Solvent Properties of Dichloromethane. VI. Dielectric Properties of Electrolytes in Dichloromethane

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The dielectric properties of solutions of R_4NClO_4 (R = Et, Pr, Bu, Hex and Dec), Pr_4NI, Bu_4NI, Ph_4AsI and $[(Ph_3P)_2N]ClO_4$ (abbreviated [PNP]ClO_4) in dichloromethane at 20.0 °C have been studied in the 0.05–10 GHz frequency range using the time domain spectroscopy (TDS) technique. The static permittivity, ε_s, of the solutions of the R_4N^+ salts increases linearly with concentration up to ~0.06 M with slopes, $d\varepsilon_s/dc$, from ~40 M^{-1} for Et_4NClO_4 to ~50 M^{-1} for Dec_4NClO_4. The $\varepsilon_s - c$ plots for Ph_4AsI and [PNP]ClO_4 are linear up to only ~0.03 M but with considerably larger slopes, viz ~150 M^{-1}. For higher concentrations the $\varepsilon_s - c$ plots level off to asymptotic values which are strongly dependent upon the size of the cation: from ~11.6 for [PNP]ClO_4 and ~12.2 for Dec_4NClO_4 to ~15.0 for Pr_4NClO. The dielectric relaxation times for the ion pair from the R_4N^+ salts are essentially independent of the concentration. The corresponding relaxation times for Ph_4AsI and [PNP]ClO_4 suggest that the ion pairs from these two salts are solvent-separated in very dilute solutions, but are gradually transformed into contact ion pairs as the concentration increases.

The results are discussed in relation to recent conductivity studies of the same salts in dichloromethane. It is concluded that the large conductivity of concentrated solutions of salts in this solvent and in other solvents of low permittivity is due to a decrease in the association constants with increasing concentration caused by the increase in the static permittivity of the solutions.

A number of solvents of low static permittivity ($\varepsilon_s < 15$) are frequently used as solvents for chemical reactions. Excellent dissolving properties combined with high thermal and chemical stability, low boiling point, negligible hygroscopicity and low price make many of these solvents advantageous compared to the usual protic and dipolar aprotic solvents.[1]

When reactions involving ionic reactants are to be examined in weakly dissociating solvents, several difficulties arise. For concentrations well below the limit given by the Fuoss equation,[2] $3.2 \times 10^{-7}\ \varepsilon_s^3$ M, in dichloromethane 2.3×10^4 M, one may safely conclude that only dissociated ions and ion pairs are present in the solution.[3-6] Few reactions, however, can be studied in the concentration range for which this simple description of the electrolytic solution is valid. For concentrations which are of practical interest

both in synthesis and for mechanistic studies a number of other species will be present,[7,8] species that may exert some reactivity toward a given substrate. Their individual concentrations seem to vary with the amount of dissolved salt, the size and structure of cation and anion and the various properties of the solvent. Unfortunately, no methods are presently available that can allow the various concentrations to be calculated with reasonable certainty. This lack of precise information concerning the exact nature of the solute species has been a major obstacle to exact mechanistic descriptions of reactions involving ionic reactants in weakly dissociating solvents, e.g. the reduction of ketones and other organic functional compounds by $LiAlH_4$ in ether,[9,10] the numerous reactions of carbanions and related species[11,12] and, more recently, substitution reactions involving transition metal complexes in halogenated alkanes.[13,14]

Kraus[8] stressed that the first step toward an improved description of electrolytes in solvents of low ε_s would be to obtain a reliable measure of the fraction that exists in the form of ions, the "ion fraction", and the type(s) of ions that contribute to this fraction. A large number of highly accurate conductivity studies have been performed with this aim.[3-5,15] The results from these studies, however, do not allow definite conclusions to be made owing to the fact that all types of ions contribute to the measured conductivity. Furthermore, no reliable relationship between conductance and concentration exists, except for very dilute solutions where the generalized equation of Fuoss and Onsager[16] is valid.

Plots of molar conductivity versus concentration, $\Lambda - c$ plots, in solvents of low ε_s exhibit in most cases a minimum at low concentration, $10^{-4}-10^{-2}$ M, and a maximum at high concentration, $10^{-1}-10^0$ M.[15,17,18] This increase in conductivity beyond the minimum was originally explained by Fuoss and Kraus[15] as being caused by the formation of conducting triple ions from nonconducting ion pairs. The triple ion hypothesis has been so widely accepted that, even in recent literature, a minimum in $\Lambda - c$ plots is considered as "proof" of the existence of triple ions.[19,20] Cavell and Knight,[21] however, proposed that quantitative estimates of the extent of triple ions formation in solutions of salts in solvents of low ε_s may be seriously in error unless the variation of ε_s with concentration of dissolved salt is explicitly taken into account. Contrary to what is observed in solvents of high ε_s, such as water,[22-23] the permittivity of electrolytes in solvents of low ε_s is known to increase with the concentration of dissolved salt.[21,24-29] Since an increase in ε_s will lead to a decrease in the association constant, K_A,[30] the high conductivity of concentrated electrolytes in solvents of low ε_s may be due to an increase in the dissociation rather than due to the formation of triple ions. Indiscriminate use of the Fuoss-Kraus triple ion hypothesis[15] when conductivity data are to be interpreted, i.e. applying large triple ion formation constants, K_T, together with concentration independent ion pair formation constants, K_A, may lead to a serious underestimate of the concentration of dissociated ions. In the solvents of lowest ε_s (ε_s being 2 to 5) this error may actually be of several orders of magnitude.[31]

Despite the obvious consequences for reactions involving ionic reactants in solvents of low ε_s, there seems to have been no detailed discussion in the literature since the studies by Cavell and Knight.[21,27,28] As an extension of our previous conductivity studies in dichloromethane[2,18] we therefore report on permittivity studies of solutions of several onium perchlorates in this solvent at 20.0 °C. The measurements were performed over a concentration range that embraced both the minimum and the maximum in the $\Lambda - c$ plots. The time domain spectroscopy (TDS) technique[32,33] was used throughout the study. A preliminary report of this study has been published.[34]

Experimental

Materials. The purification of the onium salts was performed as previously reported.[2,18] The perchlorates were found to be suitable for the present study owing to the facility with which these salts can be purified. Additionally, the results from detailed conductivity studies on several onium perchlorates in dichloromethane are available.[18] The limited solubility of Ph_4AsClO_4 in dichloromethane[2] prevented studies on solution of this salt. The very soluble iodide, Ph_4AsI, was chosen as an alternative Ph_4As^+ salt since studies on Pr_4NI and Bu_4NI gave results which agreed with those for Pr_4NClO_4 and Bu_4NClO_4, respectively, within experimental error. Et_4NClO_4 could be studied only up to ~0.07 M due to the low solubility of this salt in CH_2Cl_2. None of the Et_4N^+ halides, including Et_4NI, were significantly more soluble to allow an extension of the concentration range for Et_4N^+ salts.

Dichloromethane (*Baker Analyzed Reagent*) was distilled twice from CaH_2 prior to use.

