energy of separating ions from a distance a to infinity in a medium of permittivity ϵ, which gave an expression for the work involved of $W_{ij}(a) = bk_B T$.[31] It followed that the association constant for these contact ion pairs ln K_A should be linear with $1/\epsilon$. Although there are a few electrolyte/solvent systems for which this is true, in general it is not.

Gilkerson[32] also considered only ions in contact as pairs and applied the Kirkwood partition function[33] to arrive at an expression for the effect of solute−solvent (ion−dipole) interactions. However, no equation based on measurable quantities could be written for these effects. Writing K_A^* for the factor that expressed them, Fuoss[30] summarized Gilkerson’s result as $K_A = K_A^* \exp(b)$. This device removed the direct dependence of ln K_A on $1/\epsilon$, consistent with most experimental findings. Fuoss then presented an alternative derivation of this expression, again considering only contact ion pairs, with a distance a between their centers.[30] The Fuoss expression (see section 2.2) for K_A, which took the form K_A^* exp(b), has also been widely used and is known as the “Fuoss treatment of ion pairing”. It does not meet the reservations of Gilkerson[32] concerning the inadequacy of exp(b) as a description of the differences in experimental association constants for solvents of similar permittivities (as Fuoss’ K_A^* does not depend on ϵ), nor does it include his suggested ion−solvent (ion−dipole) interactions.

In 1954 three groups independently noted that limiting ion pairing only to ions in direct contact could not explain certain phenomena. Rather, the data under consideration indicated the presence in solutions of ion pairs separated by one or two solvent molecules. Thus, Grunwald[34] proposed the existence of a solvent-separated ion pair on the basis of electromotive force (emf) measurements, while Winstein et al.[35] described salt effects on solvolysis kinetics in terms of both "intimate" or "internal" (i.e., contact) ion pairs and "external" or "solvent-separated" ion pairs. Other terms that have been used to make this distinction are "tight" and "loose" ion pairs and, if metal ions are involved, "inner and outer sphere coordination".[36] Interestingly, Sadek and Fuoss[37] also invoked ion pairs with solvent molecules between the ions for the interpretation of some conductivity data, prior to Fuoss' restriction of ion pairing to contact pairs.[30]

A critical development in understanding the relationships between the various types of ion pairs was the work of Eigen and Tamm.[38,39] These authors suggested, on the basis of ultrasonic absorption data, that ion pairing proceeded in stages, as a result of competition between ion solvation and the electrostatic attraction between oppositely charged ions. The first stage was the formation of a solvent-separated ion pair (2SIP), where the solvation shells of *both* cation and anion remained essentially intact. This step occurred at a very fast (diffusion controlled) rate. The common representation of this kind of ion pair (Figure 1) specifies two solvent molecules on the line connecting the centers of the partner ions. It was proposed that in a second, slower, stage a partial desolvation of the ion pair occurs to form a solvent-shared ion pair (SIP) with a single solvent shell shared in the space between the partner ions. In the final, slowest, stage the solvent molecules between the partners were eliminated to form a contact ion pair (CIP) that was still solvated outside the region of contact (Figure 1). These three kinds of ion pairs were assumed to be in chemical equilibrium, described by stepwise ion association and solvent elimination equilibrium constants. If the solvent is represented by S, the cation by C^{c+}, and the anion by A^{a-}, then the stages can be represented as

$$\mathrm{C}^{c+}\mathrm{S}_m + \mathrm{A}^{a-}\mathrm{S}_n \overset{K_1}{\rightleftarrows} \mathrm{S}_p\mathrm{C}^{c+}\mathrm{S}_2\mathrm{A}^{a-}\mathrm{S}_q \overset{K_2}{\rightleftarrows} \mathrm{S}_r\mathrm{C}^{c+}\mathrm{S}\mathrm{A}^{a-}\mathrm{S}_s \overset{K_3}{\rightleftarrows} \mathrm{S}_x\mathrm{C}^{c+}\mathrm{A}^{a-}\mathrm{S}_y \quad (5)$$

where the solvation numbers are $m > p > r > x$ and $n > q > s > y$ and the overall association constant is $K_A = K_1 + K_1K_2 + K_1K_2K_3$ (see sections 2.3 and 3.5). The validity of this so-called "Eigen mechanism" was demonstrated by means of ultrasonic relaxation techniques.

For a given system not all of the steps in eq 5 may be detectable or even occur. Some authors have preferred to model ion association as a two-step process, usually omitting the formation of the 2SIP species. Indeed the concept of stepwise elimination of the solvent between the constituents of an ion pair is closely related to the notion of outer- and inner-sphere coordination compounds in solution. In their study of the association of sulfate anions with cobalt(III) amine complexes, Posey and Taube[36] found that $Co(NH_3)_5H_2O^{3+}$ formed an outer-sphere species with SO_4^{2-} virtually instantaneously. This was followed by the slow displacement of a water molecule from the inner coordination sphere of the inert Co(III) complex by SO_4^{2-}, to form an inner-sphere complex. More general considerations of inner- and outer-sphere coordination have been presented by J. Bjerrum[40] and Ahrland,[41] who discussed ways to distinguish them in aqueous solutions on the basis of thermodynamic and other criteria (see section 4.2). A detailed discussion of this problem as it relates to coordination chemistry is outside the scope of this review, but the relationship to contact and solvent-shared ion pairing is evident.

An important landmark in the development of the ion-pairing concept was the application by Justice and Justice[42] of the rigorous McMillan–Mayer[43] statistical thermodynamic theory as expressed by Rasaiah and Friedman[44] in terms of the pair correlation function $g_{+-}(r)$ for ions of opposite charges in an electrolyte solution. On this basis Justice and Justice[42] proposed an expression for the calculation of the interaction energy $W_{+-}(r)$ required for obtaining the pair correlation function $g_{+-}(r)$ still within the "restricted primitive model" (spherical hard ions of the same size in a uniform dielectric medium, neglecting many-body interactions). It involves a short-range interaction energy W^* and a long-range Coulombic term. The final result for the mean ionic activity coefficient of an associating electrolyte vindicated the Bjerrum treatment.[28] Note, however, that according to Justice and Justice[42] the short-range interaction can be included in the calculated Bjerrum integral $Q(b)$, but then the integration is from $r = 0$ rather than from $r = a$. If $W^* = \infty$ for $r \leq a$ and $W^* = 0$ for $r > a$, then the result[45] is the same as Bjerrum's.

Barthel[46] proposed what was later called the low concentration chemical model (lcCM)[47] that took up the formulations of Justice and Justice[42,45] to deal with 2SIPs and SIPs. He considered the cutoff distance for ion pairing as $R = a + nd_S$, where d_S is the linear dimension (diameter) of an oriented solvent molecule located between the pairing partners and $n = 1$ or 2. The solvation is taken into account by multiplying the Bjerrum integral (with limits from a to R) by the factor $\exp(-u^*/k_BT)$, with u^* being an adjustable parameter, independent of r (see section 2.5). The results of this approach are analogous to the Gilkerson[32] or Fuoss[30] expressions for K_A, in that the solvation parameter can explain the deviations of $\ln K_A$ from the linear dependence on $1/\epsilon$, which is expected on the basis of the RPM.

While agreement on the long-range potential of mean force (PMF), the Coulombic term, had generally been achieved by this time (end of the 1970s), no consensus has been arrived at on how to deal with the short-range interactions. In particular, the prediction of a linear relationship between $\ln K_A$ and $1/\epsilon$ from theories based on the RPM has often been refuted by the experimental findings (some early examples are in refs 32, 37, and 48, but many others have been reported). The notions of the molecular discreteness of the solvent near the ions and of dielectric saturation in the solvation shells of the ions (both ignored in the RPM) can be treated in several ways. Byberg et al.,[49] in a seldom quoted early paper, dealt with these problems by assigning radii to the solvation shells of the ions, inside which dielectric saturation took place with an arbitrarily assigned relative permittivity (5.5 in the case of hydration). Marcus[50] discussed some aspects of dielectric saturation with respect to ion pairing.

Other approaches have also been useful, for example the extended RISM (reference interaction site model). Hirata and Levy[51] employed the RISM to yield a theoretical relative permittivity ϵ_{RISM} for the Coulombic term of the PMF, $W_{+-}(r)$, and a term that comprised a Lennard-Jones type of interaction (repulsion and dispersion forces), u^*, and a solvent-mediated potential, ΔW. However, the theoretical ϵ_{RISM} yielded wrong values for methanolic solutions, so that a semiempirical approach had to be used instead: $W_{+-}(r) = z_+z_-e^2/\epsilon r + u^* + \Delta W$, employing the bulk relative permittivity ϵ_r. This, however, makes the entire calculation rather nontransparent. Rashin,[52] also applying the RISM approach, used hydrated ionic radii in calculating the PMF between ions in aqueous solutions but concluded that dielectric saturation and specific solvent structure made only small contributions. Good agreement with results from the RISM approach was reported for aqueous solutions.[52]

Simonin, Blum, and others reverted to considering only ions in contact as forming an ion pair and used the mean spherical approximation (MSA)[53−55] for their description of ion association in aqueous solutions. They took into account nonconstant solvent permittivity and the diameters of the hydrated cations, both assumed to be linearly dependent on electrolyte concentration, yielding two adjustable parameters. Using the MSA theory with these two parameters they could fit the experimental activity and osmotic coefficients of dozens of aqueous electrolytes of various charge types up to high concentrations, yielding K_A values.[53]

Recently, too, Barthel et al.[17] have reformulated the PMF for the lcCM at various distances (see section 2.6) as well as proposing[56] an MSA treatment of ion association. This approach was successfully employed for solutions of lithium perchlorate in several solvents of intermediate relative permittivities, $20 \le \epsilon_r \le 36$, and could be modified for triple ion and quadruple ion formation for solvents with $\epsilon_r < 20$. A comparison of the lcCM[17,46] and MSA[54,55] approaches was recently made by Barthel and co-workers[57] for the interpretation of aqueous magnesium sulfate conductivities. For the electrostatic part of the activity coefficients only the free ions are relevant. The nonelectrostatic part of the activity coefficients according to the MSA approach also involves the ion pairs, with the ions taken to be hard spheres, and the ratio of the activity coefficients $(f_\pm^{hs})^2/f_{IP}^{hs}$ is involved (see section 2.6).

Most present day researchers accept that ion pairs can exist not only as contact pairs but also as solvent-shared and solvent-separated ion pairs. Being at equilibrium with free ions, all of these species can still be treated by the mass action law. For detailed modeling, electrostatic forces are an important contribution to the PMF in electrolyte solutions undergoing ion pairing, but the repulsion of the partners of the pair at $r < a$ and other short-range interactions such as ion solvation need also to be taken into account. There is no consensus, however, on how these desiderata are to be achieved.

The description of ion-pairing phenomena in electrolyte solutions is still beset by unresolved problems. These include the following.

(i) What is the appropriate distance of the closest approach of ions in solution, a, to be used as the lower limit of integration in various theories of ion pairing? The choice of a is crucial for obtaining meaningful values of K_A and α .

(ii) What is the appropriate distance between *free* ions in the solution, R, below which ions are to be considered as pairs? The value of R is used as the upper limit of integration in various theories of ion pairing, leading to values of K_A and α .

(iii) Are the activity coefficients of free ions calculated from theory beyond the validity of the limiting law (as distinct from the experimentally measured stoicheometric activity coefficient of the electrolyte) sufficiently reliable to differentiate between nonspecific ion−ion interactions and ion pairing? The widely used semiempirical Pitzer expressions for activity coefficients[58] do not recognize ion pairing explicitly. However, they include a coefficient $\beta^{(2)}$ that takes care of effects otherwise deemed to be due to ion pairing and can be shown to be closely correlated with K_A values obtained by independent means (section 8.1).

There are, therefore, still many aspects of ion pair formation in electrolyte solutions that require further study.

2. Theoretical Treatments of Ion Pairing

The theoretical treatments of ion pairing dealt with here are a selection from the many published ones, on the basis of their having been used by others besides their originators or at least having been used not only for aqueous solutions but also for nonaqueous or mixed solvents. They elaborate on the brief discussion in section 1.3 on the historical development of the concept of ion pairing, where some further treatments are referred to.

2.1. Bjerrum Approach

Bjerrum[28] was the first to provide a theoretical treatment of ion pairing of "strong" electrolytes. The basis of his considerations, following the Debye−Hückel theory,[22] was the electrostatic interactions of ions, using what subsequently became known as the restricted primitive model (RPM) of electrolyte solutions. This model involved spherical hard ions of diameter a in a solvent regarded as a continuum characterized solely by its bulk permittivity $\epsilon = 4\pi\epsilon_0\epsilon_r$, with only pairwise interactions being taken into account. The electrostatic work required to separate two ions (ion i, with charge z_ie, where e is the unit charge, and ion j, with charge z_je) from a distance r apart in the solvent to infinity is a stepwise function. For $r \ge a$

$$W_{+-}(r) = -z_iz_je^2/\epsilon r \tag{6}$$

but $W_{+-}(r < a) = -\infty$. Bjerrum then calculated the probability $P_i(r,\mathrm{d}r)$ of the i-ion to be at a distance between r and $r + \mathrm{d}r$ from the j-ion:

$$P_i(r,\mathrm{d}r) = (N_Ac_i/1000)4\pi r^2 \exp(W_{+-}/k_BT)\,\mathrm{d}r \tag{7}$$

where N_A is Avogadro's number and c_i is the molar concentration of the i-ions (the factor 1000 arises from the concentration units). If the signs of z_i and z_j are the same, then the probability increases monotonically with r, because the r^2 factor increases more rapidly than the Boltzmann factor decreases the probability. However, if the signs are opposite, then the probability has a minimum at a certain distance q:

$$q = z_iz_je^2/2\epsilon k_BT \tag{3}$$

where k_B is the Boltzmann constant and T the thermodynamic (Kelvin) temperature. Bjerrum then suggested that all oppositely charged pairs of ions at distances $a \le r \le q$ are to be considered as associated ion pairs whereas pairs of ions at larger distances apart are to be considered free. That is, Bjerrum set the cutoff distance for ion pairing at $R = q$, arguing that although this distance is arbitrary, it is reasonable, since the work required to separate such ion pairs is at least twice the thermal energy. Ion pairs are dipolar, and if $z_i = -z_j$, it is generally considered (but see section 3.1) that they do not contribute to the conductivity of the electrolyte solution. Free ions participate in the ionic atmosphere and are subject to the resulting electrostatic effects summarized by the extended Debye−Hückel theory.

Bjerrum further considered that the ion pairs and the free ions thus defined are in chemical and thermodynamic equilibrium, so that the mass action law and an association constant K_A can be applied to the ion pairing as in eqs 1 and 2. At very low concentrations, the fraction of ions associated to ion pairs, $1 - \alpha$, is obtained by simple integration of eq 7 from a to q. At higher concentrations, the final expression for the association constant according to Bjerrum is

$$K_A = (4\pi N_A/1000)\int_a^q \exp(2q/r)r^2 \, dr \tag{8a}$$

If the parameter b is defined as

$$b = q/a = (e^2/2\epsilon)ak_BT \tag{4}$$

then this constant can be written as

$$K_A = (4\pi N_A/1000)b^3Q(b) \tag{9}$$

Here $Q(b) = \int_2^b x^{-4} \exp(x) \, dx$ is an integral of an auxiliary variable x that has to be solved numerically.

The relation of eq 9 to the fraction of the electrolyte present as ion pairs, $1 - \alpha$ of eq 2, requires an expression for the activity coefficient of the free ions, $y_\pm'$. Free ions, being subject to the nonspecific electrostatic ion−ion interaction effects, can be calculated by the extended Debye−Hückel (EDH) theory but with the distance of closest approach being q instead of a and the ionic strength given by αc (for 1:1 electrolytes). Thus, $y_\pm' = y_\pm^{EDH}$, where in general

$$\ln y_\pm^{EDH} = -q\kappa\alpha^{1/2}/(1 + R\kappa\alpha^{1/2}) \tag{10}$$

and $R = q$ when $q > a$ and $R = a$ if $q \le a$ (but then no association takes place and $\alpha = 1$). The quantity κ is the reciprocal of the radius of the ion atmosphere according to the Debye−Hückel theory:

$$\kappa^2 = 8\pi q\rho \tag{11}$$

where $\rho = 2000N_Ac$ is the total number density of ions in the solution (for symmetrical electrolytes). For solvents with high relative permittivity and electrolytes with low charges, the cutoff distance q is smaller than a. Therefore, no ion pairing takes place in such cases, such as, e.g., for the larger alkali halides in water, where $q = 0.357$ nm at 298.15 K. Smaller ions and ions with higher charges, especially in solvents with lower permittivities, should associate to ion pairs to extents given by eqs 2 and 9. At 298.15 K, the value of the key variable b is

$$\log b = 1.448 + \log|z_iz_j| - \log \epsilon_r - \log(a/\text{nm}) \tag{12}$$

The parameter b is inversely proportional to the distance of closest approach a, taken as the mean diameter of the ions. This should not be smaller than the sum of their crystal ionic radii: $a \ge r_+ + r_-$. The values of $\log Q(b)$ have been tabulated (e.g., in ref 14) and range from −1.358 at $b = 2.1$ (the lowest practical value at which association occurs) through zero for $b = 5.9$ and 1.125 for $b = 12$ to larger values at large b for which $Q(b) \approx \exp(b)/b$.[4]

The main criticism against the Bjerrum treatment, apart from its being based on the RPM, is the arbitrariness of the choice of the cutoff distance $R = q$. The exact value of R does not, however, affect the value of K_A strongly, as Fuoss[29] has shown. If R is appreciably larger than a and ion pairing is allowed, then even considerable variation of R from $0.5q$ to $2q$ is of small importance for $1 - \alpha$, the extent of ion pairing, according to the Bjerrum treatment.

However, if the value of $K_A°$ is obtained from experimental determination of α (or $1 - \alpha$) via eqs 2 and 10 for the activity coefficient $y_\pm'$ and is equated to the Bjerrum theory value K_A of eq 9, a calculated value of the parameter b results. This, in turn, yields a calculated value of the distance of closest approach, a, that may not be realistic (e.g., $a < r_+ + r_-$, ref 2 p 422) or which varies with ϵ_r (e.g., ref 18). This too has been raised as a criticism of the Bjerrum theory, but this roundabout manner of arriving at a value of a is rather unfair to the theory, for which the resulting value of K_A for a reasonable value of a should be calculated. This K_A may or may not agree with the experimental value, $K_A°$, and it is this comparison that ought to be made in judging the theory.

2.2. Fuoss Treatment

Fuoss, in the treatment commonly bearing his name,[30] considered only a cation and an anion in contact as an ion pair, with a distance a between their centers. He also used the RPM and discussed only 1:1 electrolytes. He modeled the cation as a conducting charged sphere of radius a and the anion as a point charge that can penetrate the cation sphere. He then considered solutions so dilute that the potential energy of an ion is negligible with respect to k_BT unless it is “trapped” by an ion of opposite charge. From electrostatic considerations, Fuoss derived from the simplified Poisson−Boltzmann equation $\nabla\psi = \kappa^2\psi$ (where ψ is the potential) the following expression of the potential energy of an anion at contact with or inside the cation sphere:

$$W_{+-}(r \le a) = -e^2/a\epsilon(1 + \kappa a) \tag{13}$$

where κ is again the familiar Debye−Hückel reciprocal of the radius of the ion atmosphere around the reference cation of the model. In a solution of concentration c M of cations (and, of course, an equal concentration of anions) of which the fraction α is free, the volume occupied by them is $(N_Ac\alpha/1000)(4\pi a^3/3)$. (The factor 1000 arises from the choice of concentration unit.) The probability of an added anion to find itself inside a cationic sphere is then proportional to the volume occupied by the cations and to the electrostatic Boltzmann factor $\exp(-W_{+-}/k_BT)$. The cations added simultaneously will show corresponding probabilities of trapping anions. On integration to the total number of ions present in the solution, the fraction of paired ions is given by

$$1 - \alpha = [(4\pi a^3/3)(N_A/1000)]c\alpha^2 \exp(-W_{+-}/k_BT) \tag{14}$$

The Boltzmann factor can be written, with the variable b defined as before (eq 4), as

$$-W_{+-}/k_BT = b - b\kappa a/(1 + \kappa a) \tag{15}$$

The second term here is the logarithm of the square of the Debye−Hückel mean ionic activity coefficient of the free ions [cf. eq 10]:

$$b\kappa a/(1 + \kappa a) = -\ln(y_{\pm}')^2 \qquad (16)$$

The resulting expression for the association constant is, therefore

$$K_A = (1 - \alpha)/c\alpha^2(y_{\pm}')^2 = (4\pi N_A/3000)a^3 \exp(b) \qquad (17)$$

This is the final Fuoss expression for the association constant for (contact) ion pairing.[30] The pre-exponential factor depends only on the ions via the parameter a whereas the exponent depends both on the ions and, via its permittivity ϵ, on the solvent. It follows that, for a given electrolyte, log K_A should be linear with $1/\epsilon$, but for many series of solvents or solvent mixtures this is found not to be the case.

Justice and Justice[42] criticized the Fuoss treatment on a more fundamental basis. They pointed out that this treatment allowed for the anions to be at any distance $0 \le r \le a$ from the center of the cation and that the integration of $d\psi/dr$ was carried out from 0 to a for the evaluation of $W_{+-}(r)$. Therefore, this treatment did not actually pertain to "contact" ion pairs. Furthermore, cation−anion distances $r < a$ are highly improbable due to the infinite repulsion potentials at such distances, and the contact configuration, $r = a$, "occurs in a vanishingly small part of configuration space"; that is, it is also highly improbable. This last conclusion was reached by Fuoss himself—several decades earlier.[29]

2.3. Multistep Ion Pairing

Eigen and Tamm developed their multistage ion association treatment for the interpretation of sound absorption relaxation processes in electrolyte solutions.[38] There is a change in the molar volume of the electrolyte on ion pairing, due to diminution of the solvent electrostriction near the ions (see sections 4.3 and 6.1). The sound waves cause alternate compression and expansion of the solution as a function of time, t. Hence, the momentary concentration of the ion pair, c_{IP}, responds to the pressure changes and differs from its equilibrium concentration, c_{IP}^{eq}, in a time-dependent manner:

$$dc_{IP}/dt = (c_{IP} - c_{IP}^{eq})/\tau \qquad (18)$$

where τ denotes the relaxation time. The reciprocal of τ can be expressed in terms of the forward and backward rate coefficients of the ion pairing.

To explain the time dependence of c_{IP}, Eigen and Tamm assumed a multistage ion pair formation process to take place, from solvent-separated ion pairs (2SIPs) through solvent-shared ion pairs (SIPs) to contact ion pairs (CIPs), according to

$$C^{z+}S_m + A^{z-}S_n \overset{K_1}{\rightleftarrows} S_pC^{z+}S_2A^{z-}S_q \overset{K_2}{\rightleftarrows} S_rC^{z+}SA^{z-}S_s \overset{K_3}{\rightleftarrows} S_xC^{z+}A^{z-}S_y \qquad (5)$$

Then, if the relaxation times of the three stages are related as $\tau_1 \ll \tau_2 \ll \tau_3$, the three stages can be discerned separately. This condition is fulfilled if stage 1 proceeds very rapidly, being diffusion controlled, whereas the elimination of solvent molecules between the ion partners is a chemically controlled slower reaction.

