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Ion association in aqueous and non-aqueous solutions probed by diffusion and electrophoretic NMR

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Abstract

The results of diffusion and electrophoretic NMR (eNMR) measurements are reported for a series of tetramethylammonium (TMA) electrolytes (with sulphate, fluoride, acetate, chloride, bromide, nitrate, iodide and perchlorate as anions) in deuterated solvents such as water, dimethylsulphoxide (DMSO), acetonitrile, methanol and ethanol. In addition, similar data are presented for aqueous solutions of tetraalkylammonium salts with increasing alkyl chain length. The combination of diffusion NMR and eNMR yields the effective charge for the TMA cation. Relative to the nominal charge of $z_{nom}=1$ of TMA, the effective charge in the different solvents is found to be progressively smaller in the order water > DMSO > methanol > acetonitrile > ethanol. A part of this observed trend is ascribed to regular ion-ion interactions incorporated in the Onsager limiting law. Indeed, in solvents with high dielectric constants such as water, DMSO and methanol, the Onsager limiting law describes well the observations for all tetraalkylammonium ions. For ethanol and acetonitrile, there is a significant difference between the experimental data and the expected limiting-law behavior that is attributed to ion association (ion pairing) not taken into consideration by the Onsager limiting law.

Keywords: effective charge, ion mobility, ion pairing.

Introduction

The behavior of ions in electrolyte solutions is a topic that has attracted a considerable attention since the beginning of the past century. In particular, a large number of models describing ion transport in solution have been developed, aimed traditionally at explaining data obtained by conductometry, a long-favored tool. Even though initial studies focused more on aqueous solutions[1], a considerable interest for investigating ions and their ion pairing behavior in other solvents/media has also been shown.[2, 3] More recently, new techniques have been developed to study the same problem including spectroscopic methods[4] and molecular dynamics (MD) simulations.[5] Besides corroborating evidence, these new tools are also suitable to investigate new aspects of ion transport that, in turn, contributes to renewed interest for this field.

Ionic mobility in solution depends on several types of interactions.[6] Ion-solvent interactions are usually described by the Stokes model (hydrodynamic model) where the frictional forces in a fluid of known viscosity are interpreted in terms of the hydrodynamic radius R_h of an object that is assumed to include the central ion and those coordinating solvent molecules that are hydrodynamically coupled (that is, sufficiently long relative to the elementary steps of Brownian translation) to that. Crucially, the hydrodynamic radius is not corresponding to the crystallographic radius of the ion. Early attempts to account for this difference[7-9] within the framework of continuous dielectric models (dielectric friction) were shown to be inadequate.[10, 11] In other words, solvation and its molecularly specific details have a very significant effect which, more recently, has also been highlighted by molecular dynamics (MD) simulations.[12]

Another factor influencing ion transport is ion-ion interactions. Debye, Hückel and Onsager described two effects associated with the ionic atmosphere (or, cloud), the relaxation and electrophoretic effects[13, 14], both lowering ion mobilities. In addition to those ion-ion interactions, ion association can also take place, the resulting ion pairs having a reduced charge and an increased hydrodynamic radius relative to either of the non-associated ions. Both effects lead to a slower ion migration and thereby lower conductivity. Ion association can be a particularly important effect in solvents having an intermediate to low dielectric constant but its extent is also dependent on the nature of the ions and solvents.

Traditionally, ion association has been investigated mainly by conductometry, but recently other techniques, most importantly dielectric relaxation spectroscopy,[15, 16] have been used as well. Here, we present diffusion NMR in combination with electrophoretic NMR[17, 18] (eNMR) to provide quantitative estimates of ion pairing in electrolytes with low (~mM) salt concentrations. The method is based on measuring the average effective charge of the ions, in a manner that has already been established for polyelectrolytes and proteins in solution.[19-21] Recently, this combination of experiments provided qualitative data on ion-specific (Hofmeister) effects on ion pairing of salts of tetramethylammonium (TMA) in a 95% (v/v) ethanol-water solution.[22] Here, we expand the scope of that study and provide a more quantitative measure of ion pairing in several solvents including water, dimethyl sulphoxide (DMSO), acetonitrile, methanol and ethanol.