TDS measurements. The TDS technique is based on the study of the change in shape of a fast rising voltage step which is propagated through a coaxial line section filled with the material under study. Pulse shapes are monitored by a sampling oscilloscope controlled by a minicomputer which also performs the necessary numerical work. Details of the measuring system have been described.[32,33]

In total transmission TDS, the pulse transmitted through a sample of length l, $r(t)$, is compared to the pulse, $v(t)$, transmitted through the same length of air-filled coaxial line. Fourier transformation, $F(\omega) = {}_{-\infty}\int^\infty f(t)\exp(-i\omega t)dt$, of both pulses gives the transmission coefficient $T(\omega) =$

$R(\omega)/V(\omega)$. The apparent total complex permittivity ε_t^* can then be calculated from the transmission line equation [eqn.(1)]. Here, $\varrho = (1 - \varepsilon_t^{*1/2})/(1 + \varepsilon_t^{*1/2})$ and c is the velocity of light in free space.

$$T(\omega) = \frac{(1 - \varrho^2)\exp - (i\omega l/c)(\varepsilon_t^{*1/2} - 1)}{1 - \varrho^2\exp - (2i\omega l/c)\varepsilon_t^{*1/2}} \quad (1)$$

Imperfections in the coaxial line and sampling system will lead to the occurrence of unwanted spurious reflections. The influence of these on the calculated permittivity spectra can be reduced if the pulse transmitted through a liquid with known dielectric parameters is used as reference. In a study of the change in dielectric spectrum with solution composition, the appropriate reference liquid is the pure solvent. The transmission coefficient, $T_{ref}(\omega)$, for the reference liquid can then be calculated from eqn. (1) and the unknown spectrum obtained by solving eqn. (2).

$$\frac{R(\omega)}{R_{ref}(\omega)} = \frac{T(\omega)}{T_{ref}(\omega)} \quad (2)$$

In a sample showing dc conductivity σ, the total permittivity is generally described by eqn. (3), where $\varepsilon^*(\omega)$ gives the dielectric contribution and

$$\varepsilon_t^*(\omega) = \varepsilon^*(\omega) - i\sigma/\omega\varepsilon_0 = \varepsilon' - i\varepsilon'' - i\sigma/\omega\varepsilon_0 \quad (3)$$

$-i\sigma/\omega\varepsilon_0$ the ionic conductance contribution to the apparent ε_t^*. ε_0 is the permittivity of free space while ε' and ε'' represent the real and imaginary parts of $\varepsilon^*(\omega)$.

For a dielectric showing dc conductivity, the pulse transmitted through the sample will not reach the final level of the incident step pulse. The asymptotic value of the time domain transmission coefficient, $r(t)/v(t)$, is given by eqn. (4):

$$t_\infty = \lim_{t \to \infty} r(t)/v(t) = \lim_{\omega \to 0} T(\omega) \quad (4)$$

This eqn., combined with eqns. (1)–(3) gives eqn. (5):

$$t_\infty = (1 + \sigma l/2c\varepsilon_0)^{-1} \quad (5)$$

If a time window is used, which allows a complete relaxation of all dielectric processes, the time domain data will give σ directly.

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A 20 mm sample cell, obtained by closing off the coaxial line with matched teflon beads, was used in all measurements. In this cell, holes are drilled in the line to facilitate cleaning and insertion and change of sample without disassembling. All solutions within a series were inserted consecutively without change in instrument setting. This procedure ensures the detection of small systematic changes in the dielectric parameters with sample composition. A time window of 20 ns was used for all measurements. The temperature was kept at 20.0 °C by means of a water cooled jacket which surrounded the coaxial line.

The literature value for the static permittivity, ε_s, of dichloromethane at 20 °C is 9.1.[35] Its dielectric relaxation is sufficiently fast to put the major part of the dispersion above the TDS frequency range $\leq$10 GHz. However, by using $\varepsilon_\infty = n_D^2 = 2.0$ and fitting the experimental data from the use of eqn. (1) to a Debye model function [eqn. (6)], a value $\tau = 2$ ps could be obtained. The permittivity spectrum $\leq$10 GHz is not sensitive to the precise value of τ, and the given parameters ($\varepsilon_s = 9.1$, $\varepsilon_\infty = 2.0$ and $\tau = 2$ ps) were used together with the model function, given by eqn. (6), as the reference in solving eqn. (2) for the solution spectra.

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau} \quad (6)$$

Results

The pulse shapes were Fourier transformed and permittivities determined at 35 frequencies between 50 MHz and 10 GHz. The chosen frequencies were evenly distributed on a logarithmic scale. As a typical example the permittivity spectrum of a 0.0395 M solution of Bu_4NClO_4 is shown in Fig. 1. The conductivity term, $i\sigma/\omega\varepsilon_0$, has been subtracted from the experimental data to give this dielectric spectrum.

As seen from Fig. 1, the permittivity spectrum shows an additional dielectric dispersion besides that found for the pure solvent. This is also clearly brought out in the Cole-Cole plot of the same spectrum (Fig. 2). Dissolution of salts in associated liquids such as alcohols and similar solvents has revealed a distinct influence of the ions upon the solute dielectric relaxation.[36-38] However, for a non-associated liquid like CH_2Cl_2 it can be expected that the dielectric relaxation
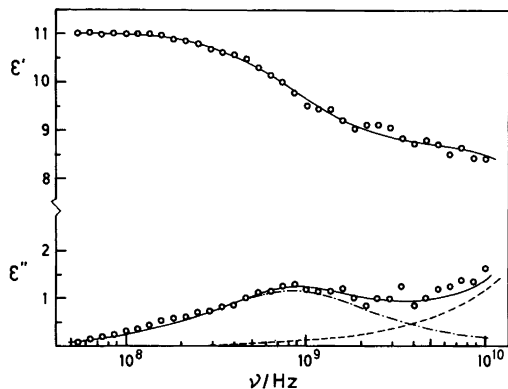
Fig. 1. Dielectric spectrum of a 0.0395 M solution of Bu_4NClO_4 in dichloromethane. The conductivity contribution has been substracted. The full line shows the theoretical spectrum [eqn. (7)], while the broken lines show the contributions to ε'' from the solvent and solute, respectively.

possibility of a distribution of relaxation times around τ_1 is allowed by the introduction of the α parameter in the Cole-Cole function. Such a distribution is usually recognizable in the Cole-Cole plot as a depression of the ε'' vs. ε' arc below the semicircle obtained with a single relaxation time. The Cole-Cole plot obtained by subtraction of the solvent relaxation term in eqn. (7) is given in Fig. 2, which shows a semicircular arc being possibly slightly depressed. Least-squares fit of the model function [eqn (7)] to the experimental data gives a slightly smaller r.m.s. deviation when assuming the Cole-Cole distribution as compared to the usual Debye model, i.e. setting $\alpha = 0$. In the case of the spectrum for Bu_4NClO_4 shown in Fig. 1 a value for α of 0.10 was obtained, which may indicate a possible narrow distribution of relaxation times.