Rather complicated expressions result for the calculation of the measurable sound absorption volume, the product $Q\lambda$ of the absorption cross section Q, and the wavelength λ, with the latter being related to the speed of sound u and the frequency $\nu = \omega/2\pi$ of the sound wave as $\lambda = u/\nu$. The final expression for the frequency dependent sound absorption volume is

$$Q\lambda = (\pi/\kappa_{S0}c)[\kappa_{S1}\omega\tau_1/(1 + \omega^2\tau_1^2) + \kappa_{S2}\omega\tau_2/(1 + \omega^2\tau_2^2) + \kappa_{S3}\omega\tau_3/(1 + \omega^2\tau_3^2)] \qquad (19)$$

where κ_{S0} is the adiabatic compressibility of the solvent, and the $\kappa_{Si\neq 0}$ values depend on the volume changes of the ion-pairing processes, ΔV_i, and the fractions α_i of the ion pairs of the corresponding kinds. A comparison of the experimental values of $Q\lambda$ with those calculated from eq 19 could lead to a determination of whether all three stages of ion pairing were represented in the solutions examined. As an approximation, on the assumption that the activity coefficients do not vary with the fractions α_i and using the quantity $\Gamma_i = \alpha_i(1 - \alpha_i)/(2 - \alpha_i)$, the compressibility coefficient for each stage is

$$\kappa_{Si} = c\Gamma_i(\Delta V_i)^2/RT \qquad (20)$$

Sets of K_i (from which the α_i are derived) and of ΔV_i (from which the κ_{Si} are calculated) are required for the calculation of the experimentally observed $Q\lambda$ values as a function of the concentration c and the frequency $\nu = \omega/2\pi$. With certain assumed values of these quantities, a satisfactory fitting of $Q\lambda(\nu,c)$ for magnesium sulfate association in aqueous solutions could be achieved.[39]

Much more recently, dielectric relaxation spectroscopic (DRS) measurements of sufficient accuracy in the multi-GHz region have become feasible and have been used for the study of ion pairing by Buchner and Barthel,[59] among others. The dispersion of solvent and solute permittivities of electrolyte solutions is generally measured at the frequencies 0.05 GHz $\le \nu = \omega/2\pi \le$ 100 GHz. The complex permittivity of a solution can be written as

$$\epsilon^*(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) + \kappa/\epsilon_0\omega \qquad (21a)$$

where, according to the Debye formula, the real part (called the dielectric dispersion) is

$$\epsilon'(\omega) = \epsilon(\infty) + [\epsilon - \epsilon(\infty)]/[1 + \omega^2\tau^2] \qquad (22)$$

the imaginary part (called the dielectric loss) is

$$\epsilon''(\omega) = [\epsilon - \epsilon(\infty)]\omega\tau/[1 + \omega^2\tau^2] \qquad (23)$$

and $\kappa/\omega\epsilon_0$ is a conductivity correction (κ is the specific conductance and ϵ_0 is the permittivity of free space).

If ion pairs are present in the electrolyte solution, then new relaxations are superimposed on the solvent relaxation process. In water, the ion-pairing relaxation times τ are of the order of 100−200 ps, compared to the solvent relaxation times of the order of 1−20 ps. Up to three ion-pair related Debye relaxation processes can generally be discerned,[26] with

$$\epsilon^*(\omega) = (\epsilon_1 - \epsilon_2)/(1 + i\omega\tau_1) + (\epsilon_2 - \epsilon_3)/(1 + i\omega\tau_2) + (\epsilon_3 - \epsilon(\infty))/(1 + i\omega\tau_3) + \epsilon(\infty) \qquad (24)$$

The ϵ_j are concentration dependent permittivities, and the τ_j are relaxation times corresponding to the stages of the ion-pairing process from the 2SIPs through the SIPs to the CIPs.

The concentrations of the individual dispersing species c_j can be evaluated from the individual amplitudes $\epsilon_j - \epsilon_{j+1}$ of the dispersion processes if the relaxation times differ sufficiently, provided the dipole moments μ_j and polarizabilities α_j of the species can be estimated.

$$c_j = (3k_BT\epsilon_0/N_A)[(\epsilon - A_j(\epsilon - 1))/\epsilon](1 - \alpha_j f_j)^2\mu_j^{-2}(\epsilon_j - \epsilon_{j+1}) \quad (25)$$

Here A_j is a geometrical factor related to the ellipsoid of rotation of the ion pair obtained from its dimensions and f_j is the field factor also dependent on the geometrical factor. These calculations have been applied to the ion pairing in aqueous solutions of Na_2SO_4 [60] and $MgSO_4$,[26] among many other studies.

2.4. The Pair Correlation Function Treatment

Justice and Justice[42] based their treatment of ion pairing on the Rasaiah and Friedman formulation of $d \ln y_\pm/dc$, the concentration dependence of the activity coefficient in an electrolyte solution,[44] at the McMillan−Mayer level.[43] This employs the integrals of the pair correlation function $g_{ij}(r)$ (i, j = + or −):

$$G_{ij} = 4\pi\int_0^\infty (g_{ij}(r) - 1)r^2\,dr \quad (26)$$

The pair correlation function can be written in a general manner as

$$g_{ij}(r) = \exp[-W_{ij}^*/k_BT - (z_iz_je^2/r\epsilon\, k_BT)\exp(-\kappa r) + \alpha_{ij}(r)] \quad (27)$$

where W_{ij}^* is the nonelectrostatic short-range part of the pair potential and $\alpha_{ij}(r)$ is the many-body effect not accounted for by the factor $\exp(-\kappa r)$ of the Coulombic term. The last term in the exponent of $g_{ij}(r)$ cannot be expressed analytically and is appreciable only in moderately concentrated solutions, so $\alpha_{ij}(r)$ was arbitrarily set equal to zero as an approximation.

The integrals in eq 26 are now split into short- and long-range parts, $G_{ij}^S = G_{ij}(0,R)$ and $G_{ij}^L = G_{ij}(R,\infty)$, with the parameters being the limits of integration. At this stage, the value of R is arbitrary, except that $W_{ij}^*(r > R) = 0$. Note that $G_{++}^L = G_{--}^L$, since they depend on the square of the charges, but $G_{++}^S \neq G_{--}^S$. On neglecting terms in $c^{1/2}$ and higher orders and denoting $G^L = G_{++}^L + G_{+-}^L$, Justice and Justice arrived at

$$d \ln y_\pm/dc = G^L/(1 + cG^L) - [G_{+-}^S + 0.5(G_{++}^S + G_{--}^S)] \quad (28)$$

The long-range term is evaluated as

$$G^L = 8\pi\int_R^\infty (\cosh(Y) - 1)r^2\,dr; \quad Y = (2q/r)\exp(-\kappa r) \quad (29)$$

The short-range term $G^S = G_{+-}^S + 0.5(G_{++}^S + G_{--}^S)$ is evaluated as

$$G^S = K_A^{Bj}\exp(-2\pi q) + 0.5(K_{++} + K_{--}) + {}^8/_3\kappa R^3 \quad (30)$$

where K_A^{Bj} is the Bjerrum association constant

$$K_A^{Bj} = (4\pi N_A/1000)\int_a^R \exp(2q/r)r^2\,dr \quad (8b)$$

but with a generalized cutoff distance R. The K_{ii} in eq 30 are similar integrals (for ions of the same signs of the charges) but with $\exp(-W_{ii}^*(r)/k_BT)$ added in the integrand and $2q/r$ being replaced by $-2q/r$. A series expansion of eq 28, using eqs 29 and 30, with truncation after the term in c and integration leads to

$$\ln y_\pm = -\kappa q + \kappa^2 qR[1 - \delta(q/R) + \delta'(q/R)] - K_A^{Bj}c + 0.5(K_{++} + K_{--})c \quad (31)$$

This expression is in agreement with that of Bjerrum[28] except for the functions δ, δ', and $(K_{++} + K_{--})$. The latter integrals were neglected by Bjerrum, since pairs of ions with the same charges at distances $<R$ were considered highly improbable in dilute solutions. The choice of the distance R is arbitrary, but it is expedient to choose such a value that makes $-\delta(q/R) + \delta'(q/R) = 0$, namely $R > 1.1q$ (whereas, for $R = q$, this quantity $\sim {}^1/_6$). The difference in the choices is unimportant.

In a second paper, Justice and Justice[45] applied these considerations to ion pair association constant calculations. Setting $K_A = K_A^{Bj}$ and expressing $y_\pm$ by eq 31 permits calculation of the fraction associated, $1 - \alpha$, according to

$$K_A = (1 - \alpha)/c\alpha^2(y_\pm')^2 \quad (2b)$$

The (unknown) short-range interaction term $\exp(-W_{ij}^*(r)/k_BT)$ in the pair correlation function enters only in the K_{ii} functions of the expression for the activity coefficient (eq 31). Alternatively, the integral $\int_0^R \exp[-(W_{ij}^*(r)/k_BT) + (2q/r)]r^2\,dr$ can be replaced by the integral $\int_{a'}^R \exp[(2q/r)]r^2\,dr$, where the new lower integration limit takes the place of the short-range interaction term. This means that the Bjerrum formulation of the association constant (eq 9) depends in a crucial manner on the proper choice of the distance of closest approach of the ions that enters the integration limit: $b = q/a$.

2.5. The Low Concentration Chemical Model

Barthel[46] proposed a model, subsequently called the low concentration chemical model (lcCM), that essentially took up the formulations of Justice and Justice[42,45] for the potential of mean force inherent in the pair correlation function (eq 27). The difference was the neglect of the many-body interaction term, $\alpha_{ij}(r)$, and the splitting of the Coulombic term into $z_iz_je^2/r\epsilon(k_BT) + \exp(-\kappa r)/k_BT$. The latter quantity was approximated as the activity coefficient factor in the expression for the association constant (eq 2). The short-range interaction was also split[17] into a solvation term, $W_{+-}^{solv}(r)$, and a correlation term, $W_{+-}^{cor}(r)$. With the restricted primitive model of electrolyte solutions, the former necessarily vanishes, whereas the latter is a hard sphere (repulsion) potential, defining the distance of closest approach, a. Consequently, the Bjerrum association constant (eq 9) is obtained. However, the lcCM departs from the restricted primitive model by recognizing ion solvation and, therefore, setting the cutoff distance instead of the Bjerrum q as $R = a + nd_S$, where d_S is the linear dimension (diameter) of an oriented solvent molecule located between the pairing partners and $n = 1$ or 2 (corresponding to SIPs and 2SIPs respectively). An average, distance independent, solvation contribution W_{+-}^{solv} is assumed for distances $a \le r \le R$ so that the resulting association constant

$$K_A^{\mathrm{lcCM}} = 4\pi N_A \exp(W_{+-}^{\mathrm{solv}}/k_BT)\int_a^R \exp[-(2q/r)]r^2\,\mathrm{d}r \qquad (32)$$

results. A more refined expression would result if $W_{+-}^{\mathrm{solv}}(r)$ was not treated as a constant but its dependence on the distance was allowed for.[61] Furthermore, under certain conditions, contact ion pairs are formed, adding the value of $n = 0$ to the definition of R. The formulation of the association constant according to eq 32 implies that the square of the mean ionic activity coefficient of the free ions is given by $(y_\pm')^2 = \exp[-\kappa q/(1 + \kappa R)]$; cf. eq 10.

2.6. The Mean Spherical Approximation Treatment

Krienke and Barthel[47,61] published a mean spherical approximation (MSA) treatment of ion association, elaborating on previous ideas of Ebeling[62] and of Turq, Blum, et al.[63] It is based on cluster expansion considerations involving the direct correlation function and addresses the problem of the many-body interaction term, $\alpha_{ij}(r)$ in eq 27. It involves also the screening parameter Γ of the MSA treatment, where

$$\Gamma = [(1 + 2\kappa R)^{1/2} - 1]/2R \qquad (33)$$

resulting in the approximation $\exp[-\alpha_{ij}(R)^{\mathrm{MSA}}] \approx \exp[-4q\Gamma/(1 + R\,\Gamma)]$. An expression for the electrostatic part of the mean ionic activity coefficient of the free ions, $y_\pm'^{\mathrm{MSA}}$, then results from the MSA treatment that differs considerably from the extended Debye−Hückel expression [cf. eq 10 with $\alpha \equiv 1$], namely,

$$\ln y_\pm'^{\mathrm{MSA}} = -2q[1 + \kappa R - (1 + 2\kappa R)^{1/2}]/\kappa R^2 \qquad (34)$$

An expression for the activity coefficient of the ion pair, y_{IP}, based on the ion−dipole electrostatic interactions has also been published.[17] Furthermore, there is the hard sphere excluded volume effect, y^{HS}, that can be calculated by the MSA treatment. The expression for this effect is

$$y_\pm^{\mathrm{HS}} = (1 + 2\eta)^2/(1 - \eta)^4 \qquad (35)$$

where $\eta = (\pi/6)\rho a^3$ is the volume occupied by the ions and $\rho = 2cN_A$ is the total number density of ions (free and associated). It is assumed that $y_\pm^{\mathrm{HS}}$ is not affected by the ion pairing. The measurable mean ionic activity coefficient for an associating electrolyte is then

$$y_\pm = \alpha y_\pm^{\mathrm{HS}} y_\pm'^{\mathrm{MSA}} \qquad (36)$$

An expression for the osmotic coefficient of strong electrolyte solutions with ion pairing has also been reported.[47] See section 5.1 for the associative-MSA (AMSA) dealing with more concentrated solutions and triple ion formation.

2.7. Activity Coefficients of Charge-Symmetrical Ion Pairs

Whereas the activity coefficients of the free ions, or at least their mean, $f_\pm$, are generally taken into account by appropriate expressions (see above), those of the ion pairs f_{IP} are generally set equal to unity, for lack of better knowledge. This issue was recently discussed by Marcus.[50] Two methods for obtaining the latter quantity, one based on salting-out(in) and the other based on an analogy with zwitterions, were suggested for the calculation of f_{IP}.

The final expression for the former approach is adapted from McDevit and Long:[64]

$$\ln f_{\mathrm{IP}} = [V_{\mathrm{intr}}(V_{\mathrm{intr}} - V^\circ)/1000\kappa_T RT]z^2c \qquad (37)$$

where V_{intr} is the sum of the intrinsic volumes of the cation and anion, V° is the standard partial molar volume of the electrolyte, and κ_T is the isothermal compressibility of the solvent. Since generally V° is either negative or, if positive, smaller than V_{intr}, salting-out is predicted by eq 37, i.e., $f_{\mathrm{IP}} > 1$. For some tetraalkylammonium salts, however, $V^\circ > V_{\mathrm{intr}}$, so that salting-in, i.e., $f_{\mathrm{IP}} < 1$, is predicted.

Kirkwood[65] developed a theory for the activity coefficient of a zwitterion, but only for the unrealistic case of a spherical zwitterion rather than the more reasonable shape of a prolate ellipsoid. Still, the analogy of a symmetrical ion pair with a zwitterion, say glycine, $^+H_3NCH_2CO_2^-$, for the sake of being explicit, can be utilized. The measured dipole moment of glycine corresponds to the distance apart of the positive and negative charges, $\mu/ze = 0.239$ nm. For β-alanine, $^+H_3NCH_2CH_2CO_2^-$, the length is even larger, 0.399 nm, of similar size to common ion pairs. Tsurko and Bondarev[66] obtained the activity coefficients of the zwitterionic form of the amino acids denoted by the subscript A from emf measurements, taking into account the ionic species also formed in the presence of an electrolyte, B = HCl. Salting-out of the zwitterion at trace concentrations was deduced from

$$\ln f_A^{\mathrm{tr}} = \lim(m_A \rightarrow 0) \ln f_A = 2\chi_{AB} m_B \qquad (38)$$

with ion−zwitterion interaction parameters $\chi_{AB} = 1.112$ for A = glycine and $\chi_{AB} = 1.186$ for A = β-alanine. Charge-symmetrical ion pairs with similar distances between the partners would have similar dependences of ln f_{IP} on the concentration of the free ions.

The consequences of these approaches for the calculation of the association constants from the fractions α of the free ions obtained experimentally were illustrated[50] for cases taken from the literature. These included ion pairing of thallium(I) chloride in water and of sodium iodide and tetrabutylammonium bromide in acetonitrile, which are characterized by low or moderate values of K_A, and of magnesium sulfate in water, which has a fairly high value of K_A.

3. Experimental Methods for Studying Ion Pairing

In principle, any technique that can be used to study complex formation can be used for the investigation of ion pairing. Numerous monographs have appeared that provide comprehensive coverage of such techniques.[11−13,67−70] This review will therefore provide only a brief summary of the methods that have been most widely used, along with two relaxation techniques, which have special capabilities for the study of ion pairing. Methods that have only rarely been employed for studying ion pair formation, such as calorimetry,[71] are not dealt with here, but the above-mentioned monographs can be consulted concerning them.

3.1. Conductometry

Electrical conductivity measurements provide, along with colligative properties, the oldest experimental evidence for the existence of ion pairs in solution.[19] Conductivity ("electrical" will be omitted hereon) is a transport property. Nevertheless, such measurements can provide thermodynamic information, in the form of an association constant, because there is a direct correspondence (at least for symmetrical electrolytes) between the formation of electroneutral ion pairs and a decrease in solution conductivity. It is generally assumed,[72] although probably difficult to prove, that all solvated electroneutral ion pairs, $[C^{z+}A^{z-}S_x]^0$, where S_x represents all solvent molecules attached to the ion pair including any that may exist between the ions, have zero conductivity under normal experimental conditions. Conway,[73] on the other hand, has suggested that ion pairs may contribute to solution conductivity through a type of Grotthus mechanism.

There are several advantages in using conductivity measurements for the quantification of ion pairing. The technology is mature, and good instruments are available commercially that can measure conductivities with accuracies approaching 0.02% relative, although the best apparatus is probably still purpose built. For maximum accuracy, solution resistances should be measured as a function of frequency and extrapolated to infinite frequency.[72] Conductometry is readily applicable to all symmetrical electrolytes in almost any solvent over wide ranges of temperature and pressure. Measurements can be performed at relatively low concentrations, typically $5 \times 10^{-4} \leq c/\mathrm{M} \leq 0.05$, where the theoretical descriptions of conductance *and* activity coefficients have reasonable validity and accuracy.

The chief disadvantage of the conductometric study of ion pairs is that it is less readily applicable to nonsymmetrical electrolytes. This is because the ion pairs then produced are charged and thus contribute to the observed conductance. Furthermore, their contribution will in general be unknown and will, unlike the case of electroneutral ion pairs, vary according to their type (degree of solvation). Leaving aside this last problem, equations have been derived that can be used to analyze the conductivities of nonsymmetrical electrolytes, with the most widely used being that of Quint and Viallard.[72,74] Given the extra adjustable parameters required, the results obtained for nonsymmetrical electrolytes will be, almost inevitably, less reliable; see section 8.2.

Conductance theory is well developed and has been extensively tested. Older equations,[2,10] such as those due to Shedlovsky and others, should be regarded as superseded. A full description of the various theoretical treatments advanced at the time is given by Justice,[72] and a useful summary is given by Popovych and Tomkins.[75] It is not appropriate to discuss here the similarities and differences among the numerous equations that have been proposed, but it is important to note that the *exact* theoretical description of conductance is extremely challenging. Thus, all equations developed to date are approximations to some extent and are limited to relatively dilute solutions.

Probably the most popular of the equations developed to date is that due to Fuoss and Hsia,[76] either in its original form or as presented by Fernandez-Prini and Justice.[77] This treatment will be used here to illustrate the application of conductance measurements to ion-pairing studies.

For a partially associated electrolyte, the Fuoss−Hsia equation for the molar conductivity Λ can be written as[76,77]

$$\Lambda = \alpha\{\Lambda^\circ - S(\alpha c)^{1/2} + E\alpha c \ln(\alpha c) + J_1(R_1)\alpha c - J_2(R_2)(\alpha c)^{3/2}\} \quad (39)$$

where Λ° is the molar conductivity at infinite dilution and S, E, J_1, and J_2 are known explicit expressions, containing contributions from relaxation and electrophoretic effects, with the latter two depending also on ion-distance parameters R. The degree of dissociation α is related by eq 2 to the association constant K_A° with appropriate expressions for the activity coefficients. Over the usual concentration range for this type of study (see above), it is normally sufficient to adopt an extended Debye−Hückel equation with the distance of closest approach parameter a being set at the same value as that used for the conductivity equation. The activity coefficient of the neutral ion pair is usually assumed to be unity, which is reasonable at low c, although more sophisticated approaches have been taken occasionally. The measured molar conductivity $\Lambda(c)$ is thus a function of four unknown parameters (Λ°, K_A°, $J_1(R_1)$, and $J_2(R_2)$) that have to be determined. If R_2 and R_1 are set equal to the Bjerrum distance q (eq 3), then only three unknown parameters have to be modeled (Λ°, K_A°, and $R_1 = R_2 = q$).[78]

Whichever theoretical model is used, the essence of the conductometric quantification of ion pairing is that departures of the observed conductivities, after correction for nonspecific ion−ion interactions expressed by the terms in S, E, and J, can be attributed to ion pairing. This model works well when ion association is strong but becomes increasingly unreliable as K_A decreases. This is because of correlations between K_A and the partially arbitrary assumptions that must be made in order to apply the theory.[72] The value of K_A at which such correlations become significant depends on the charges on the interacting ions, the properties of the solvent (especially its relative permittivity), and the accuracy of the data. Some particularly clear discussions of the problems of correlation in the interpretation of conductance measurements of weakly associated electrolytes in water are given in the papers of Duer et al.[79] and Pethybridge and Spiers.[80] One problem noted in attempts to optimize the analysis of conductivity data in terms of association is that unrealistic values of the ion size parameter may result: 0.315 nm for CsBr and 0.332 nm for CsI in water, whereas $r_+ + r_- = 0.366$ and 0.390 nm, respectively. On the other hand, the nonassociation of KCl in water is firmly established on the basis of the conductivity data;[81] see also section 8.1.

3.2. Potentiometry

There are many ways in which potentiometry can be used to study ion pairing in electrolyte solutions. Detailed consideration of all of these approaches is well beyond the scope of the present review and can be found in standard works.[11−13,67−70]

Most of the earlier potentiometric studies[11−13] employed cells without a liquid junction and, as for other thermodynamic methods, ascribed departures of the observed effects (cell potentials in the case of potentiometry), corrected for activity coefficients, to ion pairing. This approach is less successful in potentiometry than in conductivity measurements because the electrolyte concentrations required for ideal electrode behavior are typically somewhat higher than can still be used for conductometry. The results obtained for K_A then become more sensitive to the activity coefficient model adopted. As a consequence, many of the earlier potentiometric studies of ion pairing are mostly of historic interest only.

Potentiometric studies of ion pairing nowadays are performed largely using the "constant ionic medium principle".[67−70,82] This assumes that activity coefficients of the species involved in a chemical equilibrium (normally at relatively low concentrations) can be rendered constant by the addition, usually in large excess, of a supposedly "indifferent", "inert", or noncomplexing "swamping" electrolyte. The equilibrium constant is obtained as a concentration quotient and is valid strictly only in the medium in which it has been measured at its ionic strength I. Despite a widespread misconception to the contrary, such constants are thermodynamically well-defined. In essence, all that is involved is a change in the standard state from the usual infinite dilution of all species ($y_i \rightarrow 1$ as $c \rightarrow 0$) in the solvent employed to one of (near-)infinite dilution of the interacting species in the ionic medium ($y_i \rightarrow 1$ as $c_i \rightarrow 0$ at $I =$ constant). The validity of such constants is well established experimentally, and this method has for a long time been the preferred approach among the coordination and analytical chemistry communities, if not among physical chemists.

There are several advantages to the constant ionic medium approach. The most important is that it allows much greater flexibility of experimental design because it is well adapted to cells with a liquid junction. Such cells are far more versatile and allow a much wider range of electrodes to be used, especially ion-selective electrodes, ISEs, the electrochemical behavior of which is often not strictly Nernstian but still sufficiently so for reasonably accurate measurements of ion association. Electrodes are readily calibrated in terms of concentration in constant I media, and it is usually possible to vary the concentrations of the interacting species over sufficiently wide ranges while maintaining the ionic medium (and, it is presumed, the activity coefficients) essentially constant. Note that usually no attempt is made to calculate the activity coefficients. If the usual infinite dilution standard state value of $K_A°$ is required, it must be obtained by application of an appropriate activity coefficient model or by extrapolation, guided by such a model, of K_A values measured as a function of I.

The use of high I media also suppresses variations of liquid junction potentials, LJPs, which are usually highly correlated with ion association effects. If so-called "constant I cells" are used, LJPs can be calculated with a considerable degree of confidence[83] and their variation can then be taken into account.

Consider the ion-pairing equilibrium

$$\mathrm{C}^{c+} + \mathrm{A}^{a-} \leftrightarrows \mathrm{CA}^{(c-a)+} \tag{1}$$

The formation of the ion pair $\mathrm{CA}^{(c-a)+}$ can be detected most directly using either C^{c+}- or A^{a-}-sensitive electrodes (in principle, both can be used simultaneously, but in practice, such an approach rarely offers any advantages). Ignoring the sign convention, typical galvanic cells used for this purpose can be written

$$\mathrm{CE}|\mathrm{C}^{c+}, \mathrm{A}^{a-} \text{ in } I(\mathrm{MX})||\mathrm{RE} \tag{I}$$

$$\mathrm{AE}|\mathrm{C}^{c+}, \mathrm{A}^{a-} \text{ in } I(\mathrm{MX})||\mathrm{RE} \tag{II}$$

where CE and AE represent C^{c+}- and A^{a-}-responsive electrodes, respectively, RE is the reference electrode, and I(MX) indicates that the ionic strength is being held constant by addition of appropriate amounts (ideally in large excess) of the supposedly indifferent swamping electrolyte MX.