Experimental

TMA salts with anions: sulphate (>98 %, TCI Europe); fluoride (97 %, International Laboratory USA); acetate (>98 % TCI Europe); chloride (≥99 %, Fluka); bromide (≥99 %, Merck); nitrate (98 %, Alfa Aesar); iodide (99 %, Alfa Aesar) and perchlorate (analytical grade, Alfa Aesar) were used as received. Tetraethylammonium bromide (99 %) was purchased from Alfa Aesar, Tetraethylammonium chloride (>98 %), tetrapropylammonium bromide (98 %), tetrapropylammonium chloride (98 %), tetrabutylammonium bromide (≥99 %), tetrabutylammonium chloride (≥97 %), tetrapentylammonium bromide (99 %), tetrapentylammonium chloride (99 %) were from Sigma-Aldrich and were used as received. D_2O was from Isotec Inc. (99.9 % D) and d6-dimethyl sulphoxide (99.9 % D), d3-acetonitrile (99.8 % D), d4-methanol (99.8 % D) and d6-ethanol (99.5 % D) were from Sigma-Aldrich. In all experiments the salt concentration was 2 ± 0.2 mM and the water (H_2O) concentration (that is, except in the case of water as solvent) was set to 120 ± 20 mM. The reason for having this solvent composition was to avoid effects of a water content that was changing during the course of the experiment by water having been adsorbed from the air by dry and hygroscopic solvents like DMSO. Some experiments were performed with dry solvents and salts, see more details in Electronic Supplementary Information ESI. The acetonitrile samples contained 2 % (v/v) hydrogenated acetonitrile, added in order to obtain a stronger eNMR solvent reference signal (see below). Additional experiments with 10 mM TMA salts in D_2O were also performed.

NMR experiments were performed on a Bruker Avance 500 spectrometer with ^{1}H resonance frequency of 500 MHz equipped with a conventional high-resolution probe with *z*-gradient coils (with maximum gradient of 50 G cm^{-1}) at 299.1 K. Diffusion NMR and eNMR experiments using the ^{1}H signal of the TMA moiety were performed using either double-stimulated-echo[23, 24] or single-stimulated-echo[25] (for D_2O) pulse sequences. In the diffusion experiments the diffusion time Δ and the duration of gradient pulses δ were set to 75 ms and 3 ms, respectively and the amplitude of the gradient was stepped up in 24 equal steps. The gradient strength was calibrated using the known value of trace ^{1}H diffusion coefficient in heavy water.[26] Diffusion coefficients were obtained by analyzing the dependence of the NMR signal integral on the amplitude of the gradient pulse. The eNMR experiments were performed as previously described.[27] In particular, the effect of convection driven by thermal gradients and electro-osmotic forces was suppressed by recording the phase difference between the TMA and the solvent ^{1}H NMR signals; the slope of the assumed linear variation of that phase with the electric field stepped up. The electrophoretic drift time Δ_E and the duration of the gradient pulses δ were 200 ms and 1 ms, respectively. The electric voltage providing the electric field along the sample cell was stepped up in 10 equal steps up to a maximum of 400 V while the amplitude of gradient pulses was kept constant at a value between 17 and 31 G cm^{-1}, depending on the solvent. A slight temperature increase due to Joule heating (in the order of 0.1-0.2 K) was noted in the eNMR experiments and the obtained diffusion coefficients were corrected for this effect by exploiting the known temperature dependences of the viscosity of the solvents.[28-32]

Theoretical background: limiting laws

If ion association certainly alters diffusion and electrophoretic mobility, the long-range nature of electrostatic and hydrodynamic effects can also modify the dynamics of ionic species. In electrolyte solutions, the two most important factors are referred to as the relaxation and electrophoretic effects[14], introduced by Debye, Hückel and Onsager in their theory of conductivity. As a central element there, an ion is assumed to surround itself by a cloud of counterions, an arrangement favored by electrostatic interaction over thermal motion. Upon the application of an electric field, oppositely charged ions will move in opposite directions. Having hence displaced relative to its cloud, each ion tries to rebuild its counterion environment but this process takes some time, termed the relaxation time. If the electric field is persistent, the position of the central ions will not be at the center of the counterion cloud. That difference between positions imposes on any ion in the electrolyte an extra force that is opposite to the applied external field. This is termed the relaxation effect. The electrophoretic effect arises when ions moving in an electric field drag solvent molecules along. Ions then experience an additional drag from the solvent shells of the oppositely charged ions, as those shells move in the opposite direction. Hence, the electrophoretic effect is negligible for diffusion in dilute solutions.