Although computer fitting of a Cole-Cole function is always possible, we do not find the accuracy of the experimental data sufficient to justify the introduction of an additional parameter. We have therefore analyzed the data in terms of a model involving two Debye relaxation times, i.e. $\alpha = 0$ in eqn. (7). A good measure of the conductivity, σ, was obtained from the time domain data [eqn. (5)]. Nevertheless, σ was treated as a possible variable parameter in the fitting procedure. The solvent parameters, $\tau_2 = 2$ ps and $\varepsilon_\infty = 2$, were fixed as outlined above. The dielectric parameters for the various concentrations of the onium perchlorates Pr_4NI, Bu_4NI and Ph_4AsI are listed in Table 1. The results are summarized in Fig. 3, where the static permittivities of the solutions, ε_s, and the relaxation times, τ_1, are plotted versus the concentration of the dissolved salts. The circled points on the curves for

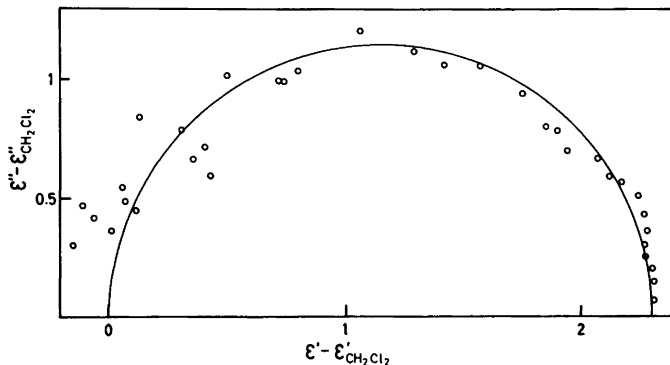time of the bulk solvent is unaffected by solute additions. The tail of the high frequency dispersion in Fig. 1 is therefore attributed to a solvent relaxation with a relaxation time, τ_2, of 2 ps.

An appropriate model function for the permittivity spectrum is then given by eqn. (7):

$$\varepsilon^* = \frac{\varepsilon_s - \varepsilon_1}{1 + (i\omega\tau_1)^{1-\alpha}} + \frac{\varepsilon_1 - \varepsilon_\infty}{1 + i\omega\tau_2} + \varepsilon_\infty \qquad (7)$$

Here, $\varepsilon_1 - \varepsilon_\infty$ gives the amplitude of the solvent relaxation, while $\varepsilon_s - \varepsilon_1$ gives the dielectric increment due to the salt addition. The corresponding mean relaxation time is τ_1. In eqn. (7), the

Fig. 2. The Cole-Cole plot of the data in Fig. 1, when the contribution from the solvent has been subtracted.

Salt	ε_s	ε_1	τ_1/ns	$\sigma \times 10^3/\Omega^{-1}m^{-1}$
Et$_4$NClO$_4$				
0.0150 M	9.9	9.2	0.14	15.7
0.0300 M	10.6	9.2	0.14	29.0
0.0601 M	11.6	9.2	0.14	58.7
Pr$_4$NClO$_4$				
0.0416	11.1	9.1	0.16	44.5
0.0833	12.3	9.1	0.16	93.8
0.1666	13.6	9.1	0.15	200.2
Pr$_4$NI				
0.1596	13.5	9.0	0.15	194.6
0.3192	14.3	8.8	0.14	398.2
Bu$_4$NClO$_4$				
0.0052	9.5	9.2	0.18	7.5
0.0158	10.0	8.9	0.19	19.0
0.0316	10.7	8.8	0.20	35.5
0.0395	11.0	8.7	0.19	45.0
0.0790	12.1	8.7	0.19	91.8
0.1580	13.1	8.6	0.18	186.6
0.3160	13.8	8.4	0.16	365.6
Bu$_4$NI				
0.0094	9.7	9.1	0.20	11.7
0.0312	10.7	9.0	0.19	33.8
0.0780	12.2	9.0	0.19	88.1
0.156	13.4	8.8	0.18	184.7
Hex$_4$NClO$_4$				
0.0316	10.7	9.1	0.27	31.0
0.0790	11.9	9.0	0.24	76.8
0.1580	12.8	8.8	0.22	151.3
0.3160	13.3	8.5	0.20	270.9
0.4540	13.1	8.1	0.19	337.9
Dec$_4$NClO$_4$				
0.0130 M	9.9	9.0	0.36	14.4
0.0212 M	10.3	9.1	0.36	22.2
0.0437 M	11.1	8.9	0.33	43.3
0.0706 M	11.6	8.8	0.30	67.4
0.0973 M	11.9	8.7	0.30	89.4
0.1410 M	12.1	8.4	0.27	121.3
0.1946 M	12.2	8.2	0.26	152.7
0.2190 M	12.1	8.1	0.25	163.0
Ph$_4$AsI				
0.0047	9.8	9.1	0.44	19.9
0.0094	10.2	9.1	0.36	35.8
0.0312	11.3	9.0	0.26	109.5
0.0779	12.1	8.9	0.21	275.3
0.1558	12.3	8.8	0.21	539.4
[PNP]ClO$_4$				
0.0095	10.3	9.0	0.43	43.4
0.0190	10.7	9.0	0.34	82.7
0.0474	11.3	8.9	0.26	199.5
0.0948	11.5	8.7	0.23	385.4
0.1896	~11.3[a]	~8.5[a]	~0.27[a]	~700

[a]Uncertain values due to the high conductivity of the solution.

Pr$_4$NClO$_4$ and Bu$_4$NClO$_4$ refer to studies on Pr$_4$NI and Bu$_4$NI, respectively.

Discussion

The permittivity of the solvent, ε_1. The static permittivity of a pure liquid is, according to the Kirkwood-Fröhlich theory,[39] given by eqn. (8), where N_1 is the number of molecules per volume unit, ε_0

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s - \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2} = \frac{N_1}{9\varepsilon_0 kT}g\mu^2 \tag{8}$$

denotes the permittivity of free space, k is Boltzmann's constant and T is the absolute temperature. μ represents the gas phase dipole moment, while g is Kirkwood's correlation factor. A deviation of g from unity is a measure of local ordering due to short range intermolecular forces.

The gas phase dipole moment of CH$_2$Cl$_2$, μ, is 1.6 D. An application of eqn. (8) with $\varepsilon_\infty = n_D^2 = 2.0$ gives a g-factor of 1.2. However, allowing a 15 % addition to n_D^2 due to atomic polarization and setting $\varepsilon_\infty = 2.3$, the correlation factor g is reduced to 1.0. It can be concluded that the solvent molecules can be considered unassociated and that the assumption made in the spectral analysis of negligible influence on the bulk solvent relaxation by the solute is valid.