Potentiometric determination of moderately strong ion pairing (say, $K_A > 20\ \mathrm{M}^{-1}$) is reasonably straightforward,[67,69] providing a satisfactory C^{c+}- or A^{a-}-responsive electrode is available. Alternatively, it is sometimes possible to utilize competitive equilibria to obtain the constant of interest. The most widely used example of this approach employs measurements with H^+-sensitive electrodes of equilibria involving weak acid anions:

$$\mathrm{C}^{c+} + \mathrm{HA}^{(a-1)-} \leftrightarrows \mathrm{CA}^{(c-a)+} + \mathrm{H}^+ \tag{40}$$

Evaluation of the ion-pairing constant from such measurements requires knowledge of the association constant for the equilibrium

$$\mathrm{H}^+ + \mathrm{A}^{a-} \leftrightarrows \mathrm{HA}^{(a-1)-} \tag{41}$$

which can be obtained from a separate set of measurements in the usual way.[67,68]

When K_A is small, however, more care is needed to separate the effects of ion pairing from changes due to activity coefficients and LJPs. Experimentally, the optimal conditions for determining K_A by potentiometry are $[\mathrm{A}^{a-}] \gg [\mathrm{C}^{c+}]$ for measurements using a C^{c+}-responsive electrode (cell I) and $[\mathrm{C}^{c+}] \gg [\mathrm{A}^{a-}]$ for those with an A^{a-}-responsive electrode (cell II), as these conditions produce the greatest experimental effects. The use of ion-selective (membrane) electrodes, which generally have much lower limits of detection than traditional redox-based indicator electrodes, often enables such conditions to be met without substantial replacement of the ionic medium by the interacting ions. For example, it has been shown[84] that, at $I = 1.0$ M, K_A values for $\mathrm{M}^+ + \mathrm{F}^-$ association as low as 0.2 could be detected with acceptable accuracy using a F^- ISE with $[\mathrm{C}^{c+}] = 0.1$ M (10% replacement) and insignificant concentrations of F^-. Even smaller K_A values have been determined successfully, albeit with higher medium replacement levels.[85]

3.3. Salt or Solvent Activity Measurements

It can be shown from solution thermodynamics[2,86,87] that, for a 1:1 electrolyte CA, the degree of dissociation α is given by

$$\alpha = \gamma_\pm/\gamma_\pm' \tag{42}$$

where $\gamma_\pm$ is the *stoicheometric* mean molal ionic activity coefficient and $\gamma_\pm'$ the mean molal ionic activity coefficient calculated for the *free* ions of CA(solv). Since $\alpha \leq 1$, the effect of ion association is to lower the observed value of $\gamma_\pm$, relative to what it would be if all the ions were free, i.e., if CA was fully dissociated. Similar but more complicated expressions are obtained for other electrolyte types.

If $\gamma_\pm'$ can be estimated by an appropriate theoretical expression, then, from eqs 2 and 42, noting the change from the molar scale (using c and $y_\pm$) to the molal scale (using m and $\gamma_\pm$) and setting $\gamma_{IP} = 1$,

$$K_A° = (1 - \alpha)/m{\gamma_\pm}^2 \tag{43}$$

it follows that $K_A°$ can be obtained from measurement of $\gamma_\pm$ by any of the usual methods,[2,10,86,87] such as isopiestic equilibration, freezing point depression, vapor pressure lowering, potentiometry, etc. As such measurements can be made with good accuracy, the error in $K_A°$ depends only on the reliability of the theoretical estimation of $\gamma_\pm'$.

As for other methods of quantifying ion association, there is little problem in evaluating $K_A°$ when it is large ($\alpha \ll 1$), but as $\alpha \rightarrow 1$, i.e., $\gamma_\pm \rightarrow \gamma_\pm'$, the value of $K_A°$ becomes highly correlated with the (semi-)empirical parameter(s) of the activity coefficient model. A very realistic appraisal of the problems involved in the estimation of low $K_A°$ values from activity coefficient measurements by some experienced and capable practitioners is given in refs 81 and 88.

3.4. Solubility Measurements

The increase in solubility of a sparingly soluble salt AB upon addition, usually in considerable excess, of a soluble electrolyte YZ (not containing a common ion) is a useful method for measuring K_A values.[12,13] The observed solubility increase, after correcting for activity coefficient variations caused by the presence of YZ in solution, can be attributed to ion association between Y^+ and B^- and/or of Z^- and A^+, respectively.

Ideally, AB should have a solubility that is as low as possible, commensurate with the desired ease and accuracy of its determination, and should have no tendency to self-association. Equally ideally, YZ should be fully dissociated and only one of its ions (say, Z^-) should associate with the counterion (A^+) of the sparingly soluble salt. Under such circumstances, the solubility equilibrium can be recast:

$$\mathrm{AB(s)} + \mathrm{Z^-(solv)} \leftrightarrows \mathrm{A^+Z^-(solv)} + \mathrm{B^-(solv)} \quad (44)$$

For example, let AB(s) be the sparingly soluble $TlIO_3$(s), and YZ be aqueous KCl.[89] Then the ion pair Tl^+Cl^- is formed on dissolution of the $TlIO_3$, increasing the content of thallium in the solution over what it is in saturated aqueous $TlIO_3$:

$$\mathrm{TlIO_3(c)} + \mathrm{KCl(aq)} \leftrightarrows \mathrm{Tl^+Cl^-} + \mathrm{K^+(aq)} + \mathrm{IO_3^-(aq)} \quad (45)$$

This increase is readily evaluated in terms of the association constant of Tl^+Cl^-, taking into account the activity coefficients of the species in the solution,[12,13] but see also the discussion by Marcus.[50]

In practice, such desiderata are rarely fully met and it is usually necessary to make allowance for self-association of both AB and YZ and possibly YB.[12,13] Also, as lower and lower values of the association constant $K_A(A^+Z^-)$ are sought, it becomes necessary to use higher concentrations of YZ, which increases the difficulty of separating K_A and activity coefficient effects; see section 8.1.

3.5. Relaxation Methods

There are many relaxation methods that can be used, at least in principle, to study ion pairing. Such methods share the common feature of measuring the return of a system to its equilibrium state following an externally imposed perturbation of some kind. Most of these techniques, such as the *T*- and *P*-jump methods, have been used only for kinetic studies and so will not be considered here. In contrast, dielectric relaxation and ultrasonic relaxation have been shown to have unusual capabilities for the study of ion-pairing phenomena. Because of their relative unfamiliarity, a reasonably detailed description of these two techniques is presented below. This section should be read in conjunction with the theoretical description in section 2.3.

3.5.1. Dielectric Relaxation

Dielectric relaxation spectroscopy (DRS) involves measuring the response of a sample to perturbation by an applied electromagnetic field, broadly over the microwave region of frequency ν in the range 0.01−1000 GHz.[90,91] The frequency-dependent complex dielectric response, $\epsilon^*(\nu)$, of a solution is directly related to the cooperative motions of all dipolar species present, including the solvent. In addition, there is a contribution to $\epsilon^*(\nu)$ from the polarizability of the electron clouds of all molecular-level species. This relatively small contribution, which becomes important at higher frequencies, must be carefully subtracted from the data to obtain the purely dipolar response. For electrolyte solutions, there is an additional contribution at low frequencies, arising from the electrical conductivity of the ions that must be taken into account. This is discussed in more detail below.

A feature of DRS is that the response is sensitive to the *square* of the dipole moment (μ) of any dipolar species present, bearing in mind that ion pairs are by definition dipolar. This makes DRS particularly sensitive to very weakly associated ion pairs (species with $K_A < 1$ have been quantified,[92,93] but see section 8.1). More importantly, DRS is able to distinguish between the various types of ion pair since the dipole moment ($\mu = zed$, where ze is the charge on the ions, assumed equal, and d is their separation) depends on the separation between the charge centers (the ions), which decreases as solvent molecules are ejected from between the partners of the ion pair (cf. Figure 1). For this reason, and *uniquely among all the currently available techniques* for studying ion pairs, DRS has a sensitivity toward the various ion-pair types in the following order: 2SIP > SIP > CIP.

DRS is, in essence, applicable to any electrolyte solution, but there are a number of problems that have inhibited its wider application.[17,94,95] First, it is technologically demanding to achieve the levels of accuracy desirable for the reliable study of ion-pairing behavior. The best present-day instruments typically achieve an accuracy of ca. 1−2% in $\epsilon^*(\nu)$, which is sufficient for most purposes, but 0.1−0.2% over the entire frequency range would be ideal (a similar desideratum has been noted for ultrasonic relaxation; see section 3.5.2 below). The instrumentation required to achieve even the present modest accuracies is commercially available only in part and is expensive. Equipment covering the ideal range of 0.01−1000 GHz would typically require several purpose-built instruments and would cost ca. 1 million USD at current prices. Fortunately, applications of the required signal generators and processors to electronic and surveillance networks have produced technological progress in this area that may change this situation significantly.

Second, the theory of DR is rather complicated and, unlike the case of NMR spectroscopy, there are no commercially available computer packages that enable the nonspecialist to exploit the great capabilities of the technique. Third, DR spectra are very broad and rather featureless. Because the major peak(s) in most solution spectra is (are) associated with the solvent molecules, and invariably overlap(s) with the ion-pair contribution(s), decomposition of a DR spectrum into its component parts is often difficult and detracts from the attainable accuracy.[26]

A fourth problem, exclusive to the DRS of electrolyte solutions, relates to the presence of ions. Although common ions such as those considered in this review are not dipoles, and thus do not directly contribute to the dielectric response, they may have an important effect. The complex dielectric response of a sample is given by

$$\epsilon^*(\omega) = \epsilon'(\nu) + i\epsilon''(\nu) + \kappa/2\pi\epsilon_0\nu \tag{21b}$$

where $\omega = 2\pi\nu$ and $\epsilon'(\nu)$ and $\epsilon''(\nu)$ are respectively the frequency-dependent in-phase and out-of-phase responses to the applied field ($i = \sqrt{-1}$). The real component $\epsilon'(\nu)$, which is usually referred to as the dielectric dispersion, reflects the relative permittivity of the solution, while the imaginary component $\epsilon''(\nu)$ measures the dielectric loss (absorption) in the solution. For an electrolyte solution of conductivity κ, only the total loss, $\eta''(\nu) = \epsilon''(\nu) + \kappa/(2\pi\nu\ \epsilon_0)$, is observable. The conductivity term $\kappa/(2\pi\epsilon_0\nu)$ arises from the movement of ions under the influence of the applied field. It becomes dominant at low frequencies and ultimately swamps the dielectric response. In effect, this restricts DRS measurements to electrolyte solutions with $\kappa \lesssim 10$ S m^{-1}, which in aqueous solutions close to ambient temperatures corresponds to concentrations of 1−2 M for a 1:1 salt. Even at such relatively high solute concentrations, the still-dominant solvent peak(s) must be dealt with in an appropriate manner (see below).

For these reasons, DR spectra covering the common experimental frequency range of $0.1 \leq \nu/\text{GHz} \leq 100$ are typically limited to a concentration range of $0.01 \lesssim c/\text{M} \lesssim 1$ for 1:1 electrolytes in water. The lower concentration limit is determined by instrument sensitivity and the upper limit by the conductivity contribution. Obviously, the concentration range will vary according to the desired frequency range, electrolyte, solvent, and temperature. Because even strong electrolytes usually show a maximum in their electrical conductivity as a function of concentration (often as a result of ion pairing (!) but also due to viscosity increases), it is sometimes possible to make measurements at very much higher concentrations.[91]

Two sets of data, one each for $\epsilon'(\nu)$ and $\epsilon''(\nu)$, are obtained from the measurements at each concentration. The $\epsilon''(\nu)$ curves look more like conventional spectra, although data are also sometimes presented as Cole−Cole (Argand) plots of $\epsilon'(\nu)$ against $\epsilon''(\nu)$. A typical DR $\epsilon''(\nu)$ spectrum is given in Figure 2.[26]

Typically, DRS data are analyzed by simultaneous fitting of the in-phase and out-of-phase components with models consisting of n distinguishable relaxation processes. Each of them is described by a Havriliak−Negami equation, that for most processes, fortunately, can be described by the more simple Debye equation; that is, each $\epsilon''(\nu)$ curve is Lorentzian (but deviations are possible).

$$\epsilon^*(\nu) = \sum_{j=1}^{n} \frac{\epsilon_j - \epsilon_{j+1}}{1 + i2\pi\nu\tau_j} + \epsilon_\infty \tag{46}$$

where ϵ_∞ ($= \epsilon_{n+1}$) is the infinite-frequency permittivity, which in principle reflects only contributions from intramolecular polarizability. Note that $\epsilon_j - \epsilon_{j+1} = S_j$ is the amplitude (relaxation strength) of the jth dispersion step corresponding to the formation of the jth dipolar species. The static (zero-frequency) permittivity of the sample is $\epsilon = \epsilon_\infty + \sum S_j$. The quantities ϵ_j and τ_j are respectively the limiting (zero-frequency) permittivity and the average relaxation time for the jth dispersion step (including both solvent- and solute-related processes). The major difficulty in the data analysis is to find the correct value of n. Achieving this goal is made harder by the weakness (small amplitude relative to the solvent dispersion) and broadness of the dispersion steps. Even with this level of simplification, care needs to be exercised in the fitting of the data to ensure that the models are physically meaningful and produce consistent fits for all the data.

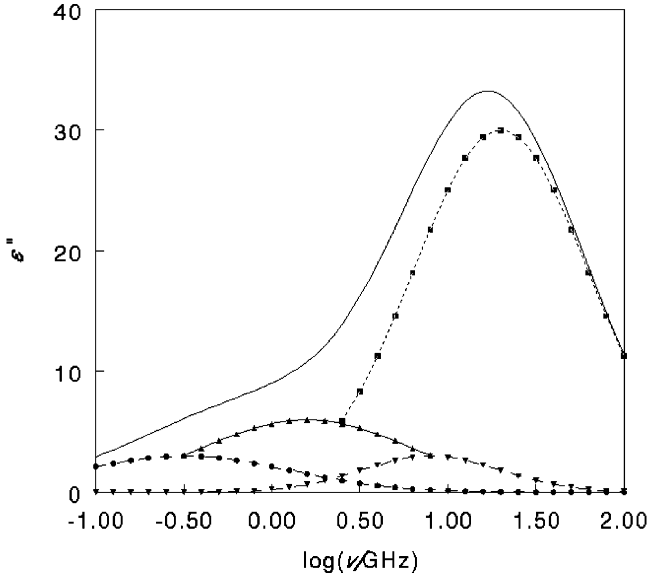


Figure 2. Dielectric loss $\epsilon''(\nu)$ (continuous curve) of 0.363 M aqueous $MgSO_4$, as deconvoluted into the contributions from the solvent (squares), 2SIPs (circles), SIPs (upright triangles), and CIPs (downward triangles). Adapted from data and Figure 2 in ref 26.

Ion pairing is detected in DRS as in most forms of spectroscopy by the observation of new features in the spectra (peaks in $\epsilon''(\nu)$ and steps in $\epsilon'(\nu)$), although these may not be fully resolved, and their variation with concentration. The amplitude of each process is related to the concentration of the particular dipolar species associated with that process, c_i, and is usually determined via the modified Cavell equation[96,97] (see also eq 25):

$$c_i = \frac{3(\epsilon + (1-\epsilon)A_i)}{\epsilon} \frac{k_B T\epsilon_0}{N_A} \frac{(1-\alpha_i f_i)^2}{g_i \mu_i^{\,2}} S_i \tag{47}$$

Note that the subscript j pertains to a relaxation process whereas the subscript i pertains to the resulting species. In eq 47 α_i, f_i, g_i, and μ_i are the polarizability, field factor, correlation factor, and dipole moment; A_i is a geometric factor reflecting the ellipsoid of rotation of the ion pair (which can be obtained from the dimensions of the ion pair);[60,98] and other symbols have their usual meanings. Note that, strictly speaking, only apparent concentrations, $c_i g_i$, are directly accessible from DRS measurements. However, as long as c_i values are reasonably low, it can be assumed that correlations with other dipoles are negligible, i.e., $g_i = 1$.

Since DRS provides, in principle, values of c_i for each ion-pair type present, the values for K_i (eq 5) and $K_A = K_1 + K_1K_2 + K_1K_2K_3$ are obtained as concentration quotients. The values obtained as a function of the electrolyte concentration (or I) can be fitted to an appropriate activity coefficient expression to estimate the corresponding standard values $K_i°$ and $K_A°$ at $I = 0$. A point to note in this context is that DRS values for K_i and K_A at finite I appear to be invariably lower than those obtained by potentiometric methods in the presence of an excess of an indifferent electrolyte at the same I. Because the standard values are in good agreement, this has been attributed to differences in activity coefficients between the “self-medium” of the pure electrolyte invariably employed in DRS measurements and the mixed electrolyte systems usually used in potentiometric studies (section 3.2).

The interested reader is advised to consult reviews or recent papers in the field for more details.[90−95] A typical fit for a solution of $MgSO_4$(aq) in which all three ion-pair types are detected[26] is shown in Figure 2.

3.5.2. Ultrasonic Relaxation

Ultrasonic relaxation (UR)[38,39,99−101] involves the measurement of the interaction of a sample with sonic waves, typically over the range from audio (ca. 10 kHz) to hypersonic (ca. 10 GHz) frequencies. Such waves create very small, essentially adiabatic, perturbations (of ∼1 kPa in P and ∼2 mK in T) in the equilibrium conditions of the sample. Such perturbations can couple to *any* type of chemical equilibrium that has a time constant between ∼20 μs and ∼20 ps. Like its dielectric counterpart, UR is of almost universal application to solutions and the type of information obtained is broadly similar. Again, as is the case for DRS, the equipment required for UR is barely available commercially (especially with regard to sample cells) and the mathematics are rather complicated. The major disadvantage of UR relative to DRS is that it detects *equilibria* rather than *species*. Thus, interpretation of sonic absorption spectra requires (reasonable) assumptions about the species involved. In practice, this is not a major disadvantage and data such as K_i and K_A values obtained by competent practitioners using either technique are generally in good agreement even for quite complicated systems (see, for example, ref 26). The major advantage of UR is its ability to measure the rates of the forward and reverse reactions for all of the steps in eq 5: It is probably the only technique available with this general capability.

There are two experimental approaches for studying UR: dispersion methods, in which the sound velocity (u_s) is measured as a function of frequency (ν), and absorption methods, in which the sonic energy loss is determined against frequency. Since the frequency dispersion of the velocity requires data of very high accuracy (better than 0.1%[101]) which is not readily attainable, most measurements to date have employed absorption methods.

In such measurements, the quantity usually plotted against frequency is the so-called “excess absorption per wavelength:[101]

$$(Q\lambda)^E = Q\lambda - B\nu \tag{48}$$

where Q is the attenuation coefficient of the sonic wave in the sample (not to be confused with the Q of the Bjerrum treatment, section 2.1) and $\lambda = u/\nu$ is its wavelength, where u is the velocity of the sound wave. The $B\nu$ term in essence corrects the observed absorption for “classical” losses that arise from microviscosity and heat-dissipation effects among the solvent molecules. Because $(Q\lambda)^E$ is quite small, typically $\lesssim$ 0.01, accurate data are again necessary.

For n kinetically independent reactions, typical of ion-pairing processes, $(Q\lambda)^E$ can be obtained as a sum from i = 1 to i = n of discrete Debye-type relaxation terms;[101] see also eq 19:

$$(Q\lambda)^E = \sum A_i 2\pi\nu\tau_i/[1 + (2\pi\nu\tau)^2] \tag{49}$$

In this expression, A_i are the relaxation amplitudes, depending on the heat capacity of the solution, c_p, and the relaxation contribution of each species to it, δc_{pi}, the isobaric thermal expansion of the solution, α_p, and the enthalpy and volume changes, ΔH_i and ΔV_i, for the formation of the species. These have to be estimated independently. The relaxation time constant, τ_i, also depends on the relaxation heat capacity, δc_{p_i}, and on ΔH_i but, most importantly for the present purpose, also on the concentrations, c_i, of the species. The latter, in turn, are related to the ion pair formation constants K_i.

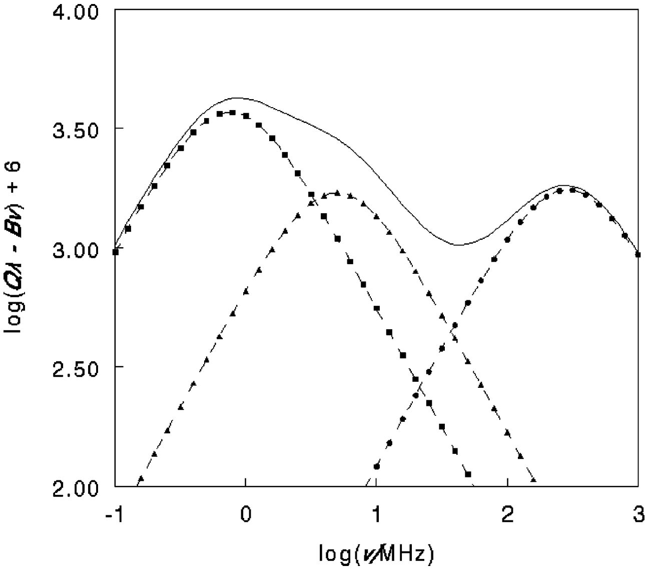


Figure 3. Excess ultrasound absorption per wavelength (continuous curve) of 0.033 M aqueous $Sc_2(SO_4)_3$, as deconvoluted into the relaxation effects for the formation of 2SIPs (circles), SIPs (triangles), and CIPs (squares). Adapted from data and Figure 4 in ref 102.

An alternative treatment of the UR results is discussed in section 2.3 in terms of the measurable sound absorption volume, the product $Q\lambda$ of the absorption cross section Q, and the wavelength λ. For further details of the calculations and more detailed discussions of specific systems, the interested reader is referred to the excellent review of Kaatze et al.[101] By way of example, Figure 3 gives the absorption spectrum for the scandium sulfate system that exhibits all three ion-pair types.[102]

As already noted, not all steps in eq 5 necessarily occur or are detectable in a given system, with the formation of 2SIPs being undetectable for some systems. It is noteworthy that under such circumstances the rate constant for the formation of CIPs from SIPs in aqueous solutions is approximately equal to the rate constant for the exchange of water molecules in the first coordination shell of the cation, as determined by NMR spectroscopy.[100]

3.6. Spectroscopic Methods

The common forms of spectroscopy—electronic (UV−vis), vibrational (IR and Raman), and nuclear magnetic resonance (NMR)—have been widely used for the study of complex formation and ion association. Such techniques typically rely on the observation of a new spectral feature corresponding to each new species formed in solution. Ideally, such features should be unique well-separated peaks, but in practice, they may occur only as modifications of the features corresponding to the ions themselves. A great advantage of spectroscopic methods is that they are readily applicable to most solute/solvent combinations without the need for significant theoretical development (unlike traditional methods such as conductometry or more recent ones such as relaxation methods). Details of the use of spectroscopic methods for the study of complex formation/ion association are given in standard works and so do not need to be repeated here.

It is, however, necessary to add a word of warning regarding the use of conventional spectroscopic techniques for the study of multistep ion-pairing reactions, such as that shown in eq 5. This is because, in general and with some exceptions, conventional spectroscopies detect only CIP species. If CIPs are the only type of ion pair present, there is no problem and spectroscopic methods can be used in the normal way. However, when other types of ion pairs (SIPs and/or 2SIPs) are also present or suspected, considerable caution must be exercised. In such situations, the results obtained from conventional spectroscopic measurements may be misleading.[25,26,103]

Consider for example a system that in reality conforms to eq 5 but which is investigated by a spectroscopic technique that detects only CIPs. The equilibrium sensed is (for a 1:1 salt)

$$C^{+}* + A^{-}* \leftrightarrows C^{+}A^{-}\ (\mathrm{CIP}) \tag{50}$$

where the * indicates the "free" species, as detected by the spectroscopic measurement. Generally, the concentrations $c_{C^{+*}} = c_{A^{-*}} = c_T - c_{CIP}$, where c_T is the total salt concentration and $c_{CIP} = [\mathrm{CIP}]$ is the ion pair concentration as detected spectroscopically, are used in the equilibrium calculations. The species marked with * thus include ionic species associated electrostatically with a counterion, i.e., 2SIPs and SIPs. Ignoring activity coefficients, the equilibrium constant observed spectroscopically is then

$$K_{\mathrm{spec}} = [\mathrm{CIP}]/(c_T - [\mathrm{CIP}])^2 \tag{51}$$

and thus, remembering that the equilibria in the system in fact conform to eq 5,

$$K_{\mathrm{spec}} = K_1K_2K_3[C^+]^2/(c_T - K_1K_2K_3[C^+]^2)^2 \tag{52}$$

where $[C^+] = [A^-]$ are the "true" free ion concentrations in the solution.