We limit the discussion to the lowest order in concentration of the asymptotic laws, known in the literature as Onsager limiting laws for diffusion and electrophoretic mobility.[33, 34] The great advantage of those laws is that they only require known physical quantities: the dielectric constant ε_R and the dynamic viscosity η of the solvent, the absolute temperature T and the diffusion coefficient of the ions at infinite dilution, D_i^0. The latter can be obtained from the limiting molar conductivity

$$\lambda_i^0 = z_{nom,i}\mu_i^0 F , \tag{1}$$

using the Nernst-Einstein relation

$$D_i^0 = \frac{k_B T \mu_i^0}{z_{nom,i} e} \tag{2}$$

with μ_i^0 representing the electrophoretic mobility at infinite dilution, $z_{nom,i}$ is the nominal charge of the ion, e the elementary charge, k_B the Boltzmann factor, and F the Faraday constant. The limiting laws in 1-1 electrolytes for, respectively, the electrophoretic mobility and diffusion are given as

$$\mu_+ = \mu_+^0\left(1 - \frac{l_B\kappa}{6}\frac{\sqrt{2}}{1+\sqrt{2}}\right) - \frac{\kappa e}{6\pi\eta} \tag{3}$$

and

$$D_+ = D_+^0\left[1-\frac{l_B\kappa}{3}\left(1-\frac{1}{2}\sqrt{\frac{1+3\delta}{1+\delta}}\right)\right] \tag{4}$$

where $\delta = D_-^0 / D_+^0$, $I_B = e^2/4\pi\varepsilon_0\varepsilon_R k_B T$ is the Bjerrum length, $\kappa = \sqrt{8\pi I_B n}$ the reciprocal Debye length, and n is the particle number density (or, concentration). Indices + and – denote the cations and anions, respectively. These laws are valid for small κa values, where a is the closest approach distance between ions. For higher concentrations, additional contributions have to be taken into account.[35] Practically, the limiting law for diffusion holds for a 1-1 electrolyte up to 10 mM.[36]

The measurements of the TMA self-diffusion coefficient D_+ and electrophoretic mobility μ_+ make it possible to obtain the effective charge z_{eff} of the TMA ion in solution as

$$z_{eff} = \frac{k_B T\mu_+}{D_+ e} \tag{5}$$

which can be evaluated in terms of Eqs.(3)-(4). In the case of similar diffusion coefficients for the anion and the cation ($\delta \approx 1$) in a 1-1 electrolyte, the relaxation contributions to the diffusion coefficient and to the electrophoretic mobility cancel out in the ratio leading to the following simple limiting law for the effective charge:

$$z_{eff} = 1-\kappa R_h \tag{6a}$$

where

$$R_h = k_B T / 6\pi\eta D_+^0 \tag{6b}$$

is given by the Stokes-Einstein equation evaluated at infinite dilution; the term κR_h is caused solely by the electrophoretic effect. The difference between the nominal and effective charges for the 1-1 electrolytes can be further expressed as

$$p = 1 - z_{eff} \tag{7a}$$

For 1-1 electrolytes with similar diffusion coefficients for the anion and the cation ($\delta \approx 1$), the limiting law hence provides

$$p = \kappa R_h \tag{7b}$$

In the dilute regime explored here, any significant deviation of p from the value given by Eq.(7b) indicates more specific interactions such as ion association.

The effect of ion association characterized with an association constant K on p can in turn be estimated as follows. First, because of fast exchange between the ion pair and free ion states, the observed electrophoretic mobility and diffusion coefficient of a particular ion can be estimated as

$$\mu_{obs} = \frac{1}{c_0}\left(c_i \mu_i(c_i) + c_{IP}\mu_{IP}\right) \tag{8a}$$

$$D_{obs} = \frac{1}{c_0}\left(c_i D_i(c_i) + c_{IP}D_{IP}\right) \tag{8b}$$

where c_0 is the total concentration of electrolyte, c_i is the concentration of free ions, and c_IP the concentration of ion pair. While the electrophoretic mobility and diffusion coefficient of the free ions depend on concentration, 1:1 ion pairs are uncharged and therefore one can expect a very weak dependence of D_IP on the electrolyte concentration $D_{IP} \approx D_{IP}^0$. For the same reason, the ion-pair contribution cancels out in the mobility expression. Assuming then a weak association $Kc_0 << 1$, $c_\mathrm{IP} \approx Kc_0^2$ and $c_\mathrm{i} \approx c_0(1-Kc_0)$, Eq.(8) simplifies to