The dispersion $\varepsilon_1 - \varepsilon_\infty$ is interpreted as due to the solvent relaxation. On salt addition, the amplitude of this solvent dispersion is reduced with increasing salt concentration (cf. Table 1, column 3). This agrees with eqn. (8), in that a lowering of N_1 will reduce the static permittivity contribution from the solvent. The number of solvent molecules, N_1, per volume unit, V_u, is given by eqn. (9), in which $V_{\varphi 1}$ is the molar volume of a solvent

$$N_1 = \frac{V_u}{V_{\varphi 1}} - c_s\frac{V_\varphi}{V_{\varphi 1}} \tag{9}$$

molecule in the solvent, c_s is the concentration of solute and V_φ is the apparent molar volume of the solute at a concentration of c_s. The apparent molar volumes of the studied salts seem to obey Masson's equation[40] in dichloromethane[41] [eqn. (10)]:

$$V_\varphi = V_\varphi^0 + S_v c_s^{1/2} \tag{10}$$

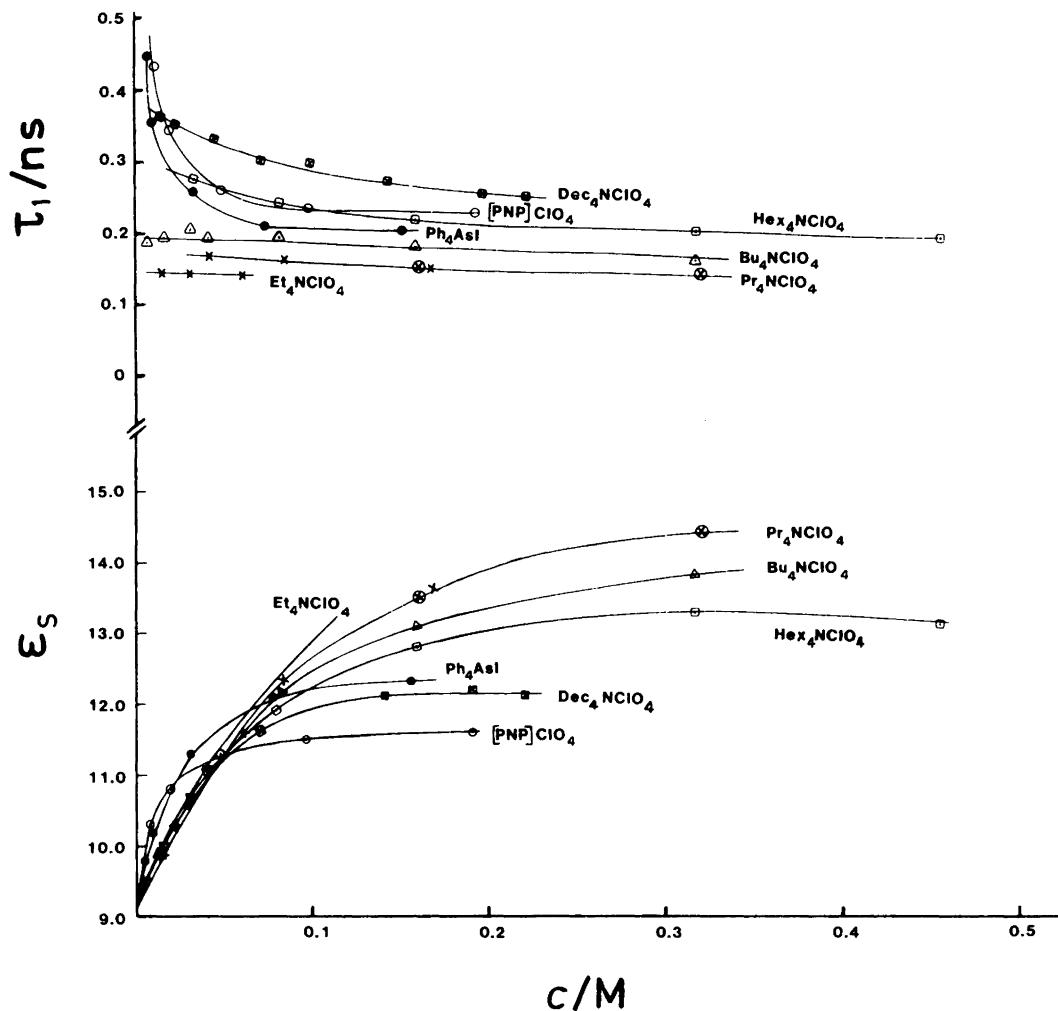V_φ^0 in eqn. (10) represents the partial molar vol-

Fig. 3. The static permittivity, ε_s, and the relaxation time, τ_1, as a function of the concentration of onium salts in dichloromethane at 20.0 °C (circled points on curves for Pr_4NClO_4 and Bu_4NClO_4 refer to studies on Pr_4NI and Bu_4NI, respectively).

ume at infinite dilution, which in dichloromethane ranges from 167 cm³ mol⁻¹ for Et_4NClO_4 to 716 cm³ mol⁻¹ for Dec_4NClO_4.[41] Since S_v values for onium salts in dichloromethane are small,[41] the percentage reduction in N_1 is approximately equal to $c_s V_\varphi^0 \times 10^{-1}$. For 0.1 M solutions this reduction in N_1 will vary from ~1.7% for Et_4N-ClO_4 to ~7.2% for Dec_4NClO_4. The negligible decrease in ε_1 for Et_4NClO_4 and Pr_4NClO_4, and the significant decrease in ε_1 for the salts of the larger cations are thus as expected from this simple analysis based upon eqns. (9) and (10). A nu-

merical estimate shows that a 10 % reduction in N_1 will give an ε_1 of 8.4, which is in fair agreement with the experimental results (cf. Table 1).

By differentiation of eqn. (9) with respect to the concentration one obtains eqn. (11):

$$\frac{dN_1}{dc_s} = -\frac{V_\varphi^0}{V_{\varphi 1}} - \frac{3S_v}{2V_{\varphi 1}} c_s^{1/2} \qquad (11)$$

Since the reduction in ε_1 is essentially proportional to the reduction in N_1, a plot of ε_1 versus $c_s^{1/2}$ should be linear. This linear relation has been

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observed by Cavell[27] for Bu$_4$NBr in acetone and appears to be satisfied by the present data for Bu$_4$NClO$_4$ and Dec$_4$NClO$_4$, the salts most extensively studied. It should be emphasized, however, that the limited accuracy of ε_1 combined with the relatively small variations in this parameter do not merit a detailed discussion.

The static permittivity of the solutions, ε_s. As shown in Fig. 3, ε_s increases with concentration for all salt solutions. This accords with results arrived at in similar studies in solvents of low permitivity.[29] The $\varepsilon_s - c$ plots appear as smooth curves with steadily decreasing slopes. For dilute solutions of the R$_4$N$^+$ perchlorates ($<\sim0.06$ M) the permittivity increases fairly linearly with concentration with slopes, $d\varepsilon_s/dc$, ranging from ~40 M^{-1} for Et$_4$NClO$_4$ to ~50 M^{-1} for Dec$_4$NClO$_4$. For higher concentrations the curves level off toward asymptotic values for ε_s. The rate at which this levelling off in the $\varepsilon_s - c$ curves takes place and the asymptotic permittivity of the solutions are strongly dependent upon the size of the cation, the latter ranging from ~12.3 for Dec$_4$ NClO$_4$ to almost 15 for Pr$_4$NClO$_4$. The corresponding value for Et$_4$NClO$_4$ could not be determined owing to the limited solubility of this salt in dichloromethane. The shape of the $\varepsilon_s - c$ curve at low concentrations, however, indicates that the asymptotic value for this salt will exceed that for Pr$_4$NClO$_4$.