As shown elsewhere,[25] further consideration of the stoicheometric relationships for this simplified system produces an algebraic solution to K_{spec} in terms of K_i. If all the K_i values are known, it is possible to calculate K_{spec} via eq 52 but it is *not* possible to deduce the K_i values from measurements of K_{spec} under these circumstances. Note too that K_{spec} is ill-defined thermodynamically because the values of $[C^{+}*]$ and $[A^{-}*]$ in eq 50 contain unknown contributions from 2SIPs and SIPs. Such technique-specific constants are of little utility in speciation calculations or in understanding the nature of ion pairing. However, spectroscopy does provide direct evidence for CIP formation, not available from conventional (conductivity, potentiometry) measurements, and although such evidence is available from relaxation techniques, these are not widely accessible and they still require assumptions and simplifications. Failure to recognize this limitation of conventional spectroscopic methods has led to confusion in the literature.[103] The following example illustrates the problem.

The modest association of $MgSO_4$(aq) has been much studied by the traditional methods of potentiometry and conductivity (for citations of the earlier work, see refs 25, 26, and 57). Although the results are not in exact agreement due to the marked dependence of K_A on I (as expected from the Debye−Hückel equation), coupled to uncertainties in activity coefficient models for 2:2 electrolytes (especially the distances of closest approach, a), a value of $\log K_A^\circ = 2.2 \pm 0.2$ encompasses all the reliable reported data.[103] This value of K_A° is confirmed independently by both ultrasonic absorption[104] and dielectric relaxation[26] studies. The latter techniques also produce K_i values for the formation of the individual ion-pair types in good agreement with each other.[26] Careful investigations by numerous groups using Raman spectroscopy (see ref 25 for a recent survey) show clear evidence for the formation of a new species from variations in the position and shape of the strong $\nu_1(SO_4^{2-})$ mode. This interpretation is confirmed by other more subtle changes that can be detected in high quality spectra.[25] However, the value of K_R obtained in the usual way from the Raman spectra is an order of magnitude lower than those obtained by all other techniques. This is because only the CIP is "seen" by Raman spectroscopy: the chemical environments of the SIPs and 2SIPs are too similar to that of the free SO_4^{2-}(aq) to produce detectable changes in the Raman spectrum. In an *apparent* paradox, although K_R is not equivalent to K_i, the concentration of the CIP species directly detected by Raman spectroscopy is (and must be) in good agreement with the results obtained by other techniques such as DRS.[25,26]

Similar considerations apply to UV−vis and NMR spectroscopies. A somewhat extreme illustration is given by the aqueous Ni^{2+}/SO_4^{2-} system. The electronic spectra of $NiSO_4$(aq) are virtually indistinguishable from those of the essentially unassociated $Ni(ClO_4)_2$(aq).[103] However, both conductivity and potentiometry, recently confirmed by DRS,[105,106] indicate appreciable ($\log K_A^\circ \approx 2$) ion pair formation. The discrepancy is due partly to the presence of 2SIPs and SIPs and to the insensitivity of the spectrum of Ni^{2+} to the presence of SO_4^{2-}, even in the CIPs that do form.

The restriction of conventional spectroscopies to the detection of CIPs can be turned into an advantage. By combining such data with other techniques, it may be possible to better quantify a particular system.

4. Thermodynamic Consequences of Ion Pairing

Ion pairing in solutions has certain consequences that are manifested in measurable thermodynamic quantities. However, even if the ion pairing is deduced from nonthermodynamic measurements, such as conductivity or spectroscopy, the ion pairing is expressed in terms of a thermodynamic association constant, K_A or K_A°, for the equilibrium between the paired and free ions. The standard molar Gibbs energy of formation of the ion pair IP in a solvent S is, as usual, obtained from its association constant:

$$\Delta_{\mathrm{IP}}G^\circ(\mathrm{IP,S}) = -RT \ln(K_A^\circ/\mathrm{M}^{-1}) \tag{53}$$

Derived quantities, such as the standard molar enthalpy, entropy, or volume of ion pairing, are defined by the usual thermodynamic relationships. The thermodynamic quantities applicable to ion pair formation are discussed briefly in the following section.

4.1. Activity and Osmotic Coefficients

When the stoichiometric activity coefficients of families of salts with common cations or common anions in aqueous solutions are examined, certain generalizations that relate to ion pairing can be made. Thus, contrary to the activity coefficients of highly hydrated salts that increase beyond a minimum with increasing concentration, "moderately low activity coefficients ... are explained by ... ion pair formation. ...[For example] potassium salts of oxyacids ... have low activity coefficients probably [arising] from ion pairs" (ref 2 pp 218 and 219). The mean molar activity coefficients of the free ions are given at not too large concentrations by, for example, the extended Debye−Hückel expression

$$\ln y_{\pm}' = -\kappa q/(1 + \kappa R) \tag{54}$$

analogous to eq 10, where for these free ions $\alpha \equiv 1$ can be set. Here κ is given by eq 11 and q by eq 3. Then, if the activity coefficient of the ion pair is approximately set to unity, $y_{\mathrm{IP}} \approx 1$, it follows that the measurable nominal activity coefficient of the salt in the solution on the molar scale is (cf. eq 42)

$$y_{\pm} = \alpha y_{\pm}' \tag{55}$$

Since $\alpha \leq 1$, ion-paired salts of a given charge type in a given solvent (defining q) have smaller activity coefficients than nonpaired salts. It is still necessary to specify a value for the cutoff distance R in eq 54, see section 2, for modeling α in terms of $y_{\pm}$ or vice versa.

The osmotic coefficient of dilute solutions of strong electrolytes, i.e., where complete dissociation occurs and all ions are free, is usually given according to the extended Debye−Hückel theory as

$$\varphi = 1 - (q\kappa/3)\sigma(\kappa a) \tag{56}$$

Here, as before, q is the Bjerrum cutoff distance, eq 3, κ is the reciprocal of the diameter of the Debye−Hückel ionic atmosphere, eq 11, a is the distance of closest approach of the ions, and the function $\sigma(\kappa a)$ is

$$\sigma(\kappa a) = [3/(\kappa a)^3]\int_0^{\kappa a}[x/(1 + x)]^2\, dx = [3/(\kappa a)^3][(1+\kappa a) - (1 + \kappa a)^{-1} - 2\ln(1 + \kappa a)] \tag{57}$$

When ion pairing occurs, and assuming effects of only the free ions on the activity of the solvent (effects of the ion pairs being neglected), the necessary changes for obtaining the osmotic coefficient φ from eq 56 are replacement of κa in the argument of the function $\sigma(\kappa a)$ by $\kappa\alpha^{1/2}R$.

For more sophisticated modeling of $y_{\pm}$, see section 2.4 and eq 31 due to Justice and Justice[42] and section 2.6 and eq 36 due to Krienke and Barthel.[47] These authors also presented expressions for the osmotic coefficients resulting from their respective treatments.

4.2. Enthalpy and Entropy

The temperature derivative of the standard association constant for ion pair formation yields the standard molar entropy and enthalpy changes of ion pairing according to the usual expressions.

$$\Delta_{\mathrm{IP}}H°(\mathrm{IP,S}) = -RT^2[(\partial \ln(K_{\mathrm{A}}°/\mathrm{M}^{-1})/\partial T)_P - \alpha_{\mathrm{P}}] \tag{58}$$

$$\Delta_{\mathrm{IP}}S°(\mathrm{IP,S}) = [\Delta_{\mathrm{IP}}H°(\mathrm{IP,S}) - \Delta_{\mathrm{IP}}G°(\mathrm{IP,S})]/T \tag{59}$$

The solvent isobaric expansivity, α_{P}, needs to be subtracted in eq 58, as $K_{\mathrm{A}}°$ is expressed on the temperature-dependent molar scale, M^{-1}. The enthalpy change upon ion pairing can be obtained experimentally from calorimetric titrations or from heat of dilution measurements on the electrolyte solution. For the latter, the observed enthalpy changes must be compared with those expected from a completely dissociated electrolyte of the same charge type and in the same solvent, calculated using the Debye−Hückel theory or one of its variants, and only the excess can be attributed to the ion pair formation. The vast majority of data on enthalpies of ion pairing, however, were obtained by the application of the van't Hoff equation (eq 58).

A representative set of $\Delta_{\mathrm{IP}}G°$ values for the formation of ion pairs in several solvents, from eq 53, is shown in Table 1. These values are in almost all cases negative, since otherwise the ion pair has not formed to a significant extent. If $\Delta H°$ and $\Delta S°$ have been measured for the formation of a given ion pair, they where generally determined in a single solvent only. It may be noted that the formation of several ion pairs, e.g., the 2:2 ion pairs in water, the charged ion pairs in methanol, and the small ions in ammonia and 1-propanol, is entropy driven, as seen by the (unfavorable) positive $\Delta_{\mathrm{IP}}H°(\mathrm{IP,S})$ values. The desolvation of the ions in the process appears to cost more enthalpy than is gained by the electrostatic interactions. In the other cases reported, the enthalpy changes are negative so that it can be deduced either that little desolvation of the ions occurs or that such desolvation is more than compensated by the electrostatic or coordinative bonding interaction between the ions.

The standard molar enthalpy change on ion pairing $\Delta_{\mathrm{IP}}H°$ can be employed as a criterion for whether solvent-separated ion pairs 2SIPs and SIPs (outer-sphere complexes) or CIPs (inner-sphere complexes) are formed. An illustration of this is the association of lanthanide ions with chloride and bromide in *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMA).[124,125,128] In the case of the bromide association in DMF, $\Delta_{\mathrm{IP}}H°(\mathrm{IP,S}) \leq 5$ kJ mol^{-1} and 2SIPs or SIPs are formed, whereas, for the other cases, $\Delta_{\mathrm{IP}}H°(\mathrm{IP,S}) \geq 10$ kJ mol^{-1} and CIPs or inner-sphere complexes are formed. However, the association may not stop with the first counterion (ligand), and the question as to whether ion pairing or complex formation occurs for the first ligand is rather semantic. It should also be noted that this enthalpy criterion does not distinguish between 2SIPs and SIPs and thus is of limited use.

The positive values of $\Delta_{\mathrm{IP}}S°(\mathrm{IP,S})$ noted in the large majority of cases in Table 1 signify that several solvent molecules are released to the bulk solvent from the solvation shells of the ions on the formation of an ion pair. This release is minor for the formation of a 2SIP and more significant when an SIP or a CIP is formed. A quantitative estimate of the number of solvent molecules thus released was made by Marcus;[130] see section 6.1.

Negative values of $\Delta_{\mathrm{IP}}S°(\mathrm{IP,S})$ are noted in Table 1 in very few cases only (mostly the thallium(I) halides). Such cases comprise poorly solvated ions forming the pair, so that only a few solvent molecules are released on forming even the CIP. The coming together of two ions to form one particle, the ion pair, produces a negative entropy change of only $-R \ln 2 = -5.8$ J K^{-1} mol^{-1}. Much larger negative values of $\Delta_{\mathrm{IP}}S°(\mathrm{IP,S})$ signify that the ion pair is more solvated than the separate ions.

The simpler electrostatic theories of ion pairing—those of Bjerrum (section 2.1) and Fuoss (section 2.2), the latter pertaining to CIPs only—can be used to derive theoretical

Table 1. Standard Molar Gibbs Energies, $\Delta_{IP}G°$/kJ mol^{-1}, Enthalpies, $\Delta_{IP}H°$/kJ mol^{-1}, and Entropies, $\Delta_{IP}S°$/J K^{-1} mol^{-1} (from Eqs 58 and 59) of Ion Pairing of Various Electrolytes in Several Neat Solvents at 298.15 K unless Otherwise Noted

solvent	ion pair	$\Delta_{IP}G°$	$\Delta_{IP}H°$	$\Delta_{IP}S°$	ref
water	TlCl	−21.3	−26.3	−16.8	107
	TlBr	−31.4	−34.6	−10.7	107
	TlI	−41.4	−71.1	−99.6	107
	$LiB(OH)_4$	−6.0	1.0	23.5	108
	$NaAl(OH)_4$	+7.1	5.4	−5.7	109
	$GaCl^{2+}$	−5.9	4.8	35.9	110
	$NaSO_4^-$	+0.5			111
	$MgSO_4$	−12.6	5.8	61.7	112
	$CaSO_4$	−13.0	6.7	66.1	71
	$MnSO_4$	−13.0	7.8	69.8	71
	$CoSO_4$	−13.2	5.7	63.4	71
	$NiSO_4$	−13.3	5.4	62.7	71
	$ZnSO_4$	−13.2	6.2	65.1	71
	$CdSO_4$	−13.6	8.4	73.8	71
	$Cd(H_2O)_5SO_4$[a]	−3.0	6.2	30.9	112
	$LiCrOx_3^{2-}$	−5.2	6.4	37.6	113
	$NaCrOx_3^{2-}$	−8.6	−0.8	26.2	113
	$KCrOx_3^{2-}$	−9.0	−0.5	28.5	113
	$RbCrOx_3^{2-}$	−9.1	−1.3	26.2	113
	$CsCrOx_3^{2-}$	−9.3	−1.5	26.2	113
	$Co(NH_3)_6SO_4^+$	−20.3	2.5	76.5	114
	$Coen_6SO_4^+$	−20.0	2.7	76.1	114
methanol	$CaClO_4^+$	−11.9	16.9	96.6	115
	$SrClO_4^+$	−13.0	17.2	101.3	115
	$BaClO_4^+$	−13.9	16.3	101.3	115
	$CoClO_4^+$	−11.4	12.1	78.8	115
	$NiClO_4^+$	−10.9	14.0	83.5	115
	$CuClO_4^+$	−11.3	19.5	103.3	115
	$ZnClO_4^+$	−10.3	15.5	86.5	115
	$CdClO_4^+$	−10.4	16.4	89.9	115
	Hx_4NBr	−8.8			116
	Hp_4NBr	−8.8			116
	Bu_4NBPh_4	−10.6			116
1-propanol	NaBr	−14.3	22.1	122.1	71
	NaI	−13.2	18.9	107.7	71
	$NaClO_4$	−14.8	16.5	105.0	71
	KI	−14.7	19.1	113.4	71
	RbI	−15.5	17.5	110.7	71
	Et_4NI	−15.6	6.62	74.5	17
	Pr_4NI	−15.5	6.00	72.1	17
	Bu_4NI	−15.6	5.67	71.3	17
	Pe_4NI	−15.6			71
	i-Pe_4NI	−15.8			71
	Me_2Bu_2NI	−16.2			71
	$MeBu_3NI$	−15.8			71
2-methoxyethanol	KPic	−14.7	−0.2	48.6	117
	$KBPh_4$	−13.6	−9.4	14.1	117
	Bu_4NBPh_4	−14.7	−7.5	24.1	117
	Ph_4AsPic	−15.0	1.9	56.7	117
	Ph_4AsCl	−13.5	−11.6	6.4	118
	Ph_4PCl	−13.4	−11.0	8.0	118
	$LiBF_4$	−14.2	−17.8	−12.1	118
	$LiClO_4$	−13.3			119
	$NaBF_4$	−13.8	−8.0	19.5	118
	$NaClO_4$	−14.1			119
	$KClO_4$	−14.5			119
	$RbClO_4$	−14.8			119
	$CsClO_4$	−15.0			119
	Ph_4PBr	−14.3	−5.0	31.2	118
2,2-dimethoxyethane	LiCl	−50.1			120
	LiBr	−40.8			120
	$LiBF_4$	−39.9			120
	$LiClO_4$	−35.0			120
tetrahydrofuran	$LiBF_4$	−40.3			121
	$LiAsF_6$	−28.0			121
	Bu_4NBr	−37.2			121
	Pe_4NBr	−38.9			121
	Hx_4NBr	−38.2			121
	Hp_4NBr	−37.8			121
propylene carbonate	TlCl	−64.5	−77.3	−42.9	107
	LiBr	−7.5			122[b]
	TlBr	−61.9	−70.4		107
	NaI	−1.0			122[b]
	KI	+1.3			122[b]
	TlI	−57.0	−46.6		107
	$LiClO_4$	−5.3			122[b]
	$NaClO_4$	0.0			122[b]
	$KClO_4$	−0.8			122[b]
	Me_4NClO_4	−1.8			122[b]
	Et_4NClO_4	−1.6			122[b]
	Et_4NBr	−3.3			122[b]
	Pr_4NBr	+4.0			122[b]
	Bu_4NBr	−2.9			122[b]
	Hx_4NBr	−8.1			116
	Hp_4NBr	−8.0			116
	Bu_4NBPh_4	−8.7			116
acetonitrile	Et_4NCl	−7.8			122[b]
	Et_4NBr	−7.4			122[b]
	Et_4NI	−7.0			122[b]
	Et_4NClO_4	−5.7			122[b]
	Pr_4NBr	−6.4			122[b]
	Bu_4NBr	−6.7			122[b]
	Pe_4NBr	−5.5			122[b]
N,*N*-dimethylformamide	LiCNS	−1.3	1.8	10.4	123[b]
	TlCl	−49.0	−30.5	62.0	107
	TlBr	−45.3	−29.4	53.3	107
	TlI	−39.1	−26.9	40.9	107
	$LaCl^{2+}$	−17.4	21.2	129.5	124
	$LaBr^{2+}$	−8.0	5	43.6	125
	$NdCl^{2+}$	−18.6	13.2	106.7	124
	$NdBr^{2+}$	−9.1	2.8	39.9	125
	$TmCl^{2+}$	−14.7	27.4	141.2	124
	$TmBr^{2+}$	−12.0	0.7	42.6	125
N,*N*-dimethylacetamide	LiCl	−9.5			126
	LiBr	−8.7			126
	LiI	−8.4			126
	$LiClO_4$	−10.1			126
	$LiBF_4$	−10.4			126
	$LiAsF_6$	−9.4			126
	$NaBPh_4$	−9.3			127
	$KBPh_4$	−9.4			127
	$LaBr^{2+}$	−11.4	25	122.1	128
	$NdBr^{2+}$	−15.2	22.3	125.8	128
	$TmBr^{2+}$	−13.8	18.2	107.3	128
	Bu_4NBPh_4	−8.5			126
	Et_4NBr	−9.6			127
	Pr_4NBr	−10.1			127
	Bu_4NBr	−9.5			126
	Pe_4NBr	−9.7			127
	Hx_4NBr	−9.9			127
	Hp_4NBr	−10.1			127
	Oc_4NBr	−9.8			127
ammonia at 238 K	KCl	−13.8	10.4	81.2	129
	KBr	−12.6	9.4	73.8	129
	KI	−11.3	4.6	53.3	129
	KNO_3	−12.8	4.6	58.4	129
	KSCN	−11.7	6.3	60.4	129
	NaSCN	−11.8	9.5	71.4	129
	NH_4SCN	−11.2	10.2	71.8	129
	Me_4NSCN	+10.0?	24.9?	50?	129
	$TlNO_3$	−11.5	26	125.8	123[b]
dimethyl sulfoxide	LiCNS	0.9	0.3	−2.0	123[b]
	LiN_3	−2.5	4.9	23.8	123[b]
	LiNCO	−11.5	1.2	42.6	123[b]
	NaNCO	−9.5	3.2	42.6	123[b]
	KNCO	−6.9	0.5	24.8	123[b]

[a] For its formation from $Cd(H_2O)_6SO_4$. [b] Also references therein.

values of $\Delta_{IP}H°(IP,S)$ and $\Delta_{IP}S°(IP,S)$. For these theories, the temperature dependence of $K_A°$ is due to that of the parameter $b = e^2/2\epsilon a k_B T$, via the factor $(\epsilon T)^{-1}$ involving the permittivity of the solvent, ϵ, provided the distance of closest approach a is assumed to be independent of the temperature. Thus, the Fuoss theoretical value is

$$\Delta_{IP}H°(IP,S)^F = RT(q/a)[1 + T(\partial \ln \epsilon/\partial T)_P + T\alpha_P(S)] \tag{60}$$

In the case of Bjerrum's theory, the cutoff distance $R = q$ is also nominally temperature-dependent, affecting the upper limit of the integral $Q(b)$, but this has little effect on the derived quantities:

$$\Delta_{IP}H°(IP,S)^B = 3RT[1 + T(\partial \ln \epsilon/\partial T)_P + T\alpha_P(S)] \tag{61}$$

On the assumption that $Q(b)$ is temperature-independent, the difference between the standard molar enthalpy derived from these two treatments is the replacement of the ratio q/a of the Fuoss theory by the numerical 3 in the Bjerrum treatment.

4.3. Volume

The volume change occurring on ion pairing is the difference between the sum of the standard partial molar volumes of the ions, $V°(\text{salt}) = V_+° + V_-°$ (for a symmetrical electrolyte), and the standard molar volume of the ion pair, $V_{IP}°$. Experimental values of this difference are obtained from the pressure derivative of the thermodynamic association constant, $K_A°$:

$$\Delta_{IP}V°(IP,S) = -RT[(\partial \ln(K_A°/M^{-1})/\partial P)_T + \kappa_T] \tag{62}$$

The solvent isothermal compressibility, κ_T, needs to be subtracted in eq 62, as $K_A°$ is expressed on the pressure-dependent molar scale, M^{-1}. Another way to obtain $\Delta V_{IP}°$ is to follow the partial molar volume, ${}^{\varphi}V(\text{salt})$, of the electrolyte to such high concentrations as needed for the ion pair to represent the major fraction of the ions in the solution:[131]

$${}^{\varphi}V(\text{salt}) = \alpha[V°(\text{salt}) + S_V c^{1/2}] + (1 - \alpha)V_{IP}° + bc \tag{63}$$

where the fraction dissociated, α, is obtained independently, S_V is the theoretical (Debye−Hückel) limiting slope as $c \rightarrow 0$, and bc is an empirical linear correction term.

Such values (mostly from eq 62) have been reported for many electrolytes, mainly in aqueous solutions but also in some nonaqueous ones. A representative list is shown in Table 2.

Analogous to the derivation of the enthalpy of ion pair formation according to the theories of Fuoss and of Bjerrum, the volume change can be formulated as[131,162]

$$\Delta_{IP}V°(IP,S)^F = RT[(q/a)(\partial \ln \epsilon/\partial P)_T - \kappa_T(S)] \tag{64}$$

and

$$\Delta_{IP}V°(IP,S)^B = RT[3 + \exp(q/a)/(q/a)^3 Q(q/a)(\partial \ln \epsilon/\partial P)_T - \kappa_T(S)] \tag{65}$$

In solvents of relatively low permittivity, when q/a is large, $Q(q/a) \approx \exp(q/a)/(q/a)^4$ and eq 65 can be simplified to $\Delta_{IP}V°(IP,S)^B = RT[3 + (q/a)(\partial \ln \epsilon/\partial P)_T - \kappa_T(S)]$.[161,162] Côté and co-workers[163] applied the Bjerrum association model to the volumes of electrolytes in solutions in water and acetonitrile. They expressed the apparent molar volumes in terms of the pressure derivative of the activity coefficient according to this model.