$$\mu_{obs} = (1 - Kc_0)\mu_i(c_i) \tag{9a}$$

$$D_{obs} = (1 - Kc_0)D_i(c_i) + Kc_0 D_{IP}^0 \tag{9b}$$

If the dependence of μ_i and D_i on concentration is described to first order by the Onsager limiting laws, the only unknown is the diffusion coefficient of the ion pair D_{IP}^0. Hence, the influence of association can then be introduced into Eq. (5) which extends Eq.(7b) by a first-order correction term for association, here specifically for the cation, as

$$p = \kappa R_{\mathrm{h}} + K c_0 \frac{D_{IP}^{\mathrm{o}}}{D_{+}^{\mathrm{o}}} \qquad (10)$$

Typically, little is known directly about the diffusion coefficient of an ion pair D_{IP}^{0} and predictive expressions[37, 38] require additional parameters such as the size of the ion pair. Moreover, ion pairing may change solvent coordination and thereby boundary condition for the diffusing pair.[39, 40] Since those parameters and conditions are not *a priori* known we can only give a semi-quantitative analysis of the effect of association. With $c_0 = 2$ mM and an estimate of $D_{IP}^{\mathrm{o}} / D_{+}^{\mathrm{o}} \approx 0.5$, the contribution of association by an association constant of $K = 10$ to p becomes 0.01. One should note that independent access to the association constant K provides, via Eq.(10), a means to measure D_{IP}^{o}.

Results and discussion

The p values obtained for different TMA salts and solvents are presented in Fig. 1 with average standard deviations from repeated experiments in each solvent presented as error bars. The raw electrophoretic mobility and diffusion data from which p was calculated from are provided in the ESI. Experimental uncertainty seemed to vary somewhat between different solvents, probably because disturbing bulk flow depends in a complex manner[41] on factors such as viscosity, conductivity, and heat capacity.

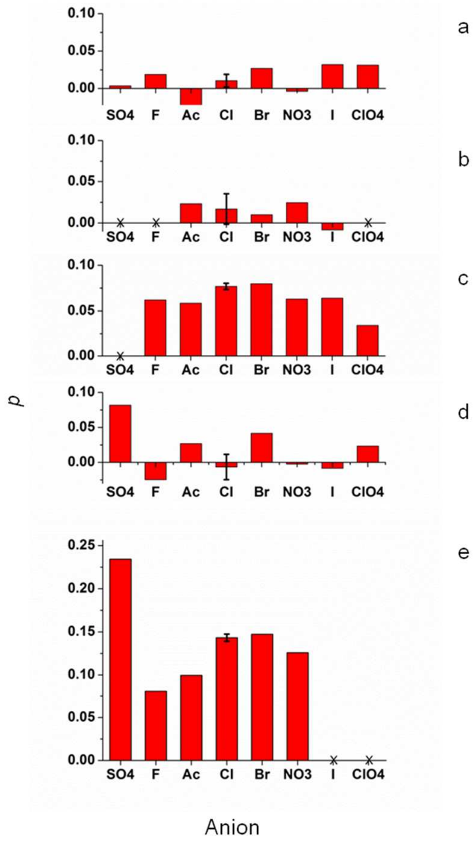

Figure 1. The difference between nominal and effective charges of the TMA cation $p = 1 - z_{eff}$ obtained at 2 mM in D_2O (a), and perdeuterated DMSO (b), acetonitrile (c), methanol (d) and ethanol (e) with anions displayed in Hofmeister order. The error bars represent the average standard deviation ($\pm\sigma$) estimated from a total of 6–18 repeated experiments. Crosses indicate salts not soluble in the actual solvent.

In Fig. 2, the parameter p is plotted as a function of the dielectric constant of the solvent. In addition to the experimental results for those salts that are soluble in all explored solvents, the p values calculated (i) from the limiting laws given in Eqs.(3-5) and (ii) with the additional approximation leading to Eq.(7b) are also reported.