The $\varepsilon_s - c$ curves for Ph$_4$AsI and [PNP]ClO$_4$ suggest that these two salts behave differently in dichloromethane. For concentrations less than ~0.03 M there seems to be a linear relationship between the permittivity and the concentration, with a slope of ~150 M^{-1}. For higher concentrations, the $\varepsilon_s - c$ curves level off significantly more rapidly than for the R$_4$N$^+$ salts. The limiting values for ε_s are ~12.5 and ~11.6 for Ph$_4$AsI and [PNP]ClO$_4$, respectively.

A number of factors are known to affect the permittivity of electrolytic solutions. In water and in related solvents of high permittivity, ε_s is known to decrease with increasing concentration of dissolved salt.[22,23] This decrease in ε_s has been explained by hydration,[22,23] by kinetic depolarization[43,44] and by the reduced number of solvent molecules, N_1, per volume unit [cf. eqn. (8)]. Since onium salts of the type studied in the present work appear to be unsolvated by dichloromethane,[2,41] one may suggest that solvation or

weaker interactions between ions and solvent molecules have no distinct effect upon ε_s. The Hubbard-Onsager kinetic depolarizing effect[43,44] is essentially proportional to the relaxation time of the solvent [eqn. (12)]. With τ equal to 2 ps the kinetic depolarization effect will be negligible.

$$\Delta\varepsilon_s = -24 \times 10^9 \pi \tau \sigma (\varepsilon_s - \varepsilon_\infty)/\varepsilon_s \qquad (12)$$

One may therefore argue that only the reduction of solvent molecules per unit of volume will cause a decrement i ε_s.

The increase in ε_s with concentration, as observed in this study and in related studies in solvents of low ε_s, is undoubtedly due to incomplete dissociation. The ions will persist as pairs for a time which is long compared to the time scale of 20 ns used in the measurements. The ion pairs, by virtue of their large dipole moments, will increase the permittivity of the solutions. The dielectric properties of the solution will thus have contributions from the dipole moment of the ion pairs present in the solution as well as from the solvent molecules. For a mixture of dipoles, the static permittivity can be calculated from eqn. (13):[45]

$$\sum_i \theta_i \frac{\varepsilon_s - \varepsilon_{\infty i}}{2\varepsilon_s + \varepsilon_{\infty i}} = \frac{\varepsilon_s}{\varepsilon_0} \frac{(\varepsilon_{\infty i} + 2)^2 N_i \mu_i^2}{9kT (2\varepsilon_s + \varepsilon_{\infty i})} \qquad (13)$$

θ_i is the volume fraction of species i with dipole moment μ_i; the other symbols are as in eqn. (8). To simplify eqn. (13) for a two-component mixture we can set $\varepsilon_{\infty 1} = \varepsilon_{\infty 2}$. For a dilute solution of dipoles μ_2 we can further assume θ_1 to approach unity. With the static permittivity of the pure solvent, ε_1, given by eqn. (8), the static permittivity of the mixture can be written as in eqn. (14):

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s} = \frac{(\varepsilon_1 - \varepsilon_\infty)(2\varepsilon_1 + \varepsilon_\infty)}{\varepsilon_1}$$
$$+ c_2 \frac{N_A \times 10^3 (\varepsilon_\infty + 2)^2 \mu_2^2}{9 \, \varepsilon_0 kT} \qquad (14)$$

where N_A is Avogadros number and c_2 is the concentration in mol l^{-1}. The initial increase in static permittivity with dipole solute concentration will then be expressed by eqn. (15):

$$\frac{d\varepsilon_s}{dc} = \frac{N_A(\varepsilon_\infty + 2)^2 \varepsilon_1^2 \times 10^3}{9 \, \varepsilon_0 kT (2\varepsilon_1^2 + \varepsilon_\infty^2)} \mu_2^2 \qquad (15)$$

From the slopes of the $\varepsilon_s - c$ plots for the solutions of the R_4N^+ salts for concentrations less than 0.06 M (from ~40 to ~50 M^{-1}), application of eqn. (15) with $\varepsilon_\infty = 2$ and $\varepsilon_1 = 9.1$ and assuming all ions to exist in the form of ion pairs, leads to dipole moments for the various R_4N^+ salts of 16 to 18 D (D = 3.3356 × 10^{-30} Cm). This is in reasonable agreement with previous estimates of dipole moments for this class of ion pairs[46] and is indicative of contact ion pairs.

The similar slopes in the $\varepsilon_s - c$ plots for low concentrations of all R_4N^+ perchlorates indicate that the dipole moments are not very dependent upon the size of the cation. This observation implies that the radii of the cations cannot be as different as expected from the length of the alkyl groups. This conclusion conforms with the results from a recent conductivity study of several R_4N^+ perchlorates in dichloromethane,[18] in which a Bjerrum treatment[30] of the conductivity data led to distances of closest approach of from 4.9(3) Å for Et_4NClO_4 to 5.8(3) Å for Dec_4NClO_4. A recent viscosity study on R_4N^+ salts in dichloromethane has similarly shown that R_4N^+ cations with large R-groups "curl up" to form "hard spheres" in this solvent.[47] However, when eqn. (15) was used to calculate the dipole moments it was assumed that all ions were associated. As shown in the conductivity study,[18] this assumption is not correct. In the concentration range where the $\varepsilon_s - c$ plots are linear, some 8 % of Et_4NClO_4 and 12–13 % of Dec_4NClO_4 remain dissociated.[18] The procedure outlined above for the calculation of dipole moments will thus lead to dipole moments which are slightly underestimated, particularly for the salts of the larger cations.

Ph_4AsI and $[PNP]ClO_4$ show a much faster increase in ε_s than the tetraalkylammonium salts. This points to a higher dipole moment for the ion pairs of the former salts. The slope in the $\varepsilon_s - c$ plots for concentrations less than 0.03 M, ~150 M^{-1}, inserted into eqn. (15), but without taking into account that these two salts are considerably more dissociated than the R_4N^+ salts,[18] gives a dipole moment of 30 D. This large dipole moment indicates a greater charge separation, presumably due to solvent molecules being retained in the ion pairs. In the conductivity study it was also concluded that Ph_4As^+ and $[PNP]^+$ salts form solvent-separated ion pairs in dilute solutions in dichloromethane.[18]

In Fig. 3 the permittivity of the solutions is plotted *versus* the concentration of dissolved salts. While this plot gives a correct picture of the concentration dependence of ε_s, it is to be emphasized that the increase due to the ion pairs is opposed by the reduction in solvent dipoles [cf. eqn. (9)]. The permittivity increment due to the ion pair dipoles is therefore slightly larger than shown in Fig. 3. This effect is more pronounced for the salts of the larger cations and for the more concentrated solutions (cf. Table 1). In the concentration range in which the slopes of the plots are constant, however, ε_1 is not significantly different from ε_s and will thus not influence the estimated dipole moments.