Table 2. Volume Changes on Ion Pairing, $\Delta_{IP}V°(IP,S)/cm^3\ mol^{-1}$, Mostly from Eq 62

solvent S	ion pair IP	$\Delta_{IP}V°(IP,S)$	ref
water	LiF	7.9	132
	NaF	4.6	132
	KF	3.4	132
	RbF	4.0	132
	CsF	4.2	132
	$LiB(OH)_4$	9.1	132
	$NaB(OH)_4$	8.4	132
	$KB(OH)_4$	6.5	132
	$RbB(OH)_4$	7.6	132
	$CsB(OH)_4$	6.9	132
	$LiSO_4^-$	5.8	133−135
	$NaSO_4^-$	7.3 (8.3)	133−135
	KSO_4^-	5.9	134, 135
	$NH_4SO_4^-$	3.4	135
	$RbSO_4^-$	3.3	135
	$CsSO_4^-$	6.2	135
	$MgSO_4$	7.4 (9.0, 7.8) (7.2−8.5)	136 (83, 137)
	$CaSO_4$	11.7 (10.1)	138 (139)
	$MnSO_4$	7.4 (9)	136 (140)
	$CoSO_4$	10.9 (11.5)	141 (138)
	$NiSO_4$	11.4 (11.6, 8.6)	141 (138, 142)
	$CuSO_4$	11.3 (10.0, 11.4)	141 (143, 144)
	$ZnSO_4$	10.0 (8.0)	140 (145)
	$CdSO_4$	9.3 (3.4, 20.6)	146 (140, 147)
	UO_2SO_4	20.6	148
	$LaSO_4^+$	21 (26)	149 (150)
	$EuSO_4^+$	25.6	149
	$RbNO_3$	6	151
	$TlNO_3$	15	151
	$MgCl^+$	4.0 (8.2)	134, 135 (152)
	$LaFe(CN)_6$	8.0	48
	$Coen_3Cl^{2+}$	5.4	153
	$Coen_3Br^{2+}$	5.2	153
	$Coen_3I^{2+}$	5.0	153
	$Coen_3NO_3^{2+}$	5.0	153
	$Coen_3ClO_4^{2+}$	4.7	153
	$Coen_3SO_4^+$	23.3	153
	$Coen_3C_2O_4^+$	30.3	153
	$Coen_3Cit$	59.2	153
methanol	LiCl	18	131
	LiBr	17	131
	KCl	29	154
ethanol	LiCl	17	131
1-propanol	LiCl	16	131
2-propanol	LiCl	17.4 (19, 21.8)	155 (131, 156)
	NaI	15	157
	Bu_4NCl	11.7	155
	Bu_4NBr	8.8	155
	Bu_4NI	8.7	155
	Bu_4NClO_4	7.8	155
acetone	LiI	21	147
	NaI	25 (31.2)	147 (158)
	KI	23 (30.7)	147 (158)
	CsI	24 (30.4)	147 (158)
diethyl ether	Bu_4NPic	115	159
benzene	Bu_4NPic	62 (59)	159 (147)
dichloromethane	R_4NX	negligible	160

The multistep process of ion pairing discussed in section 2.3 involves the volume changes occurring during the distinct steps for the formation of the 2SIP, SIP, and CIP species; see eq 5 and Figure 1. For the first step, the electrostatic association of cation and anion, the value obtained from the Bjerrum model was thought to be adequate, but for the further steps, the values had to be assumed.[39] Whether a three-step or a two-step process takes place was discussed by Hemmes[161] from the point of view of the volume changes involved. It is generally agreed, however, that the volume changes leading to the CIP are due to the release of solvent molecules from between the partners of the ion pair to the bulk solvent.

The volume change on ion pairing was interpreted in terms of the number of solvent molecules released. This can be calculated on the notion that solvent molecules electrostricted in the solvation shells expand to their ordinary molar volumes when released, accounting for the observed positive values of $\Delta_{IP}V^\circ(\mathrm{IP,S})$.[162]

5. Triple Ions and Further Aggregation

There is no doubt that nominal triple ions such as $AgCl_2^-$ [67] or AlF_2^+,[164] where significant covalent bonding is present, have an independent existence in solution. However, the evidence for similar species held together by purely electrostatic forces is less clear-cut. As discussed below, the existence of triple ions (and higher aggregates) has been invoked already long ago to account for certain experimental observations, mainly concerning conductivities of electrolytes in solvents of low permittivity. However, alternative explanations are frequently possible and some researchers have regarded these aggregates as little more than mathematical conveniences. The following section should be considered in this context.

5.1. Triple Ion Formation

The equivalent conductance of a salt in a solvent of very low permittivity may exhibit a minimum conductivity at a certain, low, concentration. Ion pairing and variations of the activity coefficient of the free ions alone cannot explain this behavior. Fuoss and Kraus[165−167] reported and discussed conductivity data of tetraisopentylammonium nitrate and thiocyanate, among other salts, in benzene ($\epsilon_r = 2.27$), in dioxane ($\epsilon_r = 2.21$), and in dilute mixtures of benzene with 1,2-dichloroethane (13.3 wt %, $\epsilon_r = 2.8$) and of dioxane with water (≤14.95 wt %, $\epsilon_r \le 9.0$), where such minima were encountered. They explained quantitatively[166] the presence of the minima and the values of the equivalent conductivity and concentration at the minimum in terms of the formation of triple ions at equilibrium with free (single) ions and ion pairs:

$$C^+ + A^-C^+ \leftrightarrows C^+A^-C^+ \quad \text{and} \quad A^- + C^+A^- \leftrightarrows A^-C^+A^- \qquad (66)$$

By considering the low permittivity solutions at sufficiently low total salt concentrations ($c < 1$ mM), Fuoss and Kraus[166] could reasonably assume that the fraction of the dissolved salt dissociated into free ions, α, was so low that corrections for activity coefficients and the effects of interionic forces on the mobility of the ions could be neglected. Since $\alpha \ll 1$, the concentration of the ion pair (the "nondissociated" salt) essentially equals c. The equilibrium constant for ion pair formation $C^+ + A^- \leftrightarrows C^+A^-$ is then $K_{IP} = 1/\alpha^2 c$ and that for triple ion formation from the ion pair (assumed to be the same for the two equilibria (eq 66)) is $K_{TI} = \alpha_{TI}/c\alpha$, with α_{TI} being the fraction of the salt present as triple ions. The equivalent conductivity is then given by

$$\Lambda = \alpha\Lambda_0 + \alpha_{TI}\Lambda_{TI} \qquad (67)$$

where Λ_0 is the limiting equivalent conductivity at zero concentration (i.e., of the completely ionized salt) and Λ_{TI} is the equivalent conductivity of the triple ions, again not distinguishing between their two forms. Walden's rule—$\Lambda_{01}\eta_1 \approx \Lambda_{02}\eta_2$ for two solvents 1 and 2, with η being the bulk solvent viscosity—was used to estimate Λ_{02} of a given salt in the solvent of interest, 2, by taking known Λ_{01} values for this salt in solvents of sufficiently high permittivity, where complete dissociation occurs. On the other hand, Λ_{TI} had to be estimated as $\sim ^1/_3$ of Λ_0 on the basis of the sizes of the single and triple ions. Fuoss and Kraus[166] then showed that plots of $\Lambda c^{1/2}$ against c were linear, as expected from the expression

$$\Lambda c^{1/2} = [K_{IP}^{-1/2}\Lambda_0] + [K_{TI}K_{IP}^{-1/2}\Lambda_{TI}]c \qquad (68)$$

resulting from eq 67 and the above equilibrium constant expressions. The concentration at which the minimum in the equivalent conductivity occurs, c_{min}, corresponded to the ratio of the intercept to the slope of eq 68, i.e.

$$c_{min} = (\Lambda_0/\Lambda_{TI})K_{TI}^{-1} \approx 3/K_{TI} \qquad (69)$$

permitting the estimation of K_{TI}.

Fuoss and Kraus[166] then went on to obtain a theoretical expression for K_{TI}, based on considerations similar to those of Bjerrum[28] for $K_{IP} = K_A$ of section 2.1. For the formation of a triple ion according to the equilibria in eq 66, a single ion should approach a dipolar ion pair, on the side of opposite charge to its own. It may do so at any angle θ, although the most stable configuration (assuming purely Coulombic interactions) is linear, where like charges are farthest away from each other. Since only 1:1 electrolytes have any useful solubility in these low permittivity solvents, the ionic charges can be omitted and thus the expression for the electrostatic potential energy is

$$W_\pm(r) = -e^2\epsilon^{-1}[r^{-1} - (r^2 + a^2 + 2ra\cos\theta)^{-1/2}] \qquad (70)$$

This becomes $W_\pm(r) = -e^2\epsilon^{-1}[r^{-1} - (r + a)^{-1}]$ for the most stable configuration where $\theta = 0$. The cutoff distance for triple ion formation R_{TI} is the root of the following equation:

$$(1 + 2r/a)/[(r/a)(1 + r/a)^2] = a/q \qquad (71)$$

where a and q have the same meanings as in the Bjerrum treatment of ion pairing (section 2.1). The triple ion association constant is a double integral $I(b)$ over the angles θ and the distances r from contact to cutoff:

$$K_{TI} = (2\pi N_A/1000)a^3 I(b) \qquad (72)$$

where $b = 2q/a$, double the value used before. Physically meaningful (non-negative) values of the integral, $I(b)$, occur above the minimal value $b = ^8/_3$. Values of $\log I(b)$ and R_{TI}/a are shown for various values of b in Table 3.

The conductance of tetraisopentylammonium nitrate in aqueous dioxane solutions showed minima up to a water content of ≤20 wt %, corresponding to $\epsilon_r \le 12$. Experimental values of K_{TI} could be obtained from eq 69 up to a water content of 9.5 wt %, where $\epsilon_r = 5.84$, and these agreed well with the values calculated from the theoretical expression (eq 72).[166] As c_{min} increased with increasing water content,

Table 3. Values of log $I(b)$ and R_{TI}/a for Triple Ion Formation at Rounded b Values[166]

b	3.5	5	10	15	20	25	30	35
log $I(b)$	0.096	0.668	1.534	2.183	2.894	3.732	4.634	5.565
R_{TI}/a	1.23	1.56	2.46	3.17	3.76	4.28	4.75	5.19

the dissociation of the ion pair to single ions increased and corrections had to be applied to the equivalent conductance expression (eq 67) for the ionic activity coefficients and effects on the ionic mobilities.[166] Whereas values of the ion-pairing constant K_{IP} were in the range 10^{17} to 10^{18} M^{-1}, those of K_{TI} were considerably smaller, of the order of 10^5 M^{-1} for various tetraisopentylammonium salts at 298.15 K.[167]

Following the pioneering work of Fuoss and Kraus, interest in triple ion formation lay dormant for many decades. It reawoke significantly only in the late 1980s as a result of the growing importance of salt solutions in solvents of low permittivity arising from their use in lithium batteries. Unfortunately, the many papers by Hojo and co-workers during this period on conductivities and triple ion formation in low permittivity solvents (e.g., refs 168−170, but there are many others) have to be discounted for two reasons. One is the use of obsolete conductivity expressions (e.g., Shedlovsky's) at concentrations where the effects of ions on the mobilities have to be taken into account more appropriately than these earlier expressions allowed. The other problem is the consideration of ions that are able to form hydrogen bonds (e.g., Bu_3HN^+) with the anions, obscuring the electrostatic interactions leading to ion pairs and triple ions.

On the other hand, Salomon and Uchiyama[171] applied a modern conductivity expression (Fuoss and Hsia's),[76] in conjunction with an extended Debye−Hückel expression for the mean ionic activity coefficients, to calculate triple ion formation from conductivity measurements. This permitted evaluation of conductivity data around c_{min} in terms of three fitting parameters: K_{IP}, K_{TI}, and $\Lambda°$, assuming $\Lambda_{TI} = {}^2/_3\Lambda°$. (Note the difference with regard to Fuoss and Kraus's estimate of $\Lambda_{TI} = {}^1/_3\Lambda°$.) The contributions of triple ions to the conductivities at 25 °C of $LiClO_4$ in dimethyl carbonate ($\epsilon_r = 3.12$), $LiBF_4$ in 1,2-dimethoxyethane ($\epsilon_r = 7.15$), and Bu_4N^+ picrate in anisole ($\epsilon_r = 4.29$) were between 30 and 50%. In view of the cutoff distance R_{TI} defined above, no triple ions are expected to be formed below the salt concentrations $c_{cutoff}/M = 1.2 \times 10^{-14}(\epsilon_r T)^3 = 9.6 \times 10^{-6}$, 1.2×10^{-4}, and 2.5×10^{-5} for these solvents. Two problems that were knowingly ignored in this approach were the effects of increases in viscosity and permittivity of the solutions as c increases, both of which are measurable and correctable.

The latter point has been addressed by several authors. If $c_{min} \geq 0.1$ M, the increase in ϵ_r becomes appreciable and should be taken into account, as pointed out by Cavell and Knight.[172] This point was taken up by Gestblom et al.,[173] who questioned the formation of triple ions altogether in dichloromethane solutions of tetraalkylammonium and similar salts. Maaser et al.[174] also discussed this problem, but with no clear conclusion. Petrucci and Eyring[175] considered both the dependence of the solution permittivity on the salt concentration and more importantly the electrostatic interactions of the dipolar ion pairs with the ionic atmosphere around them in terms of a multibody interaction theory. This dispensed altogether with the notion of triple ions as discrete chemical species and arrived at fits of the conductance curves (in terms of the Fuoss−Hsia expression)[76] with Bjerrum-type ion pairing and expressions for the dipole−ion, dipole−dipole, ion−dipole, and ion−ion interactions. The calculations were applied to solutions of $LiAsF_6$ in methyl acetate, 2-methyltetrahydrofuran, 1,2-dimethoxyethane, and dimethyl carbonate as well as of $LiClO_4$ in these solvents, tetrahydrofuran, and 1,3-dioxolane.

Barthel et al.[17] recently tabulated K_{TI} values from the literature for the triple ions $Li^+ClO_4^-Li^+$ and $ClO_4^-Li^+ClO_4^-$ (assumed to be equal) that ranged from 22 M^{-1} in methyl formate ($\epsilon_r = 8.5$) via 38 M^{-1} in methyl acetate ($\epsilon_r = 6.68$) to 412 M^{-1} in dimethyl carbonate ($\epsilon_r = 3.11$). However, it should not be concluded from this that triple ion formation is confined to solvents of low permittivity. For instance, Barthel et al.[90] concluded from conductivity measurements that triple ions are formed by lithium fluoroacetates in propylene carbonate (PC, $\epsilon_r = 64.92$ at 298.15 K) at $c \leq 0.009$ M. This is a consequence of the relatively poor ability of PC to solvate the ions (see section 6). Rather more importantly, because of its general implications for *aqueous* electrolyte solutions, it has been shown recently using a combination of dielectric relaxation spectroscopy (DRS)[26] and Raman spectroscopy[25] that concentrated solutions of $MgSO_4$(aq) contain at least one triple ion, $Mg_2SO_4^{2+}$. This particular triple ion could be detected because it has a large dipole moment (the symmetry of most triple ions means that they have near-zero dipole moments), thereby making it "DRS-active",[26] and because of the unusual sensitivity of the strong $\nu_1(SO_4^{2-})$ Raman band to minor perturbations in its environment.[25]

The most recent theoretical consideration of triple ion formation is that of Barthel et al.[56] They modified the mean spherical approximation (MSA, section 2.6), formulating the associative-MSA (AMSA) to include symmetrical triple ions. They introduced the expression γ^*c (γ^* replaces the authors' γ to avoid confusion with the symbols commonly used, here and elsewhere, for activity coefficients on the molal scale) as the concentration of the ions *not* bound in a triple ion. Then the concentration of single ions is $\alpha\gamma^*c$ and that of ion pairs is $(1 - \alpha)\gamma^*c$ and the mass action law for triple ion formation is

$$(1 - \gamma^*)\gamma^{*-2} = (1 - \alpha)cK_{TI}[y_{IP}^{HS}y_{\pm}^{el}y_{IP}^{el}/y_{TI}^{el}] \qquad (73)$$

For further evaluation, K_{TI} was treated as an adjustable fitting constant, $y_{IP}^{HS} = y_{IP}^{el} = 1$ was assumed for the activity coefficients of neutral ion pairs, and $y_{TI}^{el} = \exp[-2q(R\Gamma)^3/(1 + R\Gamma)^3]$ was used by analogy with the MSA expression for $y_{\pm}^{el}$ (section 2.6). Returning to $LiClO_4$ association in the low permittivity solvents mentioned above, the experimental osmotic coefficients and equivalent conductivities were compared with those calculated from the modified MSA treatment with the assumed $K_{TI} = 1$ M^{-1} in 1,2-dimethoxyethane ($\epsilon_r = 7.08$) and dimethyl carbonate ($\epsilon_r = 3.11$) with satisfactory results, having selected reasonable values for the distance of closest approach, a.

As is apparent from the foregoing discussion, most studies of triple ion formation have utilized conductivity data of single electrolytes. A completely different approach based on the interpretation of the excess Gibbs energy, G^E (activity and osmotic coefficients), in concentrated mixtures of two electrolytes A and B with a common ion, was developed by Friedman[176] and subsequently others. These studies were mostly confined to aqueous solutions at appreciable concentrations. The value of G^E as a function of the total (molal) ionic strength I and the fraction y of electrolyte A in the mixture can be written as

$$G^E(I,y) = I^2RTy(1-y)\sum g_p(1-2y)^p; \quad p = 0, 1, 2 \ldots \tag{74}$$

In this expression, g_p is a function of I (and T and P), which is interpreted by Friedman[177,178] in terms of the cluster expansion theory and ion−ion interactions. The g_0 parameter represents predominantly pairwise interactions but also has contributions from higher-order interactions. The g_1 parameter represents mainly triple ion interactions, again with contributions from higher-order ones, etc.[179] Negative values of these parameters mean an attractive interaction of the unlike noncommon ions, lowering the Gibbs energy. In common-ion electrolyte mixtures, there are three kinds of ions, and the g_p parameters do not specify which of them interact. However, negative g_1 values (denoting triple ion formation) were assumed to arise from those shown in the equilibria in eq 66, rather than those involving three ions of the same charge. Expressions for the excess enthalpy and volume of mixing analogous to eq 74, involving parameters h_p and v_p instead of g_p, have also been discussed in relation to triple ion formation by Friedman[176,178] and by Reilly and Wood.[179] Padova and co-workers[180−182] studied various common ion electrolyte mixtures isopiestically, derived G^E and g_p values, and interpreted them in terms of ion pairs and triple ions. Contrary to the intuitive Brønsted postulate that like-charged ions would not associate, such pairs and triplets have been found in, say, aqueous $Pr_4NBr + NaBr$ mixtures.[182]

5.2. Quadruple Ions and Higher Aggregates

In solvents of low permittivity, it is sometimes observed that when concentrations rise above c_{min}, the equivalent conductivity goes through a *maximum*. Such data have been interpreted by assuming the formation of neutral quadruple ions, nominally from two ion pairs, reducing the concentration of the conducting triple ions. Examples of such behavior are the conductivities of tetrabutylammonium tetrafluoroborate in 15% phenanthrene in anisole[183] and of $LiClO_4$ in polyethylene oxide 500.[184] However, such maxima in conductivities can also be explained by an increase in the solution viscosities at the high concentrations involved: ≥ 0.7 M[183] and ∼0.4 M,[184] respectively. Quadruple ions have also been claimed in cases where no maximum beyond the minimum in the conductivity curve occurs; see, e.g., ref 185 and references therein. Such interpretations need to be regarded skeptically, since the conductivity expressions on which they were based did not allow properly for nonspecific interactions.

Thus, positive evidence of quadruple ion formation from conductivity data is sparse, although intuitively such species might be expected to form. Barthel et al.[56] treated such hypothetical cases by the MSA theory in a manner similar to the treatment of triple ion formation (see previous section).

Quadruple ion formation can be considered as the dimerization of already formed ion pairs, but note that this does not imply a mechanism of formation: it simply accounts for the coexistence of ion pairs and quadruple ions. This approach has been taken mostly for data other than conductivities, where quadruple ion formation was invoked to explain nonconstant apparent K_A values. For example, "dimerization" of KPF_6 in aqueous solutions was proposed by Robinson et al.[186] to explain the variation of K_A values (designated K_{IP} in the original paper) obtained from activity coefficient data at $0.1 \leq m/\text{mol kg}^{-1} \leq 0.5$. The data could be fitted with $K_A = 2.1\ M^{-1}$ and $K_{QI} = 2.8\ M^{-1}$ for the quadruple ion. Similarly, Wirth[187] interpreted the apparent molar volumes of Et_4NBr in water in terms of dimerization of the ion pair, fitting the data with $K_A = 1.5\ M^{-1}$ and $K_{QI} = 1.0\ M^{-1}$. Supercritical water has a low permittivity; hence, electrolytes associate in it and may aggregate to species beyond ion pairs. Calculations for 1:1 electrolytes in water at 673−1073 K and 50−400 MPa,[188] based on the restricted primitive model, indicated the formation of such species at $m > 0.5$ mol kg^{-1} at the lower pressures and higher temperatures in these ranges. Such species may be significant for many geochemical processes.

Spectroscopic methods have also provided evidence for the formation of quadruple ions in solvents of low permittivity and poor solvating ability. Chabanel and co-workers,[189−192] using vibrational (infrared and Raman) spectroscopy, have shown that isothiocyanates or perchlorates of alkali and alkaline-earth metals in solvents such as dimethyl and diethyl carbonate, methyl acetate, butyl acetate, tetrahydrofuran, and 1,3-dioxolane "dimerize" to quadruple ion structures due to dipole−dipole interactions (noting again that this is not proof of the mechanism of formation). Less dimerization of the ion pairs was noted in nitromethane, with even lower values in acetone, acetronitrile, dimethylformamide, and dimethyl sulfoxide. The dimerization was found to be entropy controlled, with the ion pair being desolvated upon formation of the quadruple ion, with concomitant positive enthalpy and entropy changes.

Further aggregation of electrolytes (i.e., beyond quadruple ion formation) in solvents that are poorly solvating and have moderate to low permittivities is to be expected in sufficiently concentrated solutions and was indeed found in some of these studies. Petrucci and co-workers[174,184,193,194] have studied salts in low permittivity solvents, mainly using relaxation methods (ultrasonic and dielectric) but also infrared spectroscopy. The systems studied included lithium and sodium thiocyanates in tetrahydrofuran, $LiClO_4$ and $LiAsF_6$ in 2-methyltetrahydrofuran, and $LiClO_4$ in polyethylene oxide dimethyl ether PEO-500. In the last system, ultrasonic and dielectric relaxation measurements led to the conclusion that the dipolar ion pairs dimerize to essentially nonpolar quadruple ions with antiparallel orientation of the two ion pairs, leading to decreased permittivity and conductivity at $c \gtrsim 0.4$ M.[184]

A recent paper by Xuan et al.[195] deals with $LiBF_4$ in acetonitrile, studied by vibrational spectroscopy and quantum chemical calculations. The latter were used to ascribe various structures to the species formed, including the dimers. The quadruple ions were claimed to have highly symmetrical structures. However, it should be noted that quantum mechanical (QM) calculations produce *gas-phase* structures, even if a few solvent molecules are included for verisimilitude. Reliable calculation of species structures in real solutions is not in general possible at present using QM calculations. The literature abounds with species for which there is no plausible evidence other than QM (or similar) calculations.

As already noted, there is no reason to suppose that the aggregation of ions in poorly solvating solvents of low permittivity should stop with triple- or quadruple-ion formation. Higher aggregates might even be considered as steps along a pathway leading ultimately to ionic liquids and seem intuitively reasonable. The solvent extraction literature is full of reports of such aggregation for long-chain substituted ammonium salts or salts of alkyl and dialkyl phosphoric or phosphonic acids in hydrocarbon solvents up to (inverted) micelles or other large aggregates. This fascinating and important subject is outside the scope of this review.

6. Solvation and Ion Pairing

Solvent effects on ion pairing have been studied right from the introduction of the concept of ion pairing of strong electrolytes by Bjerrum in 1926.[28] At the time, and for a long period subsequently, such association was taken to be determined entirely by the bulk permittivity of the solvent, ϵ, since according to the Bjerrum model, it is the electrostatic attraction between oppositely charged ions in solution that causes them to form ion pairs. For instance, Grunwald[34] considered ion pairs with $a = 0.6$ nm at 25 °C in solvents with relative permittivities $10 \leq \epsilon_r \leq 40$ on the basis of Bjerrum's theory and listed cutoff distances q ranging from 0.7 to 2.8 nm and association constants K_A from 2.6 to 4550 M^{-1}. Kraus in his review of ion pairing[18] discussed ion pairs at permittivities just below the critical value where ion pairing sets in (the Bjerrum $q \geq a$), as well as in solvents of appreciable ϵ_r. His statement that "for a given value of a at a given temperature the value of K [$\equiv 1/K_A$] is dependent only on the [relative permittivity] of the solvent medium"[18] readily followed from the understanding of that time, but even then exceptions were evident and required explanations.