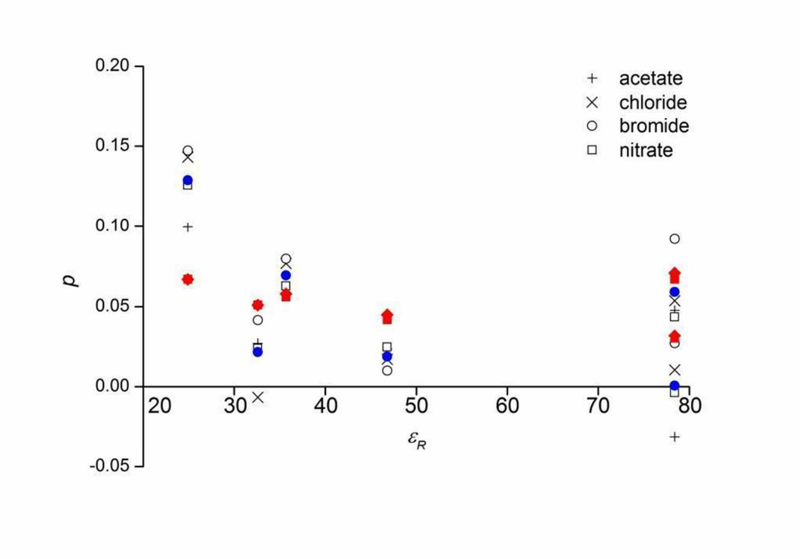

Figure 2. Measured charge difference parameter *p* for the TMA cation dissolved at 2 mM in ethanol ($\varepsilon_r = 24.9$), methanol ($\varepsilon_r = 32.6$), acetonitrile ($\varepsilon_r = 35.7$), DMSO ($\varepsilon_r = 46.8$), and water ($\varepsilon_r = 78.4$) with anions as indicated for salts that were soluble in all solvents. The average experimental value of *p* for the four salts (●) is also displayed together with *p* calculated via Eqs.(3-5) (◆) and via Eq.(7b) (■). For water, the group of displayed points with higher *p* values corresponds to experimental and calculated data for 10 mM solutions.

The material parameters used for calculating the theoretical data in Fig. 2 are collected in Table 1. In particular, one must note that the solvents used were perdeuterated. The difference in dielectric constant between deuterated and hydrogenated solvents is of the same order of magnitude (~1%) that the difference between values of dielectric constants found (for the same solvent) in the literature.[42] The dielectric constants used here were obtained from the hydrogenated experimental averages by a polynomial extrapolation.[43] On the other hand, the viscosity is significantly higher in deuterated than in hydrogenated solvents.[32, 44] The limiting molar conductivities in deuterated solvents and then the diffusion coefficients at infinite dilution were calculated using the Walden rule,[45] where the product $\lambda^{o}\eta$ is supposed to be constant. This approximation has proven to be correct (within a 2% error) for tetraalkylammonium and halide ions between D_2O and H_2O, indicating a similar solvation in the two solvents.[46] We note here that there seems to exist a small persistent discrepancy between experimental diffusion coefficients and those calculated from the Walden rule under the assumption of invariant $\lambda^{o}\eta$ product in H_2O and D_2O. This, while not being explored further here, might be related to the discrepancy between diffusion data derived from NMR measurements and from conductivity data.[47]

Table 1. Parameters used for calculating the charge difference parameter p for TMA in Fig. 2. Dielectric constants[43] ε_R and viscosity[32, 44] η were estimated directly for deuterated solvents. The displayed ratios of the anion and cation diffusion coefficients δ were estimated as the ratio $\delta = \frac{\lambda_-^0}{\lambda_+^0}$ where λ_-^0 is the average limiting molar conductivity of anions for fluoride, acetate, chloride, bromide, nitrate and iodide ions in hydrogenated solvents and λ_+^0 is the limiting molar conductivity of the TMA cation in hydrogenated solvents.

Solvent	ε_R	η (mPa s)	D_+^0 (10^{-9} m^2 s^{-1})[a]	R_h (nm)[b]	κR_h	δ[a]
ethanol	24.9	1.20	0.71	0.26	0.067	0.8
methanol	32.6	0.59	1.65	0.23	0.051	0.8
acetonitrile	35.7	0.36	2.40	0.26	0.056	1.1
DMSO	46.8	2.18	0.45	0.22	0.042	1.3
water	78.4	1.10	0.97	0.21	0.030	1.5

[a] Data for calculating D_+^0 (via Eq.(2)) and δ are from: ethanol,[48] methanol,[49-51] acetonitrile,[52] DMSO,[53, 54] and water.[55]

[b] Via Eq.(6b).