The relaxation times, τ_1. In the Debye model for a rotating spherical dipole of radius a, the microscopic relaxation time is related to the bulk solvent viscosity η through eqn. (16):

$$\tau' = \frac{4\pi a^3}{kT}\eta \tag{16}$$

This relaxation time can then be related to the observed macroscopic relaxation time by the Powles-Glarum relation[48] [eqn. (17)]:

$$\tau = \frac{3\varepsilon_s}{2\varepsilon_s + \varepsilon_\infty}\dot{\tau} \tag{17}$$

For a dilute solution of contact ion pairs this leads to a relaxation time, τ_1,[49] given by eqn. (18), where V_φ^0 is the partial molar volume of the salt.

$$\tau_1 = \frac{3\eta V_\varphi^0}{N_A kT} \tag{18}$$

Fig. 4 shows the extrapolated relaxation time, τ_1, versus $V_\varphi^0(R_4NClO_4)$ from Ref. 41. The expected correlation can indeed be observed, in fair agreement with the straight line given by eqn. (18) which is also included in the figure. Complete agreement with eqn. (18) can hardly be expected since the influence of ion pair shape factors has been disregarded.

The relaxation times, τ_1, of Ph_4AsI and $[PNP]ClO_4$ fall completely outside the picture expected for contact ion pairs. The long relaxation time at low concentrations indicates a greater charge separation and provides additional evidence for the suggestion, from both conductivity
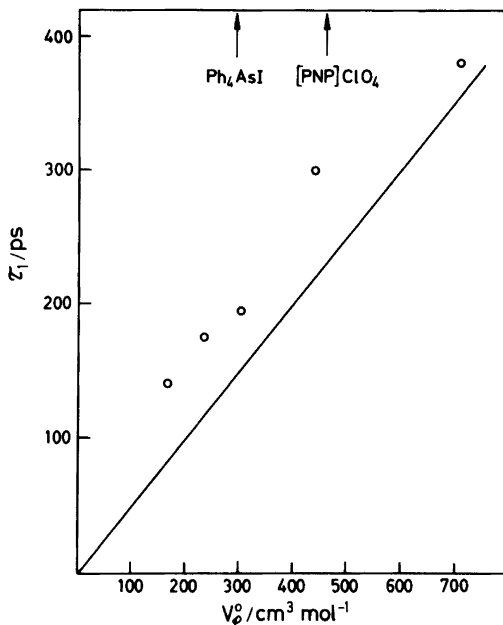
Fig. 4. The relaxation time for R_4NClO_4 (R = Et, Pr. Bu, Hex and Dec), τ_1, extrapolated to infinite dilution versus the partial molar volumes in dichloromethane, V_φ^0. As indicated, τ_1 for Ph_4AsI and $[PNP]ClO_4$ fall outside the diagram.

data[18] and dipole moments, that these two salts form solvent-separated ion pairs in dilute solutions. This agrees with the anomalously rapid increase in ε_s at low concentrations, as displayed in Fig. 3 and discussed above. With increased concentrations of these salts, the relaxation times, τ_1, fall to values similar to those for the $R_4 N^+$ perchlorates of similar size. Apparently, a gradual transformation from solvent-separated ion pairs to contact ion pairs takes place when the concentration increases. As the dipole moment of the ion pairs will change from ~30 D to ~18 D, the slope in the $\varepsilon_s - c$ plots will decrease rapidly (cf. Fig. 3).

While the relaxation times for the perchlorates of the smaller cations are only slightly dependent upon the concentration, the relaxation times for the solutions of Dec_4NClO_4 and Hex_4NClO_4 show a gradual increase as the concentration decreases. This may indicate some increase in the charge separation in the ion pairs. Presumably, in dilute solutions sufficient space will be available for the long alkyl groups to attain conformations

which are more space-demanding than in the "hard spheres". However, the ion pairs may still be considered as contact ion pairs as suggested in the conductivity study.[18]

Effects of increasing the static permittivity on the conductivity of the electrolyte solutions. According to the Bjerrum association theory,[32] the association constant for ion pair formation, K_A, is a function of the permittivity of the solvent. One of the shortcomings of the Bjerrum model is its inability to reproduce the variation in K_A with the permittivity of the solvent without requiring highly specific dependence of a, the centre-to-centre distance in the ion pair, upon the solvent.[50] Denison and Ramsey,[51] using a Born cycle,[52] Gilkerson,[53] using Kirkwood's partition function[54] and Fuoss,[55] applying a method devised by Boltzmann, arrived at the conclusion that K_A should be a continuous function of the permittivity. For a 1:1 electrolyte, K_A is given by eqn. (19), in which K_A^0, a factor characteristic for each salt,

$$K_A = K_A^0 \exp(q^2/akT\varepsilon_s) \qquad (19)$$

includes the effect of interaction between solvent and solute and the free volume of the solute, q is the electronic charge and k is Boltzmann's constant. In the so-called "new" equation by Fuoss,[2] K_A^0 is equal to $4\pi N_A a^3/3000$. Numerous association studies on very dilute electrolytes in solvents of low and medium ε_s have been performed. Bu_4NClO_4, particularly, has been the subject of detailed studies in a number of alcohols, esters, ethers, amines and halogenated hydrocarbons.[56,57] The reasonably linear relationship between the logarithm of the association constant and the reciprocal of the dielectric constant of the solvent, with the expected slope,[58–60] serves as a confirmation of the basic idea embodied in eqn. (19).

The fundamental difference between the Cavell-Knight approach[21] and the Fuoss-Kraus triple ion hypothesis[15] when conductivity data in solvents of low ε_s are to be interpreted is whether the increase in ε_s with concentration of dissolved salt is taken into account or not. The order of magnitude of this difference may be visualized by some numerical calculations. Due to the wealth of data on Bu_4NClO_4[2,18,47,56,57] we will use this compound as an example. The association constant, K_A, in dichloromethane at 25.0 °C is

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2.2×10^4.[1] When the Bjerrum equation[30] is used one arrives at a distance of closest approach, a, of 5.4(2) Å.[18] With Fuoss's "new" eqn.[2] one obtains $a = 5.76$ Å and $K_A^0 = 0.482$. The derived values for a are larger than that calculated from association constants for other solvents, viz. 4.85 Å.[56] This difference seems to be due to the fact that Bu_4NClO_4 is slightly less associated in dichloromethane than expected from the permittivity of the solvent on the basis of the $\log K_A - \varepsilon_s^{-1}$ plot.[56] We will use the Fuoss values for a and K_A^0 of 5.76 Å and 0.482, respectively, in the calculations and consider these two values to be independent of the concentration. This assumption seems to be justified by the negligible slope of the $\tau_1 - c$ plot for Bu_4NClO_4 shown in Fig. 3.