The notion that the distance of closest approach, a, can be set equal to the sum of the radii of the bare ions, $r_+ + r_-$, does not appear to be tenable in strongly solvating solvents. In such solvents, the solvation shells around the ions may remain largely intact when ions of opposite charges are attracted to each other electrostatically. In water, with $\epsilon_r = 78.36$ at 298.15 K, the cutoff distance R for 1:1 electrolytes is smaller than the distance of closest approach of the *hydrated* ions: $R \approx q = 0.357$ nm $< a = (r_+ + d_W) + (r_- + d_W)$, where d_W is the diameter of a water molecule. Thus, 1:1 electrolytes generally do not form ion pairs in water. However, 2:1 or 1:2 electrolytes associate even in water, where $R \approx q = 0.714$ nm. Electrolytes of higher charge types should certainly associate in water, as has frequently been observed. At very high temperatures, where the relative permittivity of water is considerably reduced, even 1:1 electrolytes may form ion pairs.[196]

There are in aqueous solutions two types of ion pairing not governed by the electrostatic considerations usually applied. These have been inferred by the consideration of the activity or osmotic coefficients of families of 1:1 electrolytes. Robinson and Harned[197] showed that for the alkali metal halides (except the fluorides) the activity coefficients for a given halide and at a given concentration decrease in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$, which they took to be the "regular" order. However, for the fluorides, hydroxides, formates, and acetates, the order is reversed. They explained this observation by the concept of "localized hydrolysis". They suggested that a SIP is formed: $C^+\cdots OH\cdots H\cdots A^-$, in which a high field cation C^+, with a high charge-to-radius ratio, such as Li^+, polarizes the water molecule while the anion A^- that is the conjugate base of a weak acid attracts a hydrogen atom of the polarized water molecule. This association decreases the activity coefficient in the same manner as ion pairing does due to electrostatic attraction between the ions, that occurs in any solvent, even one that is devoid of such donor and acceptor properties as water has. This idea was subsequently taken up by Diamond,[198] who elaborated on it and showed that for the lithium salts it results in the order of the activity coefficients to be $I^- > Br^- > Cl^-$, contrary to the "regular" order found for the heavier alkali metals, expected from the distances of closest approach. It should be noted, however, that the difference between "localized hydrolysis" and ion association is largely semantic. Furthermore, the limited DRS studies on such systems[3,92] suggest that 2SIPs may predominate over the SIPs assumed in the "localized hydrolysis" scenario.

The other effect, peculiar to aqueous solutions, is "water structure enforced ion pairing".[199] The order of decreasing activity coefficients for aqueous solutions of cesium halides is $Cl^- > Br^- > I^-$, and for the iodides of tetraalkylammonium it is $Et_4N^+ > Pr_4N^+ > Bu_4N^+$. Here the association is opposite to what would be expected from electrostatic attraction, increasing with the sizes of poorly hydrated ions. Such ions break the water structure around them (Cs^+ and I^-) or produce hydrophobic cages around them (R_4N^+) that disturb the ordinary water structure. By forcing such ions together to form an ion pair, the regular water structure is regained to a large extent; hence, this association is favored, i.e., the well-known hydrophobic association. Some insight for such cases may be obtained using spectroscopic[105,200] and DR[98] methods.

These two types of ion pairing are practically known only for aqueous solutions, although the first is likely to occur in solvents the molecules of which would "locally solvolize", e.g., alcohols,[201] and the second in solvents that are highly structured by hydrogen bonding, e.g., formamide.

Ion pairing in nonaqueous solvents with $\epsilon_r \lesssim 40$ has been extensively studied. This is mainly because ion pairs are common in such solvents, even if the ions are singly charged and even if they are strongly solvated. At these moderate or low relative permittivities, the electrostatic forces between oppositely charged ions are sufficiently long range to create ion pairs without necessitating the removal of solvent molecules from the solvation shells.

6.1. Solvent and Counterion Competition

Competition between counterions and solvent molecules for space in the vicinity of a given ion in an electrolyte solution is a general phenomenon. On ion pairing, solvent molecules may be sequentially released from the solvation shells at increasing electrolyte concentrations and diminishing solvent activities. This process leads via 2SIPs to SIPs to CIPs, all of which will be solvated outside the space between the partner ions, although to a smaller extent as a result of the partial charge neutralization.

Solvation effects on ion pairing were noted even in the earliest studies of ion pairing. Exceptions to the expected smooth dependence of log K_A on $1/\epsilon_r$ were evident and required explanations. For instance, for the three solvents 1,2-dichlorobenzene, 1,1,1-trichloroethane, and 1,2-dichloroethane, which have ϵ_r values of ≈ 10 within 2%, the values of K_A of tetrabutylammonium picrate at 25 °C obtained from conductivity measurements varied by more than an order of magnitude.[18] Therefore, factors other than ϵ_r were clearly operative. Solvation effects were invoked qualitatively by Gilkerson[32] to account for such variations. Deviations from the smooth dependence of log K_A on $1/\epsilon_r$ were observed especially in binary solvent mixtures, where ϵ_r could be varied continuously by changing the composition. These deviations were interpreted in terms of preferential solvation of the ions by the components of the binary solvent or, for a given ion, in terms of competition between solvation and association with its counterion. Hyne[202] pointed out that although the values of log K_A for tetrabutylammonium bromide or perchlorate in pure solvents were linearly dependent on $1/\epsilon_r$, consistent with the restricted primitive model (RPM), those for Bu_4NBr in mixtures of water and dioxane were not. In this case the RPM is not applicable and the structure of the dioxane molecules, changing from chair to boat configurations in the solvation shell of the ions, comes into play. A similar argument in terms of the *trans* and *gauche* forms of 1,2-dichloroethane explained the deviation of K_A of Bu_4NClO_4 from the line established by other pure solvents. Preferential solvation was most obvious for Bu_4NBr in mixtures of methanol and nitrobenzene.[202,203] Nitrobenzene is of appropriate size for its antiparallel dipolar association with the $Bu_4N^+Br^-$ ion pair, thus enhancing its formation. However, solvents may not only enhance ion pairing but also act against it when the solvation is sufficiently strong and extends over a wide region of space around an ion.

Further illustrations of the competition between ion solvation and ion association include the ultrasonic absorption study of lithium thiocyanate in mixtures of water and *N*,*N*-dimethylformamide (DMF). At $x_{DMF} > 0.6$, ion pairing prevails over ion solvation, while the reverse is true at $x_{DMF} < 0.6$.[58] Such a competition is enhanced as the concentration of the electrolyte increases and the ratio of solvent molecules to electrolyte decreases. The entropy of mixing of free cations, free anions, ion pairs, and free solvent molecules depends on the amount of solvent bound to the ions and ion pairs. This effect was treated by DeMaeyer and Kessling[204] for hydrochloric acid and cesium chloride in water up to saturation.

Solvent release from solvation shells upon ion pairing was studied by Marcus[130] and illustrated with entropy change data for various salts in diverse solvents. On association of two ions to form one ion pair, translational entropy is lost:

$$\Delta S_{tr}/\mathrm{J\ K^{-1}\ mol^{-1}} = 1.5R\ \ln[M_{IP}/M_+M_-] - 82.2 \qquad (75)$$

where M is molar mass and $M_{IP} = M_+ + M_-$. Rotational entropy is gained (for monatomic ions):

$$\Delta S_{rot}/\mathrm{J\ K^{-1}\ mol^{-1}} = 67.5 + R\ \ln M_{IP}/M_+M_-] + 2R\ \ln a \qquad (76)$$

where $a = r_+ + r_-$ is the contact distance of the partners in the pair. When one of the associating ions is polyatomic (e.g., sulfate or tetrabutylammonium), its rotational degrees of freedom are diminished, however, and a loss of some $^2/_3$ of its rotational entropy must be taken into account. The change of electrostatic entropy, estimated from the Born equation for distances beyond the first solvation shell of thickness d is

$$\Delta S_{el} = k[z_+^{\,2}/(r_+ + d) + z^{-2}/(r_- + d) - (z_+ - |z_-|)^2/\{(r_+r_-a)^{1/3} + d\}] \qquad (77)$$

where $k = (N_Ae^2/8\pi\epsilon_0)(\mathrm{d}\epsilon_r/\mathrm{d}T)\epsilon_r^{-2}$. For a symmetrical electrolyte, the last term in the square brackets of eq 77 vanishes. The standard molar entropy of ion pairing, $\Delta_{IP}S°(\mathrm{IP,S})$, is obtained from the temperature coefficient of the measured association constant or by calorimetry; see section 4.2. For the desolvation of the ion partners occurring in the pairing process, the entropy change is

$$\Delta_{des}S = \Delta_{IP}S°(\mathrm{IP,S}) - (\Delta S_{tr} + \Delta S_{rot} + \Delta S_{el}) \qquad (78)$$

For solvent-separated ion pairs (2SIPs), $\Delta_{des}S$ may be small, since not much solvent is expected to be removed from the ions on pairing, but is probably not zero.

The solvent molecules solvating the ions and the ion pair are translationally immobilized to them, and their release can be set analogous to the process of fusion of the solidified solvent (extrapolated to the temperature at which the terms in eq 78 are determined, generally 298.15 K). Then the number of solvent molecules released on ion pairing is

$$\Delta n_{IP}{}^{S} = \Delta S_{desolv}/\Delta_{fus}S(\mathrm{S}) \qquad (79)$$

where $\Delta_{fus}S(\mathrm{S})$ is this entropy of fusion of the solvent.[130] A corresponding quantity, the solvation number of the electrolyte, $\sum n$, is obtained from the sum of the entropies of solvation of the ions: $\sum n = \sum \Delta S_{solv}/\Delta_F S$. Such calculations were made for divalent metal sulfates in water and perchlorates in methanol and in uni- and divalent metal halides in 1-propanol, *N*,*N*-dimethylformamide, and dimethylsufoxide; see Table 4. As expected, $\Delta n_{IP} < \sum n$, with the former comprising some 30−60% of the latter. Therefore, the ion pairs studied in these solvents are still solvated to a considerable extent. As would be expected, fewer solvent molecules are released when the ion pair is charged, i.e., as in unsymmetrical electrolyte solutions. It was concluded,[130] however, that the number Δn by itself is insufficient for distinction between 2SIPs, SIPs, and CIPs.

The strong electric fields of the ions cause electrostriction of the solvent, and when the field is considerably diminished around the dipolar ion pair with no net charge, this electrostriction is loosened up. The solvent molecules released from the solvation shells revert to the bulk solvent having, then, the bulk molar volume. A recent calculation of the molar electrostriction of solvents, $\Delta V_{el}(\mathrm{S})$, that is, the volume change per mole of solvent molecules subject to electrostriction,[162] permits the estimation of the number of solvent molecules released on ion pairing, $\Delta n_{IP}°$. Evaluation of the molar volume of a completely eletrostricted solvent molecule, $V_{S,el}$, was based[212,213] on the expression

$$V_{S,el} = V_S°(\kappa_T S_V/S_\kappa) \qquad (80)$$

where $V_S°$ is the molar volume of bulk solvent and S_V and S_κ are the theoretical (Debye−Hückel) slopes of the $c^{1/2}$ term of the concentration dependence of the apparent molar volume and compressibility of the electrolyte solution. These quantities require knowledge of the first and second pressure derivatives of the density and relative permittivity of the solvent, which are available for a restricted number of solvents.[162] The value for the difference between the molar volume of bulk solvent and electrostricted solvent for S = water is $\Delta V_{el}(\mathrm{S}) = V_S° - V_{S,el} = 2.9\ \mathrm{cm^3\ mol^{-1}}$, based on modern values of the properties of water, which differs somewhat from previous estimates.[162] The ratio of the standard molar volume change on ion pairing, $\Delta_{IP}V°(\mathrm{IP,S})$, commonly obtained from the pressure derivative of the association constant (see section 4.3) and $\Delta V_{el}(\mathrm{S})$,

$$\Delta n_{IP}{}^{\circ V} = \Delta_{IP}V°(\mathrm{IP,S})/(-\Delta V_{el}(\mathrm{S})) \qquad (81)$$

Table 4. The Number Δ*n* of Solvent Molecules Released from the Individual Ions When They Form an Ion Pair, Calculated As Described in the Text

solvent S	ion pair IP	$\Delta n_{IP}{}^{\circ V}$	ref for $\Delta_{IP}V^\circ$(IP,S)	$\Delta n_{IP}{}^{\circ S}$	ref for $\Delta_{IP}S^\circ$(IP,S)
water	LiF	2.7	132		
	NaF	1.6	132		
	KF	1.2	132		
	RbF	1.4	132		
	CsF	1.4	132		
	$LiB(OH)_4$	3.1	132		
	$NaB(OH)_4$	2.9	132		
	$KB(OH)_4$	2.3	132		
	$RbB(OH)_4$	2.6	132		
	$CsB(OH)_4$	2.4	132		
	$LiSO_4^-$	1.9	133, 134		
	$NaSO_4^-$	2.5	134, 135		
	KSO_4^-	2.1	134, 135		
	$NH_4SO_4^-$	1.2	135		
	$RbSO_4^-$	1.1	135		
	$CsSO_4^-$	2.2	135		
	$MgSO_4$	2.5	205	4.9	206, 207
	$CaSO_4$	4.0	138	5.1	206, 207
	$MnSO_4$	2.5	205	5.4	104
	$CoSO_4$	3.8	141	5.1	104, 207
	$NiSO_4$	4.1	141	5.1	104, 206, 207
	$CuSO_4$	3.9	141	5.3	104, 206, 207
	$ZnSO_4$	3.5	140	5.1	206, 207
	$CdSO_4$	3.3	146	5.5	206, 207
	UO_2SO_4	7.0	148	7.8	104
	$LaSO_4^+$	6.8	149	6.3	104
	$FeSO_4^+$			8.0	104
	$EuSO_4^+$	8.8	149		
	$RbNO_3$	2.2	151		
	$TlNO_3$	5.2	151		
	$MgCl^+$	1.4	134, 135		
	$LaFe(CN)_6$	2.7	48		
	$Coen_3Cl^{2+}$	1.8	153		
	$Coen_3Br^{2+}$	1.8	153		
	$Coen_3I^{2+}$	1.7	153		
	$Coen_3NO_3{}^{2+}$	1.7	153		
	$Coen_3ClO_4{}^{2+}$	1.7	153		
	$Coen_3SO_4{}^+$	8.0	153		
	$Coen_3C_2O_4{}^+$	10.4	153		
	$Coen_3Cit$	20.4	153		
methanol	LiCl	3.0	131		
	LiBr	2.8	131		
	KCl	4.8	154		
	$MClO_4^-$ [a]			9.5−11.5	208
1-propanol	LiCl	1.1	131		
	NaBr			2.8	71
	NaI			2.5	71
	$NaClO_4$			3.7	71
	KI			2.7	71
	RbI			2.7	71
2-propanol	LiCl	0.7	155		
	NaI	0.4	157		
	Bu_4NCl	0.3	155		
	Bu_4NBr	0.3	155		
	Bu_4NI	0.3	155		
	Bu_4NClO_4	0.3	155		
acetone	LiI	0.8	147		
	NaI	1.0	147	1.9	209
	$NaClO_4$			2.0	209
	KI	0.9	147		
	CsI	0.9	147		
N,*N*-dimethylformamide	TlX[b]			0.8−1.0	107
	$CuCl^+$			2.6	210
dimethylsulfoxide	CuX^+ [b]			1.5−2.0	211
	ZnX^+ [b]			3.0	211
	CdX^+ [b]			1.6−1.8	211
	HgX^+ [b]			3.6−3.8	211
diethyl ether	Bu_4NPic	3.4	159		
benzene	Bu_4NPic	2.8	159		
dichloromethane	R_4NX[b]	∼0	160		

[a] $M^{2+} = Ca^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$, and Cd^{2+}. [b] $X^- = Cl^-, Br^-$, and I^-.

then corresponds to the number of water molecules released on ion pairing in water. The values of $\Delta n_{IP}°$ derived from the volume change on ion pairing are compared in Table 4 with values derived from the entropy change where available, with fair agreement. Unfortunately, there are not many cases where data from both approaches are known.

For the case of ion pairing of magnesium sulfate in water, the considerations of Eigen and Tamm[39] yielded discrete values for the volume changes of the three stages of association. The standard partial molar volume changes, $\Delta V°(2SIP) = 4.9$ cm^3 mol^{-1} for the formation of the double solvent-separated ion pair from the individual ions, $\Delta V°(SIP) = 3.5$ cm^3 mol^{-1} for the formation of the solvent-shared ion pair from the 2SIP, and $\Delta V°(CIP) = 0.7$ cm^3 mol^{-1} for the formation of the contact ion pair from the SIP, were estimated.[16] The sum of these values, $\Delta V° = 9.1$ cm^3 mol^{-1}, represents the volume change on formation of the contact ion pair from the individual ions. The experimental value $\Delta_{IP}V°(Mg^{2+}SO_4^{2-},aq) = 7.3$[206] or 7.8[16] cm^3 mol^{-1} at 25 °C is somewhat smaller, but in the solutions where these values were obtained, not all the magnesium sulfate was in the form of contact ion pairs. The experimental $\Delta_{IP}V°$ agrees well with that, $\Delta_{IP}V°(IP,S)^F = 7.4$ cm^3 mol^{-1}, obtained by Hemmes[161] from the differentiation of the logarithm of the Fuoss expression for the association constant K_A^F (cf. section 2.2) with respect to the pressure, eq 64.

The Bjerrum treatment of ion pairing, in this case of magnesium sulfate in water, involves the cutoff distance $q = 1.43$ nm, which is more than the distance between the centers of the ions separated by two water molecules, ~ 0.9 nm, but it is expected that little volume change occurs when the partner ions are subject to ion pairing at distances apart of $0.9 \leq r/\text{nm} \leq 1.43$. The expression for the volume change according to this treatment, eq 65,[155,161] leads to a calculated volume change for magnesium sulfate of $\Delta_{IP}V°(IP,S)^{Bj} = 4.9$ cm^3 mol^{-1},[161] corresponding well with the $\Delta V°(2SIP) = 4.9$ cm^3 mol^{-1} reported above.

Marshall and Quist[196,214] studied ion pairing of 1:1 electrolytes in water at high temperatures and advocated the consideration of the number of water molecules released by employing "complete" equilibrium constants. For example, the association of sodium iodide in water at 500−800 °C was described by

$$Na^+(aq) + I^-(aq) \leftrightarrows Na^+I^-(aq) + kH_2O \qquad (82)$$

with $K_A° = c_{NaI}c_{H_2O}{}^k/c_{Na^+}c_{I^-}$ on the M^{k-1} scale at infinite dilution of the solute. The conventional equilibrium constant K_A could be written as

$$\log K_A = \log K_A° - k \log c_{H_2O} \qquad (83)$$

The resulting linear plot of $\log K_A$ vs $\log c_{H_2O}$ yielded the parameter $k = 9.7$ as the slope, being independent of the temperature. However, such a high number of water molecules released, signifying formation of an unhydrated CIP, is rather unlikely. The linearity of the plot of eq 83 appears to be an insufficient criterion for the elucidation of what takes place in these solutions. For instance, no allowance was made for the change in relative permittivity over this wide temperature range.

On the other hand, Zavitsas[215] evaluated the colligative properties (freezing point depression, boiling point elevation, vapor and osmotic pressures) of aqueous solutions of electrolytes at ambient temperatures up to 100 °C and up to very high concentrations. He considered the water in the hydration shells of the ions as being abstracted from the bulk water, so that the mole faction of "free" water is lower than the nominal. He then showed that these properties of electrolytes involving small inorganic ions even up to 1:3 types can be modeled by assigning hydration numbers to the ions without invoking ion pairing. In his treatment, Zavitsas ignored, however, similar ideas published over 50 years earlier by Stokes and Robinson[216] (ref 2, pp 238−251) for the interpretation of activity coefficients of aqueous electrolytes.

6.2. Transfer of Ion Pairs between Solvents

As mentioned above, in solvents with $\epsilon_r \leq 40$, ion pairs are common even if the ions are singly charged, so that ion pairing in such solvents has been extensively studied. In some of these studies, ion association was quantitatively determined in more than one solvent. The standard molar Gibbs energy of ion pair (IP) formation in a solvent S is obtained from its association constant:

$$\Delta_{IP}G°(IP,S) = -RT \ln(K_A°/M^{-1}) \qquad (53)$$

Comparison of ion pairing in various solvents is probably best made in terms of the standard molar thermodynamic functions of transfer: $\Delta_t Y°(IP,S_1 \rightarrow S_2)$, where S_1 and S_2 denote two solvents and $Y = G, H, S$, etc. The solvents may be miscible, in which case these quantities are generally obtained from separate determinations in each solvent of $K_A°$ (for $\Delta_t G°$) and $\Delta H_A°$ (from calorimetry or, less satisfactorily, the temperature dependence of $K_A°$). Entropies are generally calculated from $\Delta G°$ and $\Delta H°$ in the usual way. If the two solvents are practically immiscible, then the transfer functions may be obtained from distribution equilibria of the electrolytes in question and their temperature dependence. The latter case is dealt with in section 6.3.

Values of $\Delta_t G°$ for ion pairs were reported for $R_4N^+X^-$ (R = Me or Et; X = Cl, Br, or I) in methanol and various solvents[217] and are shown in Table 5. Unfortunately, the $\Delta_{IP}G°$ values of these ion pairs in methanol were not reported. The results were interpreted in terms of the Kamlet−Taft linear solvation energy relation:

$$\Delta_{solv}G° = \Delta G°_0 + s\pi^* + a\alpha + h\delta_H{}^2 \qquad (84)$$

where π^* is the polarity/polarizability of the solvent, α is its hydrogen bond donation ability (zero for aprotic solvents), $\delta_H{}^2$ is the cohesive energy density (square of the Hildebrand solubility parameter), and s, a, and h are the susceptibilities of the ion pairs to these solvent characteristics. $\Delta G°_0$ is a constant that would vanish if $\Delta_t G°$ were used and the differences between π^*, α, and $\delta_H{}^2$ of the solvent and methanol were employed in eq 84. It was noted[217] that the change of R_4N^+ from tetramethyl- to tetraethylammonium had only a small effect on the ion pairing but changing the anion had a larger one. The average ratios for $X^- = I^-/Br^-/Cl^-$ of the a coefficients were 1.00:1.68:2.12, and those of the s coefficients were 1.00:1.20:1.28. The susceptibilities of the anions to solvation increase in this order, more for the hydrogen bonding coefficient a than for the polarization coefficient s. It was noted that the s, a, and h coefficients for the ion pairs were about 0.4−0.5 times those for the transfer of the separate cation and anion. The strong cation−

Table 5. Standard Molar Gibbs Energies of Transfer, $\Delta_t G°(IP,MeOH\rightarrow S_2)$/kJ mol^{-1}, of Tetraalkylammonium Halide Ion Pairs from Methanol to Diverse Solvents[217]

solvent S_2	Me_4NCl	Me_4NBr	Me_4NI	Et_4NCl	Et_4NBr	Et_4NI	Pr_4NI
hexane	89.1	76.6	55.6	89.1	76.6	55.6	
c-hexane	85.4	72.8	51.9	85.4	72.8	51.9	
water	−12.6	−8.4	−5.4	−7.5	−2.9	0.4	9.2
ethanol	6.3	5.4	3.3	6.7	5.9	4.6	0.8
1-propanol	7.9	6.7	4.6	7.9	6.7	5.9	
i-propanol	9.6	8.8	6.7	10.9	9.6	8.4	
1-butanol	9.2	8.4	6.3	8.8	7.5	6.7	2.5
t-butanol	16.3	15.5	13.0	16.3	15.1	13.8	
ethyl ether	63.2	52.3	33.5	63.2	53.1	34.7	30.5
acetone	27.6	18.0	6.7	27.6	18.0	7.9	5.0
2-butanone		19.7	8.8		23.0	11.3	6.7
ethyl acetate	37.7	28.0	17.2			20.1	18.4
acetonitrile	18.8	9.2	1.7	21.3	12.1	5.0	4.2
nitromethane	13.0	6.7	−0.8	20.9	13.8	4.2	6.3
DMF[a]	14.6	7.9	−2.1	19.2	13.0	2.1	2.5
NMPy[b]	19.7	11.7	−0.4	22.6	13.8	2.1	
DMSO[c]	12.6	5.9	−3.3			0.8	

[a] *N*,*N*-Dimethylformamide. [b] *N*-Methylpyrrolidin-2-one. [c] Dimethyl sulfoxide.

anion interaction leading to the ion pair makes it less prone to solvent discrimination than the separate ions, as might be expected.

Few authors have published enthalpies and entropies of transfer. An exception is the transfer of thallium(I) halides between water, *N*,*N*-dimethylformamide, and propylene carbonate.[107] If for a given ion pair there are entries in Table 1 for more than one solvent, the thermodynamic function of transfer can be obtained from the difference, but this calculation should be applied with caution, since the conditions (e.g., the temperature or concentration range) in the separate studies may have been different.