As seen from Fig.2, the overall trend is as expected; p increases as the dielectric constant decreases. The values calculated from the limiting laws, including only long-range electrostatic and hydrodynamic effects, exhibit the same general behavior. The difference between anion and cation diffusion coefficients leading to $\delta \neq 1$ clearly plays no significant role. Hence, in Fig. 3 we compare directly the experimental p values to the ones from the approximate limiting law in Eq.(7b) and find that, within experimental error, p in water, DMSO and methanol is as expected after having accounted for the effects of the ion cloud. On the other hand, TMA cations in acetonitrile and ethanol exhibit effective charges that are reduced more than expected from non-specific ion-ion interactions. We ascribe this feature to specific ion association in broad agreement with values of association constants found in the literature.[52, 56]

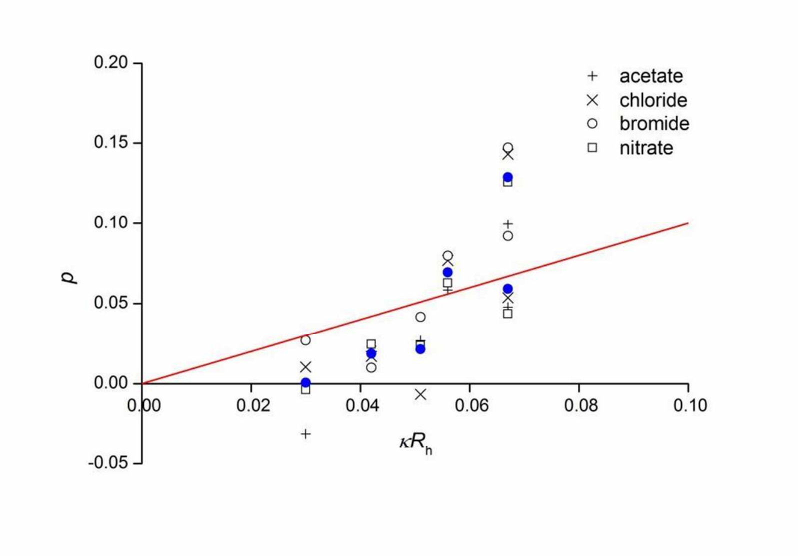

Figure 3. Measured charge difference parameter p for the TMA cation as in Fig. 2 but presented as function of κR_h with the line displaying the approximate limiting law behavior $p = \kappa R_\mathrm{h}$, recall Eq.(7b). The point at $\kappa R_\mathrm{h} = 0.067$ (data points below the line representing the limiting law) corresponds to 10 mM solutions in D_2O. The average value of p for the four salts (●) is also displayed.

For water, this result is expected as ion association is known to be weak in aqueous solutions.[1, 57] For example, a recently reported value of the association constant from conductivity measurements is $K = 2.0$ for TMABr.[58] In particular, we note that the divalent sulphate ion does not seem to associate with the TMA^+ ion to any larger extent than the monovalent anions. In addition, the lack of association in aqueous solutions is a general phenomenon for tetraalkylammonium ions irrespective of the alkyl chain length (also in agreement with previous studies[57, 58]); the data in Fig. 4 show that it is the non-specific ion-ion interaction term that dominates the observed behavior in water. (We note that the apparent jump in hydrodynamic radius between the tetrapropylammonium and tetrabutylammonium ion is, though well-documented,[58, 59] not explained.)