For a 0.2 M solution of Bu_4NClO_4 in dichloromethane, the static permittivity is ~ 13.4. The increase in ε_s will, according to eqn. (19), cause a decrease in K_A from 2.2×10^4 to 6.8×10^2, i.e. to 3.1 % of its value at infinite dilution. A comparison with Dec_4NClO_4 may not be entirely valid, since the relaxation times (Fig. 3) indicate that the distance of closest approach, a, decreases as the concentration increases. If one neglects this probable decrease in a ($a = 6.13$ Å at infinite dilution[1]), the increase in ε_s will reduce K_A from 1.4×10^4 to 1.04×10^3 for a 0.2 M solution, i.e. to 7.4 % of its value in very dilute solution. Thus, while $Dec_4N\ ClO_4$ is more dissociated than $Bu_4N\ ClO_4$ at infinite dilution,[1] the latter salt will be the more dissociated one at 0.2 M.

Fig. 5 shows plots of the ratio, $\Lambda/\Lambda°$, between the molar conductivity and the limiting molar conductivity,[18] and of ε_s versus the logarithm of the concentration for Bu_4NClO_4 and Dec_4NClO_4. While the $\Lambda - c$ curve for the former salt, as for numerous other Bu_4N^+ salts and other salts of small cations,[18] exhibits a distinct minimum and a maximum, the corresponding curve for Dec_4NClO_4 shows only an inflection. It is notable that the ratio $\Lambda/\Lambda°$ for Bu_4NClO_4 starts to exceed that for Dec_4NClO_4 at a concentration where the $\varepsilon_s - c$ curves for the solutions of the salts start to diverge. This observation can hardly be due to a coincidence and seems to confirm the basic idea in the Cavell-Knight approach[21] when conductivity data are to be interpreted.

In a solution of a salt AB one may assume that the following species are present: Single ions A^+ and B^-, ion pairs [AB], triple ions $[ABA]^+$ and $[BAB]^-$, and quadrupoles [ABAB]. In concen-

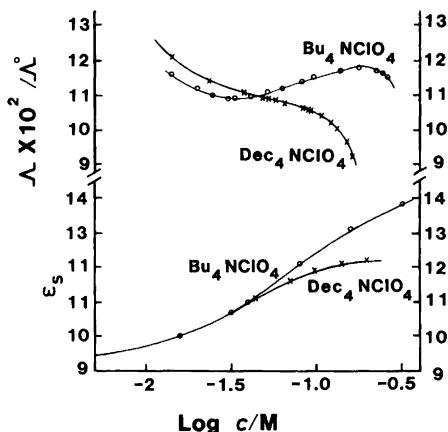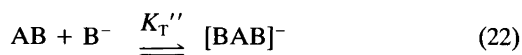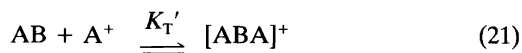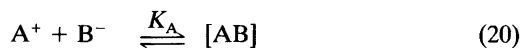Fig. 5. The ratio, $\Lambda/\Lambda°$, between the molar conductivity and the limiting molar conductivity at 25.0 °C, and the permittivity, ε_s, of the solutions at 20.0 °C versus the logarithm of the concentrations of Bu_4NClO_4 and Dec_4NClO_4 in dichloromethane.

trated solutions, larger aggregates, $[AB]_n$, may also be present. Common for the quadrupoles and the larger aggregates is that these species have negligible dipole moments, and their presence will thus not influence the permittivity of the solution.[61] For convenience we will also assume the structure and the dipole moment of the ion pairs to be independent of the concentration, an assumption that appears reasonable for the salts of the smaller R_4N^+ cations, as outlined above. Since no reliable methods are presently available that can allow the activity coefficients for any of the species to be calculated, we will further assume the activity coefficients to be unity for every species. From the equilibria of eqns. (20)–(23), the fraction of single ions (f_1), of ion pairs (f_2),

$$A^+ + B^- \underset{}{\overset{K_A}{\rightleftharpoons}} [AB] \tag{20}$$

$$AB + A^+ \underset{}{\overset{K_T'}{\rightleftharpoons}} [ABA]^+ \tag{21}$$

$$AB + B^- \underset{}{\overset{K_T''}{\rightleftharpoons}} [BAB]^- \tag{22}$$

$$AB + AB \underset{}{\overset{K_{AA}}{\rightleftharpoons}} [ABAB] \tag{23}$$

of triple ions (f_3) and of quadrupoles or higher aggregates (f_4) at a given salt concentration c can be calculated from eqns. (24)–(27) when K'_T and K''_T are assumed to be equal, K_T.[26] According to the

$$f_1 + f_2 + 3f_3 + 2f_4 = 1 \tag{24}$$

$$f_2/f_1^2 = K_A c \tag{25}$$

$$f_3/f_1 f_2 = K_T c \tag{26}$$

$$f_4/f_2^2 = K_{AA} c \tag{27}$$

Cavell-Knight approach,[21] K_T and f_3 will be small or negligible, i.e. only single ions, A^+ and B^-, will contribute to the conductivity. To confirm this approach it is necessary to be able to show that the observed increase in ε_s is of sufficient magnitude to cause f_1 to exhibit a minimum at some particular concentration for some of the studied salts in dichloromethane. Although the Onsager slope[62] in solvents of low permittivity is known to be considerable,[18] and the activity of single ions is anticipated to decrease with increasing concentration, one may expect that the molar conductivity, Λ, will exhibit a minimum at approximately the same concentration as f_1, i.e. $d\Lambda/dc = 0$ when $df_1/dc = 0$.

For numerous salts in dichloromethane the $\Lambda - c$ plots pass through a minimum at ~ 0.03 M.[18] This concentration is sufficiently small to allow approximations in eqns. (28)–(30). ε_s^c is the static

$$f_1 + f_1^2 K_A = 1 \quad (K_{AA} \text{ and } f_4 \text{ small}) \tag{28}$$

$$f_1 = (K_A c)^{-1/2} \quad (K_A \text{ large, i.e. } 4K_A \gg 1) \tag{29}$$

$$\varepsilon_s^c = \varepsilon_s + bc \quad (\text{cf. Fig. 2}) \tag{30}$$

permittivity of the solution at a concentration of dissolved salt equal to c. From eqns. (19) and (29), and after differentiation with respect to c

$$\frac{df_1}{dc} = \frac{f_1}{2c} \left(\frac{d\varepsilon_s^c}{dc} \frac{cq^2}{akT\varepsilon_s^{c2}} - 1 \right) \tag{31}$$

one obtains eqn. (31). From this equation we see that a minimum in the fraction of single ions, f_1, and presumably also in the $\Lambda - c$ curve, can only be obtained when the molar increase in the static

permittivity, $d\varepsilon_s^c/dc$, is larger than given by eqn. (32).

$$d\varepsilon_s^c/dc = \varepsilon_s^{c2} akT/q^2 c \tag{32}$$

Based only upon eqn. (32) it might be argued that f_1 will always pass through a minimum provided the concentration becomes sufficiently large. Eqns. (31) and (32), however, are only valid for fairly low concentrations [cf. eqns. (28)–(30)]. Eqn. (32) would thus suggest that a minimum in $\Lambda - c$ plots is favoured by low permittivity of the solvent. This expection is readily confirmed by the classical study of Fuoss and Kraus[15] on tetraisoamylammonium nitrate in dioxane – water mixtures, and by recent conductivity studies on Bu_4NClO_4 in numerous solvents with ε_s less than 15.[57] From eqns. (33) one would further anticipate this minimum to be more distinct the smaller the centre-to-centre distance, a, in the ion pair, i.e. when contact ion pairs from small ions are formed. The conductivity study on various R_4NClO_4 salts in dichloromethane,[18] and particularly the numerous studies on Li^+ salts in solvents of low permittivity,[19,20,31] show, indeed, that this is the case.