6.3. Transfer of Ion Pairs between Immiscible Solvents

The transfer of ions, as ion pairs, from a given solvent to an immiscible second solvent is important from two practical aspects: phase transfer catalysis and ion separations, in particular of alkali metal cations and of anions. The system employed generally comprises two substantially immiscible liquid phases (although solid/liquid, gas/liquid, and supercritical fluid/liquid systems have also been used), one of which is commonly aqueous. The other may be nonpolar, such as a hydrocarbon, but may also be highly polar, such as nitrobenzene. The general equation for the process involves the equilibrium

$$C^+{}_{aq} + A^-{}_{aq} \leftrightarrows C^+A^-{}_{org} \tag{85}$$

displaced strongly to the right, where the cation C is almost invariably monovalent, as is generally also the anion. If the organic solvent is nonpolar, the ion pair is poorly solvated and it has only van der Waals interactions with the surrounding solvent molecules. If the organic solvent is polar, the ion pair C^+A^- may dissociate to a small or large extent in the organic phase:

$$C^+{}_{aq} + A^-{}_{aq} \leftrightarrows C^+A^-{}_{org} \leftrightarrows C^+{}_{org} + A^-{}_{org} \tag{86}$$

6.3.1. Phase Transfer Catalysis

In phase transfer catalysis (PTC), an anion is commonly transferred from an aqueous solution into an immiscible nonpolar organic solution, where it reacts with a substrate already there. It should be noted that the reactions promoted by PTC are generally substitution reactions involving anions. A typical reaction is a cyanidation:

$$\begin{aligned} &C_8H_{17}Cl_{org} + Q^+{}_{aq} + CN^-{}_{aq} \leftrightarrows \\ &\quad C_8H_{17}Cl_{org} + Q^+CN^-{}_{org} \leftrightarrows C_8H_{17}CN_{org} + Q^+{}_{aq} + Cl^-{}_{aq} \end{aligned} \tag{87}$$

where Q^+ is the phase transfer catalytic cation, $Q^+CN^-{}_{org}$ indicates a more or less fully ion-paired salt in the organic phase (the salts are essentially fully dissociated in the aqueous phase), and the octyl chloride serves as the organic solvent as well as the substrate in this example.[218]

Two separate kinetic stages can be discerned—transfer of the anion from the aqueous phase and its subsequent reaction in the organic phase—with each being able to be rate determining. The role of the catalyst is to lower the kinetic barriers as far as possible. The transfer of the anion can be facilitated by means of an amphiphilic cation that is soluble in both phases, being largely in a dissociated state with respect to the anion of interest in the aqueous phase but ion paired with it in the organic phase. However, hydrophobic (i.e., lipophilic) cations can also be used, approaching from the organic solvent side to the interface, where they pick up the anion from the aqueous phase. The ion pair formed in the organic phase should be sufficiently reactive for the required purpose; one feature that can make it so is the absence of any significant solvation by the nonpolar solvent. The cation can be chosen at will and, if chiral, can lead to chiral products. Two types of cation have been employed for PTC: substituted quaternary ammonium cations and, less commonly, small cations embedded in crown ethers or cryptands, mainly dibenzo-18-crown-6 with K^+. However, the possible variety is almost infinite, as is the variety of anions that can be transferred.

The rate of transfer of the anion to form an ion pair in the organic phase in PTC increases up to a point and then diminishes when the number of carbon atoms, n_C, in the chains of a substituted quaternary ammonium cation, Q^+, increases. The rate depends on the cation bulk for two reasons. One is the distance of approach of the cation to the interface, being larger for a symmetrical quaternary ammonium cation, such as tetrahexylammonium, (Hx_4N^+), n_C

= 24, than for an unsymmetrical one, such as methyltrioctylammonium ($MeOc_3N^+$), $n_C = 25$, or didecyldiethylammonium ($Dc_2Et_2N^+$), $n_C = 24$. The latter two cations provide for easier pickup of the anion from the interface. The other cause is the coverage of the interface by the cations, with there being space for more if the bulk is smaller. Thus, with a proper choice of Q^+ and its lipophilicity, the maximal concentration of the anion in the organic phase, and hence the maximal rate for transfer-controlled reactions, can be achieved.

However, a too-intimate approach of the anion to the cation leads to stronger electrostatic interactions between them and hence to a lower reactivity of the anion. The rate of reaction of the anionic part of the ion pair with the substrate can be estimated from the q' value (not to be confused with the cutoff distance q), which should optimally be <1 for higher anion reactivity. This value (for quaternary ammonium PTCs) is the sum of the reciprocals of the number of carbon atoms in the chains, being $4 \times {}^1/_6 = 0.667$ for Hx_4N^+, $3 \times {}^1/_8 + 1 = 1.375$ for $MeOc_3N^+$, and $2 \times {}^1/_{10} + 2 \times {}^1/_2 = 1.200$ for $Dc_2Et_2N^+$. On the other hand, if the intrinsic rate of the reaction is fast, then the rate can be transfer controlled, and then $1.5 \leq q' \leq 2.0$ is optimal.[219] This aspect of the PTC can be handled in terms of the Hansch lipophilicity (hydrophobicity) parameters that are group-additive, being negative for hydrophilic groups and positive for hydrophobic ones.[220]

Further consideration of phase transfer catalysis is outside the scope of this review.

6.3.2. Ion Pair Extraction

Whereas in phase transfer catalysis the emphasis is on the transfer of anions by means of hydrophobic cations, the reverse is often true for ion pair extraction, where the focus is on the transfer of hydrophilic cations by means of amphiphilic or lipophilic anions. For many practical purposes, the cations transferred are the alkali metal cations that do not form complexes with the chelating agents that are used for the extraction of more highly charged cations.[221] However, for anion separation, lipophilic cations are of course required.[222] The exchange equilibrium involving the two (monovalent) cations $C^{\alpha+}$ and $C^{\beta+}$,

$$C^{\alpha+}{}_{aq} + A^-{}_{aq} + C^{\beta+}A^-{}_{org} \leftrightarrows C^{\beta+}{}_{aq} + A^-{}_{aq} + C^{\alpha+}A^-{}_{org} \quad (88)$$

is sometimes invoked in this connection, where the seemingly redundant $A^-{}_{aq}$ on both sides serves to show that the equilibrium conditions require electroneutrality in the aqueous phase. It was found expedient[221,223] in such cases to discuss the transfer of individual (cat)ions and to describe the systems and predict the position of the equilibrium in terms of the standard molar Gibbs energies of transfer of individual ions, $\Delta_t G°(C^+,W{\rightarrow}S)$, or the distribution electrochemical potential $\Delta\varphi° = \Delta_t G°/F$, where F is the Faraday constant.

Consider a single electrolyte CA present in the aqueous phase that distributes according to eq 85 with an equilibrium quotient (constant, if activity coefficients remain constant) $K_{exIP} = c_{C_{org}}/c_{C^+{}_{aq}}c_{A^-{}_{aq}}$. Then, since the concentration c remaining in the aqueous phase is $c = c_{C^+{}_{aq}} = c_{A^-{}_{aq}}$, the limiting distribution ratio D_C depends on c as follows:

$$\lim(c{\rightarrow}0)\, D_C = c_{C_{org}}/c_{C_{aq}} = K_{exIP}c \quad (89)$$

This would be the case with organic solvents of low polarity and relative permittivity. But if appreciable dissociation of the ion pair in the organic phase can occur (eq 86 with an equilibrium constant K_{exdi} (for dissociated ions)), then there should be no dependence of $\lim(c{\rightarrow}0)\, D_C$ on the concentration c. Therefore, plots of log D_C against log c would have slopes of +1 and 0, respectively, in these limiting cases. These slopes can serve as diagnostic tools for the extent of ion pairing in the organic phase, assuming that activity coefficients remain essentially constant. This is attainable in the aqueous phase by adding a nonextracted swamping electrolyte at sufficiently high and constant concentration.

There are two further aspects to the extraction of ions as ion pairs from aqueous solutions that should be considered. One is the total extractability, i.e., the magnitude of the distribution ratio D, and the other is the selectivity, i.e., the ratio D_β/D_α for the exchange (eq 88) or similarly for the exchange of anions. As the basicity (electron donor ability) of the solvent increases, measured for example by the Kamlet–Taft β parameter (cf. the discussion around eq 84 above), the magnitudes of the distribution ratios of salts with a given anion increase.[221] Conversely, as the hydrogen bond donating (electron acceptor) ability of the solvent increases, measured by the Kamlet–Taft α parameter, the distribution ratios of salts with a given cation increase.[222] However, the selectivity is not much affected by such uniformly increased D values. On the contrary, selectivity is largest when, say, $D_\beta \gg 1$ and $D_\alpha \ll 1$, a condition that depends more on the sizes of the ions than on the properties of the solvents.

Moyer and Sun[221] explored this point with respect to the selectivity for cesium over sodium in ion pair extraction. They concluded on the basis of $\Delta_t G°(C^+,W{\rightarrow}S)$ data that, without consideration of the anion, selectivity would be largest in solvents with low Kamlet–Taft β values or solvents that are soft. Among water immiscible solvents, dichloromethane, 1,2-dichloroethane, and nitrobenzene should have such preferences for cesium. If the relative permittivity is relatively high (water-saturated nitrobenzene, $\epsilon_r = 34.8$ at 298.15 K), eq 86 would be operative and the anion would have no effect, as found experimentally. However, if ϵ_r is low (1,2-dichloroethane, $\epsilon_r = 10.4$ at 298.15 K), eq 85 shows that the anion has a considerable effect. A bulky, hydrophobic anion will lead to high distribution ratios but not necessarily to large selectivity. Nitrophenolates (e.g., picrate or dipicrylaminate), tetraphenylborates (e.g., with fluoro- or trifluoromethyl groups on the aromatic rings), and dicarbollides have been suggested for attaining large selectivity for the extraction of Cs^+.[221,223] The larger the distance of the cation from the negative charge center of the anion, the better would be the selectivity for the larger cesium cation in ion pair extraction.

Mutatis mutandis, similar considerations apply to the selective extraction of anions, although ion pair extraction has been less intensively studied for them[222] than for cations. The primary solvent factor that provides a large driving force for the extraction of anions with a given cation is the solvent hydrogen bond donation ability, measured by the Kamlet–Taft α parameter, favoring the extraction of the smaller anions. Other considerations have already been discussed in section 6.3.1. An instance of selective and efficient extraction separation of fluoride anions from other halides is the extraction of the potassium salts with dibenzo-18-crown-6 into *m*-cresol shown by Marcus and Asher.[224] The selectivity in this case derives from the better extractability rather than the ion pairing, since this is least for the K^+-crown complex with F^- in the strongly solvating *m*-cresol relative to the other halides.

6.4. Hydration vs Ion Pairing in Molten Salt Hydrates

Molten salt hydrates are a special case of very concentrated aqueous solutions. The hydration numbers of crystalline salt hydrates are typically 2−9, they dissociate (in dilute solutions) to 2−4 ions, and the mean ratio of water molecules per ion in the melts ranges from 1:1 to 9:2. The molalities of the melts range from 6 to 27 mol kg^{-1}. The mean distance apart of the centers of ions, d/nm, in a c M solution of a symmetrical electrolyte is

$$d = [10^{-3}\ (\mathrm{m^3/dm^{-3}}) \times 10^{27}\ (\mathrm{nm^3/m^3})/2 \times c\ (\mathrm{mol/dm^{-3}}) \times N_A\ (\mathrm{mol^{-1}})]^{1/3} \quad (90)$$

In a 1 M solution, $d = 0.94$ nm, permitting water molecules (diameter 0.28 nm) to be located between the hydration shells of some hydrated ions. In a 3 M solution, the mean distance is $d = 0.65$ nm only, and in a 10 M solution, $d = 0.44$ nm only. It is, therefore, to be expected from geometrical considerations that the near surroundings of a given ion in the melt must include both water molecules and at least one counterion associated with it as an ion pair. Solutions containing such high concentrations of ions are encountered in nature as well as in industrial processes and laboratory practice.

Consider, for example, the Dead Sea shared by Israel and Jordan, consisting essentially of an aqueous solution of magnesium, calcium, sodium, and potassium chlorides.[225] The sum of the concentrations of the ions is 8.8 M (replacing $2c$ in the denominator of eq 90, since some of the salts are asymmetric), and their mean distance apart is $d = 0.57$ nm. On the basis of the primary and secondary hydration numbers, this brine contains some 28% “free” water. The hydrated alkali metal cations are separated from the chloride anions by “free” water, but the hydration shells of the divalent alkaline earth cations already overlap that of the chloride anion. In an industrial process involving the Dead Sea, an “end brine” is produced that contains 15 M ions (total) with $d = 0.48$ nm and has a deficit of −31% of “free” water. In this brine, the hydrated alkali metal cations are in contact with (partly dehydrated) chloride anions, but the latter penetrate the secondary hydration shell of the magnesium ions and even the primary hydration shell of the calcium ions. SIPs and, on average, some CIPs are, therefore, present in these brines merely due to geometrical causes, before any consideration of electrostatic attraction.[225]

A different way to look at molten salt hydrates is to consider them as being represented by a quasi-lattice consisting of two interleaving sublattices, one occupied by cations and the other by anions and water molecules. Systems that have been studied[226] consist of a solvent salt B^+D^-, where $B^+ = NH_4^+$, (Li^+,K^+) at the eutectic composition, or $^1/_2Ca^{2+}$ and $D^- = NO_3^-$; water, denoted by W; and a solute salt C^+A^-, where $C^+ = Ag^+$, $^1/_2Zn^{2+}$, $^1/_2Cd^{2+}$, $^1/_2Hg^{2+}$, or $^1/_2Pb^{2+}$ and $A^- = Cl^-$ or Br^-. The quasi-lattice is characterized by a coordination number Z and the ratios of solute salt and water per solvent salt B^+D^- are denoted by R_A and R_W. The Z lattice sites around a cation A^+ are occupied by D^-, W, or C^-, but at small solute concentrations and R_W values, only one C^- and W will be present there. The following exchange equilibria occur in these systems:

$$C^+D^- + B^+A^- \leftrightarrows C^+A^- + B^+D^- \quad (91)$$

with an energy change of e_E per reaction unit and

$$C^+D^- + B^+W \leftrightarrows C^+W + B^+D^- \quad (92)$$

with an energy change of e_H per reaction unit These exchange energies were considered to be independent of the other occupants of the sites near the ions involved. These systems were studied potentiometrically with an electrode reversible to A^- to yield the potential difference ΔE in the presence and absence of C^+. The association constant is thus obtained:

$$K_{CA} = \lim(R_C \rightarrow 0)[(F/RT)(\partial \Delta E/\partial R_C)_{R_W}] = Z \exp(-e_E/k_BT)/[1 + R_W \exp(-e_H/k_BT)] \quad (93)$$

The values of the energies e_E and e_H were derived from the dependence of K_{CA} on R_W. The competition of the two cations for water in the melt is expressed by e_H. The results[16] show, for instance, that Cd^{2+} is preferred by the water over K^+, Li^+, and NH_4^+ but that Ca^{2+} is preferred over Cd^{2+} as long as R_W is low (not in molten $Ca(NO_3)_2 \cdot 4H_2O$). Water is preferred by Zn^{2+} and Hg^{2+} over NH_4^+, but the latter is preferred over Pb^{2+}.

Other techniques have also been applied to the study of ion association in molten salt hydrates, including X-ray diffraction,[225] Raman spectroscopy,[227] and NMR;[228] the references given are to illustrative early reports. In 5 mol kg^{-1} aqueous solutions, where the mean distance is $d = 0.55$ nm, X-ray diffraction did not detect any ion−ion contacts in LiCl and NaCl solutions, but such contacts were found in CsCl solutions. The “irregular cation hydration” noted in $MgCl_2$ and $CaCl_2$ solutions and a hydration number of the chloride ions lower than 6 were interpreted as indicative of some ion pairing.[225] In melts of $Mg(NO_3)_2 + (R_W)H_2O$, Raman spectroscopy showed that if $R_W \geq 6$, the primary hydration shell of the Mg^{2+} remains intact but 2SIPs and SIPs were formed as R_W was reduced below this limiting value. When R_W was < 6, the nitrate anion penetrated the hydration shell of the Mg^{2+}, and at $R_W = 2.5$, a specific rearrangement of the quasi-lattice of the melt took place, there being then two distinguishable nitrate anions (presumably coordinated by one and two oxygen atoms).[227] NMR chemical shift data in equimolar melts of $Ca(NO_3)_2 \cdot 4H_2O$ with other nitrates (at 369 K) show that the Ca^{2+} ion took up 90% of the available water when the other salt was KNO_3 but only 83% when it was Me_4NNO_3. When, at the same water content, a fifth of the Ca^{2+} ions were replaced by Mg^{2+} ions, the former took up only 68% of the available water whereas the latter took up the rest.[228]

7. Ion Pairing in Polyelectrolytes

Polyelectrolytes are common in nature (proteins, DNA) as well as in chemical practice (ion-exchange resins, polyphosphate detergents) and have interesting properties that have been described in many books and reviews. It is inexpedient to repeat here much of this information, even not that part that pertains to ion pairing of mobile counterions with fixed ionic groups of the polyelectrolyte. Only a few of the earlier and seminal studies of the latter phenomena can be highlighted here, in addition to some recent publications that address the main issues.

A typical polyelectrolyte has a polymeric backbone to which are attached at intervals ionogenic groups. These may be completely ionized and, hence, consist of a so-called fixed ion covalently attached to the backbone and a mobile counterion that is free to diffuse in the solution that surrounds the polyelectrolyte, although it may bind electrostatically to the fixed ion (or cooperatively to several fixed ions). When extensively ionized, the polyelectrolyte is in its fully extended form, due to the mutual electrostatic repulsion of the fixed ionic charges. It can then be modeled as an infinitely long rod with charges at its surface at a uniform charge density, e.g., according to Fuoss, Kachalsky, and Lifson.[229] Another kind of polyelectrolyte has weakly acidic or basic fixed groups attached to the backbone that are not ionized unless neutralized with a base or protonated, respectively. If ionized, the counterions behave as for the kind of polyelectrolytes described above. If the degree of ionization is low, the polyelectrolyte will take up a more coiled conformation that maximizes the entropy. The polymeric backbone may be long or relatively short (e.g., in polyphosphates) and may be cross-linked to form a gel. The surrounding solution may contain in addition to the counterions one or more other electrolytes but need not do so. Until recently, the discussion of polyelectrolytes and, in particular, their association with counterions was limited to aqueous solutions, but more recently, experimental information and theoretical treatments of polyelectrolytes in nonaqueous or mixed solvents have become available.

Three types of polyelectrolyte solutions are briefly discussed here: a linear, weakly acidic polyelectyrolyte, such as (partly) neutralized polyacrylic acid; a linear, strongly acidic polyelectyrolyte, such as polystyrenesulfonic acid; and a polyelectrolyte gel, such as the cross-linked polymethacrylic acid ion exchanger. Two distinct phases exist in the latter type of gel polyelectrolyte in equilibrium: the gel phase and the outer solution. The treatments of polybases, e.g., (partly) protonated polyvinylpyridine as an example of a linear, weak electrolyte, and the cross-linked polystryrene benzyl trimethylammonium salt strongly basic anion exchanger are completely analogous to the examples discussed here and need not be treated separately. A distinct class of polyelectyrolytes (polyampholytes), however, involves polypeptides and proteins that have both basic and acidic functions, such as arginine and glutamic acid moieties, on the same polymer chain. These, however, will not be discussed here at all.

Consider an aqueous solution of polyacrylic acid that is being titrated with an aqueous sodium hydroxide solution in the absence of added soluble salt. As the titration proceeds, the degree of ionization of the polyelectrolyte, α, increases up to the equivalent point. Since such a polyelectyrolyte tends to be polydisperse, i.e., has polymer chains of different lengths, it is convenient to specify its concentration c in terms of the total number of monomeric titratable groups per unit volume. Three types of “sites” on the polymer chain can be discerned, the relative abundance of which depends on the degree of ionization α and the concentration c of the polyacrylic acid that is being titrated. These sites are not-yet-neutralized protonated carboxylic groups, ionized carboxylate groups, and carboxylate groups ion paired with the sodium counterions. When the titration is carried out in the presence of excess salt, say sodium chloride, it is assumed that the chloride anions remain completely mobile but that the association of the sodium cations with the polyelectrolyte is enhanced due to the common ion effect. The main point to note is that, even in very dilute solutions of the polyelectrolyte, the environment of a given sodium cation at an appreciable value of α consists of many anions with which it can associate. The ionic atmosphere does not become infinitely dilute with decreasing concentrations of the polyelectrolyte, $c \rightarrow 0$.

The operative expression for description of the course of the titration is

$$\mathrm{pH} + \log a_{\mathrm{Na^+}} + \log[(1 - \alpha)/\alpha] - \log f = \mathrm{p}K_a - \mathrm{p}K_s \qquad (94)$$

where f is the degree of binding of the sodium counterion, K_a is the intrinsic dissociation constant for the acid, and K_s is that of the ion pair (the reciprocal of its association constant). This treatment by Harris and Rice[230] assumed random distribution of the three types of sites along the polyelectrolyte chain, but restrictions could be introduced, such as requiring an ionized site adjacent to the one where ion pairing took place. The mutual interaction of neighboring ionized sites was taken into account by Lifson,[231] but the final result was the same as eq 94, i.e., as for the case where no such interaction was considered.

However, if the electrostatic potential of the polyelectrolyte is high, the interactions with counterions need not follow the mass action law. The electrostatic potential around the polyelectrolyte chain was calculated according to several models. Gregor and Gregor[232] proposed a model involving a rod of infinite length of radius a and along which the fixed charges are located at random intervals, and a solution region extending up to a distance R from the center of the rod in which counterions are affected by the potential. Counterions of different sizes, with radius r_s of the smaller one and r_l of the larger one, can approach the rod to different distances. A selectivity constant (ratio of binding constants) arises from this difference in the distance of closest approach. The quantity $\lambda = -e(1/b)/4\pi\epsilon_0\epsilon_r k_B T$ is defined, where $1/b$ is the average charge per unit length of the rod (note the change from the symbol Q used in ref 232 that is used below in another sense). Another quantity, α, is implicitly defined by $2(\alpha^2 + 1)R^{-2}(4\pi\epsilon_0\epsilon_r k_B T/e^2) = c_l + c_s$, where the subscripts l and s denote the larger and the smaller counterion. Then the selectivity coefficient between the two kinds of ions is

$$K^{l}_{s} = [\lambda(c_l + c_s)/c_s]/ \\ [1 + \alpha \cot \alpha \ln\{(a + r_l)/R\} - \tan^{-1}\alpha] - (c_l/c_s) \qquad (95)$$

This expression was tested by Gregor and Greff[233] with a completely ionized polymethacrylate gel cross-linked to various extents, 0.2−24 mol %, by ethyleneglycol dimethacrylate (EGDM). They studied the exchange of the small cation K^+ (assigned $r_s = 0.175$ nm) and the large cation Me_4N^+ (assigned $r_l = 0.347$ nm) or Et_4N^+ (assigned $r_l = 0.400$ nm), on this rodlike polyelectrolyte, which was taken to have a radius $a = 0.21$ nm and a charge density of $1/b = 3.23$ unit charges per nm. The experimental selectivity coefficient, $K^{l}_{s,\mathrm{expt}}$, has a contribution from the osmotic pressure and the difference in the partial molar volumes of the ions: $\exp[\pi(V_l - V_s)/RT]$, a factor multiplying the electrostatic contribution expressed by eq 95. The values of π and R are obtained from the swelling of the polyelectrolyte gels in water. The testing of eq 95 against the experimental selectivity could not, however, be carried out completely, since an important variable—the permittivity of the water in the annular region around the polyelectrolyte defined by R—could not be estimated independently. Taking eq 95 as valid, Gregor and Greff[233] obtained a value of the permittivity in the vicinity of the polyelectrolyte rod of $\epsilon = 30 \pm 3$ from the K^+/Me_4N^+ exchange for cross-linking with 4−24 mol % EGDM. However, when the data for the K^+/Et_4N^+ exchange were employed instead, the lower value $\epsilon = 15 \pm 5$ was obtained, for no apparent reason.