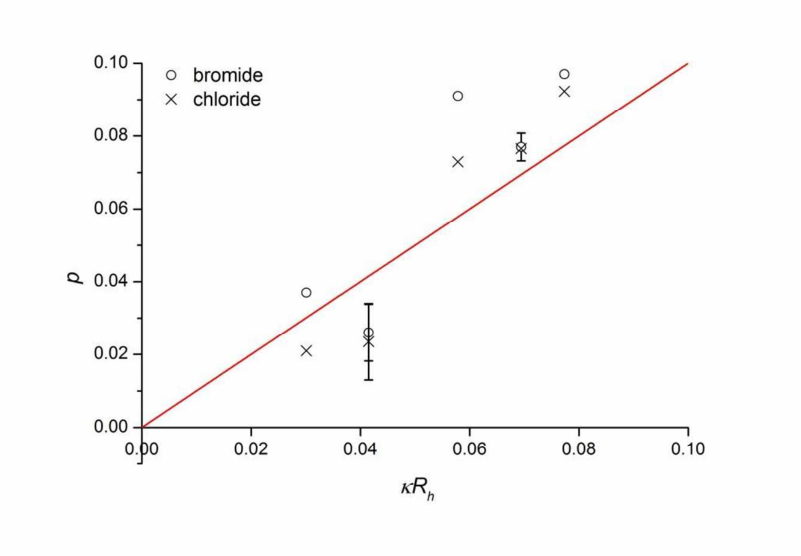

Figure 4. Measured charge difference parameter p for the different tetraalkylammonium cations with methyl (κR_h=0.030), ethyl (κR_h=0.042), propyl (κR_h=0.058), butyl (κR_h=0.070) and pentyl (κR_h=0.077) as alkyl groups, dissolved at 2 mM in D_2O with bromide and chloride as anions. The data are presented as function of κR_h with the line displaying the approximate limiting law behavior $p = \kappa R_h$, recall Eq.(7b). The values of κR_h were calculated using the dielectric constant and viscosity of D_2O in Table 1 with tabulated limiting molar conductivities for tetraalkylammonium salts.[55]

In DMSO (Fig. 1b), the extent of ion association detected was low which is in accordance with a conductivity study where no ion association at all was detected for dilute <10 mM TMABr and TMAI solutions.[60]

As is clear from Fig. 3, there is significant ion association both in acetonitrile and in ethanol. For acetonitrile, Barthel reported an association constant of 40 for TMAI and 29.5 for $TMAClO_4$.[52] A value of the association constant can be estimated from our data by taking the difference between the measured p and the p predicted by Onsager limiting law. Based on Eq.(10), deviations from the limiting law by 0.04 ($p \approx 0.11$) and 0.03 ($p \approx 0.10$) are expected for TMAI and $TMAClO_4$, respectively. Clearly, our current data (Fig. 1c) are not consistent with the association constants found previously, that may be a sign of experimental error. For ethanol, the extensive ion association is consistent with previous findings for alkali metal halides[56] and with an older study where the association constants of tetramethylammonium halides were found to be higher than 100.[48] The more recent study of Barthel provides association constants in the order K = 50 for alkali metal halides.[56] From this value, the association parameter p can be estimated to be close to $p = 0.12$ which is consistent with our observed p values. The monovalent ions exhibit a Hofmeister-type relation in ion association (Fig. 1e) similar to that previously found for 95 % (v/v) ethanol-water solution.[22]

Interestingly, the ion association of the TMA^+ cation in methanol was found to be negligible. On one hand, this is perhaps not as expected (i) because of the low dielectric constant of methanol ($\varepsilon_R = 32.6$) and (ii) because the small R_h of TMA in methanol that would seem to permit short ion-ion separation in ion pairs. Indeed, previous conductometric results indicated similar magnitudes of ion pairing for TMA salts in acetonitrile[52] and in methanol.[51] We cannot verify that finding.[51] One possible reason for this discrepancy is experimental error in our experiments; in general, our p values are, for solvents like water and DMSO, below the limiting law values. Another possible explanation is that, similarly to water, methanol is dipolar and has a molecular structure that facilitates the formation of hydrogen bond networks. Hence, if that aspect of molecular structure is important one would expect that methanol would behave similarly to water with ion pairing suppressed. On the other hand, sulphate in methanol is more associated than the monovalent anions which could not be observed in water.