At the minimum in the $\Lambda - c$ plots for R_4NClO_4 in dichloromethane, the static permittivity of the solutions is ~ 10.6. From the right hand side in eqn. (32) one calculates $d\varepsilon_s^c/dc$ for Bu_4NClO_4 and Dec_4NClO_4 to be 39 and 41 M^{-1}, respectively. The experimental values for R_4NClO_4 in dichloromethane are from 40 to 50 M^{-1} (cf. Fig. 3). Apparently, in dichloromethane, with a permittivity of 9.1, the slope is just sufficiently large to allow a minimum to be detected for Bu_4NClO_4. The lack of a minimum in the $\Lambda - c$ curve for Dec_4NClO_4 in dichloromethane[18] is presumably due to the viscosity of the solutions,[47,62] or to quadrupole formation constant, K_{AA}, which is sufficiently large to invalidate the approximation made in eqn. (28). In 1,1-dichloroethane and in 1,2-dichlorobenzene, ε_s in both solvents being 9.9, the $\Lambda - c$ plots for Bu_4NClO_4 exhibit no minimum but only an inflection.[57] In the case of Bu_4NClO_4 it appears that only in solvents with $\varepsilon_s = 9.1$ or less will the association constant, K_A, and the ion pair fraction, f_2, be sufficiently large to create the necessary molar increment in ε_s according to eqn. (32).

The linearity in the $\varepsilon_s - c$ plots for fairly low concentrations (Fig-3) suggests that the fraction

existing as ion pairs, f_2, is rather constant, i.e. $df_2/dc = 0$. As viewed by the permittivity of the solutions, the ion pair concentrations at higher salt concentrations level off gradually to values which are smaller the larger the cations are. The ion pairs are apparently consumed as quadrupoles or as larger aggregates.[67] Above a certain concentration, characteristic for each salt-solvent combination, the formation of quadrupoles and larger species will cause the concentration of ion pairs, f_2c, the permittivity of the solution, ε_s^c, and the association constant, K_A, to remain essentially constant. Thus, the fraction of free ions, f_1, will start to decrease and the $\Lambda - c$ curves will pass through a maximum. This maximum will occur at a concentration which is strongly dependent upon the cation, as can be deduced from the $\varepsilon_s - c$ plots in Fig. 3. This expectation has been confirmed experimentally.[18] These considerations lead to the conclusion that for concentrations above c_{min}, the quadrupole formation constant, K_{AA}, will be the determining factor with regard to the shape of the $\varepsilon_s - c$ and the $\Lambda - c$ plots. Petrucci and co-workers[20] have argued that $\varepsilon - c$ curves of the type shown in Fig. 3 can be rationalized by the existence of two equilibria, one for the formation of ion pairs [eqn. (29)] and one for the formation of quadrupoles from ion pairs [eqn. (30)]. It is apparent that knowledge of the factors determining K_{AA} will be of key importance to further understanding of salt solutions in solvents of low ε_s.

The equilibrium constant for the first equilibrium, K_A, can be obtained by means of the Cavell-Knight approach[21] based upon the Bjerrum equation.[30] The quadrupole formation constant, K_{AA}, however, is not as easily arrived at. If one assumes that the deviation from linearity in the $\varepsilon_s - c$ plots (Fig. 3) is entirely due to the formation of quadrupoles, application of eqns. (24) and (27) allows an estimate of K_{AA}; f_1 in eqn. (24) can be set equal to ~0.1 on the basis of the conductivity data for R_4NClO_4 in dichloromethane. Table 2 summarizes the results for R_4NClO_4 for three arbitrary concentrations, viz. 0.068, 0.100 and 0.150 M, for which the necessary corrections in ε_s due to ε_1 were extrapolated from the data in Table 1. The calculations were based upon the following slopes in the $\varepsilon_s - c$ plots: 40 M^{-1} for Et_4NClO_4 and Pr_4NClO_4, 45 M^{-1} for Bu_4NClO_4 and 50 M^{-1} for Hex_4NClO_4 and Dec_4NClO_4.

Admittedly, the values for K_{AA} listed in Table 2

Table 2. The quadrupole formation constants, K_{AA}, at three concentrations of R_4NClO_4 in dichloromethane at 20.0 °C.

	0.068 M	0.100 M	0.150 M
Et_4NClO_4	≤0.5	≤0.8	~0.8
Pr_4NClO_4	≤0.8	~1	~2.0
Bu_4NClO_4	~1.5	3.0	3.4
Hex_4NClO_4	2.7	5.2	6.1
Dec_4NClO_4	3.3	5.8	7.7

are only to be considered as approximate values. It is notable that K_{AA} increases with the size of the cation and thus with the dipole moment of the ion pair. This is the expected order. The data in Table 2 seem to indicate a trend towards larger values for K_{AA} as the concentration increases. This is also as expected if further association to species larger than quadrupoles takes place.

The nature of the solvent will probably strongly influence K_{AA} and the formation constants of larger species. A reasonable guess is that for isodielectric solvents, the dipole moment of the solvent will be a determining factor, i.e. a high dipole moment will favour ion pairs while a low dipole moment will favour quadrupoles and larger aggregates. A detailed study on Bu_4NClO_4 in several solvents of low static permittivity but of different dipole moments is underway in an attempt to determine the factors that govern the quadrupole formation constants K_{AA}.[57]

Conclusion

The results obtained in the present study seem to suggest that the Cavell-Knight approach[21] based upon strongly concentration dependent ion pair formation constants, K_A, is valid. Although the results may not be conclusive with regard to a complete absence of triple ions, it is felt that the Fuoss-Kraus triple ion hypothesis[3,15] needs to be reconsidered. Petrucci and co-workers[20] have shown that a better fit to conductivity data is obtained when the Cavell-Knight approach is used *in addition* to the Fuoss-Kraus hypothesis. The reverse procedure appears to be more fruitful when the various peculiarities in conductivity data of electrolytes in solvents of low permittivity are to be explained. It is notable that the large conductivity of electrolytes in solvents of low ε_s

is, according to Cavell and Knight,[21] due to an increase in the fraction of single ions, while the Fuoss-Kraus approach leads to an increase in the fraction of triple ions and seriously underestimates the fraction of single ions.

The suggestion by Petrucci and co-workers[20] that $\varepsilon_s - c$ curves can be rationalized by the presence of two consecutive equilibria involving ion pairs and quadrupoles seems relevant. This suggestion, combined with the Cavell-Knight approach[21] and detailed permittivity studies, may lead to an improved knowledge of electrolytes in solvents of low ε_s. Studies of relaxation times appear to be illuminating with regard to the structure of ion pairs.

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