The problem of the estimation of the solvent permittivity near the polyelectrolyte was taken up subsequently in a number of ways, and a definite procedure was established by Lamm and Pack.[234] They calculated by finite difference Poisson−Boltzmann techniques the permittivity of water at various distances from a charged cylinder considering the effects of the surface boundary, of the presence of the fixed ions, and of the counterions and, eventually, of added electrolyte, all leading in some manner to dielectric saturation. They presented results for a cylinder of 1.0 nm radius and a charge density corresponding to B-DNA, showing the surface effect to be minor but with both the fixed and the counterions causing a large decrease of the permittivity near the charged cylinder. The total relative permittivity rose from ∼5 at the surface of the cylinder to ∼28 at a distance of 0.5 nm, to ∼45 at 1.0 nm, and to ∼58 at 2.0 nm, when there was 50 mM added salt present. In the absence of added salt, the values at 0.5 nm (∼38) and at 1.0 nm (∼54) were appreciably larger. Obviously, a low permittivity of the solvent near the polyelectrolyte is conducive to electrostatic binding of counterions to fixed ions.

The sulfonation of polystyrene to form a polyelectrolyte has the advantage that the density of fully ionized groups along the chains can be varied at will according to the degree of sulfonation, from having a sulfonic group on every phenyl ring to having only a few groups along the chain. Even with fully sulfonated polystyrene, the variability of the relative molar mass M of various preparations can be utilized. The osmotic pressures π of aqueous solutions of the acid and the sodium salt of sulfonated polystyrene of $M = 2 \times 10^4$ to 1.06×10^6 were related by Wang and Bloomfield[235] to their monomolarities c according to $\pi = RT\varphi c$, where φ is the osmotic coefficient related to the charge density parameter ξ:

$$\varphi = {}^1/_2\xi = {}^1/_2(Q/b) \tag{96}$$

where Q is twice the Bjerrum length (for univalent ions), i.e., $Q = e^2/4\pi\epsilon_0\epsilon_r k_B T$, and b is the linear charge spacing along the polyelectrolyte chain. Agreement was found with the value $\xi = 4.0$, corresponding with $b = 0.25$ nm to $Q = 1.0$ nm or $\epsilon = 56$ in the surroundings of the polystyrenesulfonate rods. The expression (eq 96) for the osmotic coefficient was previously derived by Lifson and Kachalsky[236] and by Manning[237] but was shown by Manning to pertain only to the case that $\xi > 1$. For added-salt-free polyelectrolyte solutions with $\xi < 1$, the limiting value of the osmotic coefficient is $\varphi = 1 - {}^1/_2\xi$. Only when the average distance b between the fixed charges on the polyelectrolyte is smaller than Q (i.e., when $\xi > 1$) would the electrical potential cause the (univalent) counterions to bind to (“condense on”[237]) the fixed ions, thereby reducing the effective value of ξ to the critical value of unity.

One of the quantities expressing the properties of polyelectrolyte solutions is the Donnan salt exclusion parameter Γ, describing the bias against the presence of mobile ions in the vicinity of the polyelectrolyte in the presence of a salt in the bulk of the solution (manifested in an experimentally directly measurable manner in the case of the two-phase system of a cross-linked ion exchange gel and an outer solution). If the concentration of the salt in the external solution is c_S' and that in the vicinity of the polyelectrolyte is c_S, then the limiting value of Γ for a concentration c_p of the polyelectrolyte tending to zero is formally defined by

$$\Gamma = \lim(c_p \rightarrow 0)\ (c_S' - c_S)/c_p \tag{97}$$

Manning[237] showed that $\Gamma = {}^1/_2(1 - {}^1/_2\xi)$ when $\xi < 1$ whereas if $\xi > 1$, then $\Gamma = {}^1/_4\xi$. He compared these expectations with experimental data available at that time for sodium polyvinyl sulfate and polyacrylate (of various degrees of neutralization α) and potassium polyphosphate and DNA, having ξ ranging from 0.29 to 4.20, with good results. Also, the expectations for the osmotic coefficients of the sodium polyacrylate and polymethacrylate were well vindicated.

The discussion hitherto concerned the association of univalent counterions with the fixed ions of the polyelectrolyte. The association of multivalent ions introduces complications that have been the subject of many studies. When the charge density along the polyelectrolyte chain is low, a multivalent counterion associates with a single (univalent) fixed ion, reversing the charge of this site. When the charge density is high, multivalent counterions can associate with several adjacent fixed ions, neutralizing the charge. Furthermore, when the concentration of the polyelectrolyte c is large, the multivalent counterions can act as cross-linking agents between adjacent chains.

It was recently shown by Porasso et al.[238] that not only electrostatic association of multivalent counterions with the fixed charges takes place but also coordinative bonding is possible, as for Cd^{2+} with polyacrylic acid that is being titrated with KOH. In this case, both “territorial” condensation of the divalent cation and specific binding occur, whereas in the presence of Ca^{2+} only the former kind does. A similar view of allowing for both condensation and specific binding was taken by Sabbagh and Delsanti[239] in their study of the precipitation and eventual resolubilization of polyelectrolytes in the presence of multivalent ions. They pointed out that the binding of a z-valent cation to a (monovalent) anionic site causes charge reversal to a $z - 1$ valent cationic site that then interacts electrostatically with a neighboring (negatively charged) fixed ion, leading eventually to precipitation, if the electrostatic repulsion between sites of the same charge becomes too small to keep the polyelectrolyte extended. Furthermore, when multivalent ions act as cross-linking agents between adjacent polyelectrolyte chains, this causes phase separation at sufficiently high concentrations. When the added z-valent ion concentration is increased beyond a certain threshold, however, the screening of the electrostatic attractions permits the polyelectrolyte to be soluble again. Barium ions were able to precipitate all kinds of anionic polyelectrolytes, whether carrying carboxylate, sulfonate, or sulfate fixed ions, whereas other divalent metal ions precipitated only the carboxylate-carrying polyelectrolyes.

A molecular dynamics study by Winkler, Gold, and Reineker[240] demonstrated the collapse of the extended rodlike polyelectrolyte structure in the absence of added salt to a coil-like conformation when the interaction energy of the fixed ions and counterions is increased beyond a certain threshold. For these simulations, polyelectrolytes of finite length (rather than the infinitely long rods in the models considered above) were used, and the measure for the collapse of the chain was the end-to-end extension or the radius of gyration. It is the multivalent ions that provide the sufficiently large interaction energy for a given length of polyelectrolyte and distance between the fixed charges.

Most of the discussion hitherto dealt with polyelectrolytes in aqueous solutions, although some of the authors mentioned considered also solvents of lower permittivity designated as "poor", in contrast to water taken to be a "good" solvent. Among these authors, Manning[237] was one of the earlier. A lowered permittivity of the solvent has a similar effect as the presence of multivalent counterions, in that it promotes counterion association with the fixed ions, reducing the effective charge on the polyelectrolyte chain, leading to its collapse ultimately, although with univalent counterions the additional effect of cross-linking between adjacent chains is absent. The effects of lowering the permittivity of the solvent were studied by Liu, Hu, and Tong[241] for a highly ionized linear sulfonic acid copolymer in tetrahydrofuran (THF) + dimethyl sulfoxide (DMSO) solutions by means of viscosity measurements. As the THF content increased, the reduced viscosity, $(\eta - \eta_0)/\eta_0 c$, decreased with increasing polyelectyrolyte concentration. This was explained by the decrease of the extension of the polyelectrolyte chains that can entangle with one another to more globular and mobile conformations. This change, in turn, is caused by increased counterion association, which is assumed to lead to attractive dipole−dipole interactions of adjacent dipolar fixed ion counterion pairs. Eventually, at sufficiently high THF content, precipitation occurs.[242]

8. Discussion

8.1. Weak Association vs Activity Coefficients

It is mentioned in several places in this review that, in the case of weak association to ion pairs, great care must be exercised in order to disentangle the specific effects of association between two oppositely charged ions from the general electrostatic effects on a specific ion by its ionic atmosphere. A major problem, therefore, is the appreciable correlation that exists between the association constant $K_A°$ and the activity coefficients of the dissociated ions. This occurs whether $K_A°$ is determined experimentally or is calculated theoretically; hence, the derived fraction of the electrolyte associated, $1 - \alpha$, also depends on the activity coefficients $y_{\pm}'$. This dependence and correlation is through both the distance of closest approach, a, and the cutoff distance, R, beyond which the ions are considered to be free.

As a rule of thumb, it may be stated that if the association constant $K_A° > 10$ M^{-1}, the care to be taken refers to obtaining the exact magnitude of this constant by either experiment or theory. In such cases, there would be >1% ion pairing at 1 mM and >8% ion pairing at 10 mM salt, which can be determined fairly accurately, while the activity coefficients of the free ions can be assumed to be not far from unity. Pethybridge and co-workers[80,81] and Duer et al.,[79] among others, commented on the need, when applying conductivity data to the problem of ion association, to employ consistent values of the ion size parameter that appears in the expressions for the J coefficients of the conductivity expression and in the expression for the mean ionic activity coefficients. As written, eq 39 involves the distances R_1 and R_2, which may be set equal to each other but are in effect fitting parameters that ought to be the same as R in eq 10 for the activity coefficient. The general conclusion from such studies[79−81] is that the values of K_A and R are closely correlated. Analysis[81] of very precise low concentration conductivity data led to the common value $R = 1.07$ nm for aqueous divalent metal sulfates, in fair agreement with the value $r_+ + r_- + 2d_W$ obtained from the lcCM (section 2.5) and calorimetric heat of dilution results.[71] Still, the resulting values of K_A (all >100) differ by as much as 10% when different but still reasonable values of the ion size parameter are used.

However, if $K_A° < 2$ M^{-1}, the mere existence of the ion pair may be questioned. It is expedient for this purpose to calculate, first of all, the parameter $b = q/a$ (cf. eqs 3 and 4), from eq 12, i.e., from the charges on the ion partners, the permittivity of the solvent, and, most importantly, the distance of closest approach, a. If the resulting $b < 2$, no discernible ion pairing probably takes place. For a value of $a = 0.4$ nm and univalent ions, the upper limit of the relative permittivity to allow ion pairing with $K_A° \geq 2$ M^{-1} is $\epsilon_r \sim 33$ at 298.15 K. However, this value of the permittivity depends strongly on the choice of the distance parameter, a. The correlation of the value of $K_A°$ derived from conductivity data with the selected value of a is demonstrated clearly by Duer and co-workers[79] for HCl and KPF$_6$, where association does not exist or is very weak in dilute solutions, those for which the conductivity expressions are valid.

Still, association constants as low as 0.29 M^{-1} for aqueous $Me_4N^+Cl^-$ or 0.83 M^{-1} for $Me_4N^+Br^-$ are reported,[243] as obtained by chemical trapping or ^{79}Br NMR line width methods. For $Me_4N^+Br^-$, the association constant was said to be in agreement with results obtained by dielectric relaxation spectroscopy (section 3.5.1), 3.0 ± 0.4 M^{-1}, and by conductivity, 1.24 M^{-1} (ref 244 and references therein). No information is given in these and similar studies on the values of a and R, but a value of a is implicit in the activity coefficient expression employed. From the $Ba = 1$ used,[244] $a = 0.30$ nm results (see eq 99 and discussion below), which is a very small value of the distance of closest approach for the ions of these salts.

This choice of a is not as simple as it would appear if the specification $a = r_+ + r_-$ were made, where the r are the crystal ionic radii. According to the extended Debye−Hückel expression generally employed for completely dissociated electrolytes, the activity coefficient on the molal scale is

$$\log \gamma_{\pm} = -A_m|z_+z_-|I_m^{1/2}/(1 + BaI_m^{1/2}) \qquad (98)$$

and on the molar scale it is

$$\log y_{\pm} = -A_c|z_+z_-|I_c^{1/2}/(1 + BaI_c^{1/2}) \qquad (99)$$

For these expressions, values of $a < r_+ + r_-$ were sometimes specified, albeit in cases where ion pairing was suspected. Examples in the older literature are for aqueous RbI and TlOH (ref 2, pp 246 and 410), for aqueous PbCl$_2$ and CdCl$_2$ (ref 10, p 555), or for Bu$_4$NI (ref 10, p 277) or Pe$_4$NI in benzene (ref 10, p 307). Furthermore, in more recent publications, there is a tendency to fix the product Ba in the denominator of the extended Debye−Hückel expression at 298.15 K at 1.0,[245] 1.2,[87,246] or 1.5.[247,248] These constant parameters yield, with the theoretical value $B = 29.1\epsilon_r^{-1/2}$ nm^{-1}, values of a that range from 0.46 to 0.19 nm for $30 \le \epsilon_r \le 80$. The lower values are definitely below acceptable $r_+ + r_-$ values. Therefore, eq 10 with a specified value of R has to be used instead of eq 99 for the activity coefficients of the free ions.

The situation is confounded by the fact that activity (and osmotic) coefficients could be modeled very precisely by Pitzer and co-workers over wide concentration and temperature ranges without invoking ion association at all![87,246] For a symmetrical electrolyte, the Pitzer expression is

$$\ln \gamma_\pm = |z_+z_-|f + Bm + Cm^2 \tag{100}$$

where the electrostatic term is

$$f = -A[I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})] \tag{101}$$

with an empirically selected universal coefficient of $b = 1.2$, and

$$B = 2\beta^{(0)} + (2\beta^{(1)}/\alpha_1{}^2I)[1 - \exp(-\alpha_1 I^{1/2})(1 + \alpha_1 I^{1/2} - {}^1/_2\alpha_1{}^2 I)] \tag{102}$$

with an empirically selected universal coefficient of $\alpha_1 = 2$. Then C, as well as $\beta^{(0)}$ and $\beta^{(1)}$ are fitting parameters for each electrolyte (and are temperature dependent). The magnitude of $\beta^{(1)}$ was said to be due mainly to short-range interactions of unlike charged ions; hence, it took the place of explicit recognition of ion pair formation.

For unsymmetrical electrolytes, a factor in the stoichiometric coefficients must be applied to the various terms in eqs 100−102. The expressions were employed for modeling the activity coefficients of 1:1 and 1:2 electrolytes and with the required modification also for modeling their osmotic coefficients, over wide concentration ranges.[246] It must be mentioned that these expressions had been primarily developed for aqueous electrolytes at ambient conditions, but their utility, usually with the addition of further adjustable parameters, was subsequently established also for aqueous solutions at high temperatures of lower permittivity, where ion pair formation of strong electrolytes could be appreciable. In the case of aqueous sodium chloride, nevertheless, ion pairing needed not to be invoked even at 300 °C, where $\epsilon_r = 20$.[249]

However, consideration of ion pair formation was not avoided altogether by Pitzer and co-workers in aqueous solutions at ambient conditions. They showed that the activity and osmotic coefficients of 2:2 salts[250] *could* be modeled by the addition of an additional term to the second virial coefficient B of eq 100 that involved two new fitting parameters: $\beta^{(2)}$ and α_2. The latter could be set at $32A$ (A is the Debye−Hückel coefficient in eq 101), and $\beta^{(2)}$ would equal $-0.5K_A°$ if association took place. The argument for considering the electrolytes to be completely dissociated for the purpose of the modeling was based on the consideration by Davies[12] that as the concentration increases ion pairing reaches a maximum and then decreases, as derived from

$$K_{A(m)} = [(1 - \alpha)/\alpha^2][\gamma_{IP}/m\gamma_\pm{}^2] \tag{103}$$

(with the notation used throughout this review; Pitzer and Mayorga[250] used α for the fraction associated). It was then argued that the *nominal* mean ionic activity coefficients of such electrolytes, $\gamma_\pm$, decreased more rapidly than the fraction associated, $1 - \alpha$, increased with increasing molalities m. This led to the conclusion that association did not have to be invoked for 2:2 electrolytes[250] and even for, say, a 3:2 electrolyte such as lanthanum sulfate, for modeling the activity and osmotic coefficients.[251] However, proper dealing with the association requires the *ionic* activity coefficients, $\gamma_\pm'$, eqs 2 and 10, not the nominal (stoichiometric) ones, so eq 103 as written is not correct, noting eq 42. See also ref 88, where the correct form—$K_{A(m)} = (1 - \alpha)\, m\gamma_\pm{}^2$ (setting $\gamma_{IP} = 1$)—is obtained on inversion of the dissociation constant reported there. Furthermore, the ionic strength must be adjusted for the diminished concentration of the ions. The assumed maximum in the formation of ion pairs resulting from eq 103[12,250,251] is therefore an artifact. Thus, the ability to model the activity and osmotic coefficients of electrolytes by Pitzer's expressions does not constitute in itself a denial of the formation of ion pairs under appropriate conditions.

Barthel and co-workers,[90] among others,[252] have applied Pitzer's equations for modeling the activity and osmotic coefficients of salts in nonaqueous solvents. They showed[90] that although the equations could be applied in nonaqueous solvents (e.g., the lower alcohols, acetone, acetonitrile), where terms in $\beta^{(2)}$ and α_2 had to be invoked, equally good modeling could be achieved, with fewer adjustable parameters, by the lcCM (section 2.5) that invoked ion pairing specifically. The concentration range over which the lcCM is applicable is widened when the activity coefficient of the (uncharged) ion pair is taken into account with a salting-out (or -in) type expression, $\ln \gamma_{IP} = B\alpha m$ on the molal scale; see also section 2.7.

8.2. Unsymmetrical Electrolytes

Early conductivity data, analyzed according to Onsager's limiting law equations,[23] produced association constants for a number of 2:1 and 1:2 electrolytes. For example, Righellato and Davies[253] reported standard dissociation constants for the following ion pairs, for which their reciprocals, $K_A°$/M^{-1}, are as follows: $CaNO_3^+$, 1.92; $SrNO_3^+$, 6.67; $BaNO_3^+$, 8.26; $LiSO_4^-$, 4.37; $NaSO_4^-$, 5.05; and KSO_4^-, 6.62. These data are mainly of historical interest, since the conductivity expressions on which they are based have been superseded.

The problem with conductivity data of unsymmetrical electrolytes is the presence of more than two ionic, conducting, species in the solution, say, M^{2+}, MX^+, and X^- for 1:2 salts. Quint and Viallard[74] published conductivity expressions, based on modern concepts of the relaxation and electrophoretic terms that take into account the presence of several conducting species but ignore ion association. On the basis of these expressions, Lee and Wheaton[254] published a treatment that included ion pairing. They applied their treatment to MCl_2 (M = Mg, Ca, Sr, and Ba) in methanol at 10 and 25 °C. The full expression involved six parameters—$\Lambda°(M^{2+})$, $\Lambda°(MCl^+)$, $\Lambda°(Cl^-)$, $K_{A1}°$ (for formation of MCl^+), $K_{A2}°$ (for formation of MCl_2), and a of the extended Debye−Hückel activity coefficient expression, eq 99—as well as those in the conductivity expression. The treatment ignored higher terms in the ionic strength, I^2 and $I^{5/2}$, but included terms up to $I^{3/2}$ in the range of validity of the expressions (up to $\kappa a = 0.2$). It turned out to be impossible to derive the six fitting parameters from the data, but the value of $\Lambda°(Cl^-)$ could be obtained from independent data on 1:1 salts and it was reasonably assumed that $K_{A2}° = 0$ for the very dilute solutions studied ($<8 \times 10^{-4}$ M). Hence, only four parameters had to be fitted from the data, which was done successfully. It turned out (fortuitously?) that $\Lambda°(M^{2+})/2 \approx \Lambda°(MCl^+)$ for the four salts at 25 °C and the a values ranged from 0.60 nm for $MgCl_2$ to 0.46 nm for $BaCl_2$. At 10 °C, however, a correlation between $K_{A1}°$ and a for $CaCl_2$ was noted, widening the relative standard errors to 6 and 15% respectively, compared to, at most, 2% for both parameters for the other salts and temperatures.

The Lee and Wheaton treatment[254] was subsequently employed by others to obtain the association constants of unsymmetrical electrolytes from conductivity data, but mainly in nonaqueous solutions. It appears that in aqueous solutions the concentration limit of applicability of the expressions is too low due to the high permittivity of the solvent. Solutions of $M(ClO_4)_2$ (M = Mn, Co, Ni, Cu, and Zn) in dimethyl sulfoxide[255] and of various salts in other nonaqueous solvents[256] were studied by Pethybridge in this manner. He also reviewed the various treatments proposed for such solutions,[257] while Bianchi and Fernandez-Prini[258] analyzed the levels of approximation involved in the Lee and Wheaton treatment.

Studies of ion pairing in unsymmetrical electrolytes were not confined to the analysis of conductivity data, however. Other approaches need not be complicated by the fact of there being several (>2) conducting species in the solution, although the simultaneous presence of several species in equilibrium is inherent in the problem. For instance, Puchalska and co-workers[259] studied the outer-sphere association (i.e., 2SIPs or SIPs) of nickel salts in DMSO by means of both visible spectrophotometry and conductance. Capewell and co-workers studied the ion pairing to form $NaCO_3^-$ in aqueous solutions by means of potentiometry (section 3.2) with a Na^+-specific electrode in media containing Me_4NCl, the cations of which were assumed not to form ion pairs with carbonate anions. When CsCl was used as the ionic medium, some evidence for very weak association to $CsCO_3^-$ was found.[260] Buchner and co-workers studied the ion pairing in aqueous sodium oxalate[3] and sulfate[60] by means of dielectric relaxation spectroscopy (section 3.5.1). For the oxalate system, the data did not permit an independent decision on which kind of ion pair exists, and only comparison with literature data for the stability constant could permit the conclusion that a 2SIP is the ion pair present up to saturation. In the case of the sulfate system, the data require the presence of an additional species, the SIP, to be fitted properly. These items are only an illustration of the many studies by the various methods discussed in section 3 of ion pairing in solutions of unsymmetrical electrolytes.

9. Conclusions

The formation of ion pairs in electrolyte solutions has by now been studied for 80 years. The general conclusion is that, depending mainly on the magnitude of the charges on the ions and the relative permittivity of the solvent, ion pairs can be treated as real species in the solution. If both cations and anions are univalent, then the relative permittivity of the solvent needs to be about $\epsilon_r < 30$ at ambient conditions for the existence of the ion pair to be unambiguously established. At higher values of ϵ_r, the measurable properties of 1:1 electrolyte solutions (solubility, activity coefficients, conductivity, etc.) may be dealt with without the need to invoke the formation of ion pairs, although strong evidence (from potentiometry, dielectric and ultrasonic relaxation, and vibrational spectroscopy) for their formation often exists even in water. When at least one of the ion partners has a charge larger than 1, ion pairing can be a reality in most solvents. Many methods are able to provide the necessary information concerning the fraction of the electrolyte paired, $1 - \alpha$, and the association constant K_A (section 3).

Ion pairs, when formed in the solution, need not be of the contact type (CIP); in fact, one or two solvent molecules, derived from the solvation shells of the ion partners, may intervene between them (in a SIP or a 2SIP). Few methods can distinguish between these kinds of ion pairs, but ultrasonic and dielectric relaxation can do so (section 3.5), provided certain quantities pertaining to the equilibria between these kinds of pairs can be estimated. Spectroscopic methods (section 3.6) are generally sensitive only to CIPs, so that if their use does not detect ion pairing, it cannot be concluded that ion pairs are not formed; they may be of the 2SIP or SIP kind. Thermodynamic data, such as the enthalpy and entropy changes of ion pair formation (section 4.2) can, however, indicate whether CIPs are formed (e.g., $\Delta_{IP}H°(IP,S) \geq 10$ kJ mol^{-1} is indicative of substantial solvent loss from the solvation shells and CIP formation).

Among theorists in the field, a consensus has been reached by now that the electrostatic attraction between the ion partners of the pair, being the long-range driving force for the pair formation, can be dealt with more or less on the lines proposed 80 years ago by Bjerrum (section 2). Controversies still exist on how to deal with short-range interactions, including those that involve the repulsion of the ions at very short distances and of the solvent molecules in the solvation shells. Several theories (RISM, MSA, lcCM, among others; sections 1.3, 2.5, and 2.6) vie for the attention of researchers.

The main issue from the theoretical standpoint is the accurate calculation of the activity coefficients of the free ions (and the ion pairs, even if neutral) at experimentally realistic concentrations *without the use of empirical parameters*. When using the Debye–Hückel model and its various developments for this calculation in the context of ion pairing, this amounts to properly specifying the distance of closest approach, a, and the cutoff distance, R. Ions of opposite charges being at distances $a \leq r \leq R$ are considered to be paired when residing at such a distance longer than ordinary diffusion times dictate. Without developments in theory in this area, there will be lingering doubts about the reality of ion pairing, at least for low charge electrolytes in high permittivity solvents. On the other hand, as shown throughout this review, the evidence for the existence of ion pairs in many electrolyte solutions is very strong.

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11. References

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