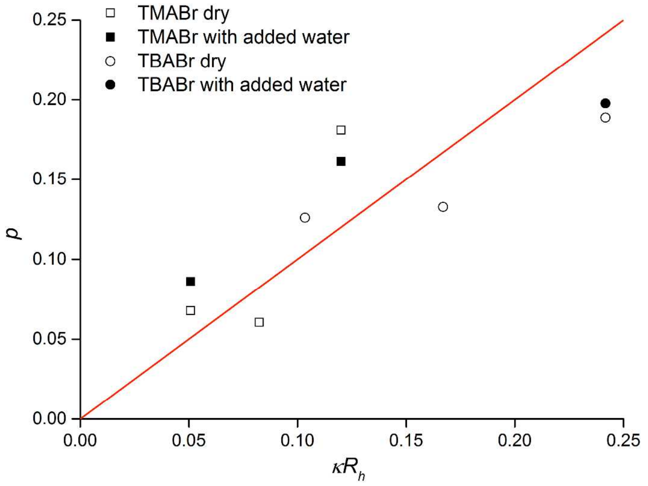

Figure 5. Measured charge difference parameter p for the tetramethylammonium and tetrabutylammonium bromide salts dissolved in dry methanol (average water content of *ca* 300 ppm, corresponding to *ca* 13 mM) and methanol with water added up to 120 mM. The data are presented as function of κR_h with the line displaying the approximate limiting law behavior $p = \kappa R_h$, recall Eq.(7b).

As concerning the other solvents, one general point is if the set 120 mM (<< 1 w %) water content has any influence on the data or not. In this context, Kiyozumi and coworkers showed a significant difference in the behavior of methanol and acetonitrile clusters when water was added, albeit at a much higher mixing ratio of 5:95.[61] None of the data there suggests that the observed preferential behavior in clustering is significant at our much lower mixing ratios. In addition, we performed eNMR and diffusion experiments in methanol with low water content and at different salt concentrations. The data, presented in Fig. 5, yield the conclusion that, within experimental error, there is no significant effect of water added at 120 mM on the observed effective charge. Additional data for other solvents (see ESI) corroborates this as a general conclusion.

It may also happen that predictions based on Onsager limiting law are inaccurate. As one reason, the concentration used in Eqs.(3-4) were set under the assumption of complete dissociation that may not be the case for all solvents. However, a slight deviation from complete dissociation has only minor effect on the limiting-law predictions because κ is dependent on the square root of concentration. (Note that the *direct* effect of having not all salt dissociated is exactly the signature of ion association that we aim to investigate.) Another limitation comes from the fact that the Debye-Hückel-Onsager approach considers the ions as point charges that leads one to underestimate the mobility.[6] Applying any correction (higher order of the laws) for taking the finite radii of the ions into account would yield a higher mobility and, consequently, a lower predicted p. However, as seen in Fig. 4, a large variation in cationic radius provides no significant deviation from the limiting law behavior in water.

Conclusions

Ion association of TMA salts in various organic solvents was characterized using a combination of diffusion NMR that yields the self-diffusion coefficient and eNMR that yields the electrophoretic mobility. This combination of data provides then the effective charge of the TMA cation and the deviation of this parameter from the nominal charge of 1 was analyzed. There are two contributing effects. First, the presence of ion clouds influences the various modes of ion motion via the so-called relaxation and electrophoretic effects, both of which can be well described in the low-concentration limit by the Onsager limiting law. For solvents with high dielectric constants such as water and DMSO we found no significant difference between the predictions of the limiting law and the experimental observation. Hence, we conclude that, as expected, there is no significant ion association in those solvents.

On the other hand, weak ion association was detected in acetonitrile whereas it was far more significant in ethanol, well in agreement with conductometric studies. In ethanol, ion association showed a Hofmeister-type correlation for the monovalent ions as association generally increased with the size of the ion.[22] Despite previous indication, we found no sign of significant ion pairing in methanol[51] where the observation was instead well reproduced by the limiting law. This calls for repeated and more accurate studies.

There are not many microscopic (that is, in contrast to macroscopic methods like conductometry) that can provide quantitative data on ion pairing. Dielectric relaxation spectroscopy seems to be best placed to be called as the current premier tool, though it is typically limited to more concentrated solutions.[15, 16, 62] We envisage that the method presented here can serve as a useful complement as it can access solutions down to mM (or, even slightly below) concentrations. As one potentially important and unique point, the methodology presented here permits one to determine the electrophoretic mobility of *individual* ions as a function of salt concentration. From such data, single-ion conductivities can be derived that may accurately yield transference numbers that are of profound importance for optimizing battery electrolytes.[63, 64] Another potential application to explore is the study of ion behaviour in mixed solvents, where modeling the dielectric response may depend on strong assumptions.

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