Solvent Properties of Dichloromethane.
VII. Viscosity Studies of Electrolytes in Dichloromethane

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The viscosity of solutions of R_4NClO_4 (R = Et, Pr, Bu, Hex, Oct and Dec),
Bu_4NX (X = BBu_4, SCN and BPh_4), Ph_4AsX (X = Cl, Br, I and SCN) and
$[(Ph_3P)_2N]X$, abbreviated [PNP]X (X = Cl, SCN and ClO_4), in dichloromethane
have been measured for concentrations up to ~0.2 M at 25 °C. The plots of the
relative viscosity, η/η_0, vs. concentration are linear for all R_4N^+ salts but are
slightly curved for Ph_4As^+ and $[PNP]^+$ salts.
    The viscosity data have been analyzed according to the Jones-Dole eqn. and
the viscosity B coefficients have been determined. The B_+ and B_- coefficients
have been evaluated by means of the $B_+(Bu_4N^+) = B_-(Bu_4B^-)$ assumption. A B_+
vs. V_φ° plot for the R_4N^+ cations, except Et_4N^+, is linear, passes through the
origin, and has a slope in agreement with the Einstein viscosity equation. From
the B_- coefficients the "solvation numbers" of the anions in dichloromethane
have been calculated.

Studies of transport properties of electrolyte so-
lutions have proved to give useful information
with regard to both solvent composition and ion-
solvent interactions. In previous studies on so-
lutions of onium salts in dichloromethane the
conductivity method has been applied.[1,2] This pa-
per describes the measurement of the momentum
transport property, i.e. the viscosity, of this
group of electrolyte solutions.

   Numerous viscosity studies of aqueous electro-
lytes made during the last century[3,4] have shown
that the viscosity of dilute solutions follows the
Jones-Dole equation,[5] eqn. (1).[6-8] η is the viscos-

$$\eta/\eta_0 = \eta_{rel} = 1 + Ac^{1/2} + Bc \qquad (1)$$

ity of the electrolyte solution, η_0 is the viscosity of
the solvent, c is the concentration, while A and B
are characteristic constants for the solute. Recent
studies have shown that the inclusion of an addi-
tional term, Dc^2, in the equation may be neces-
sary for higher concentrations, viz. $c > 0.1$ M.[4,9]
The A coefficient is a measure of long-range cou-
lombic forces, i.e. ion-ion interactions, and has a
sound theoretical background in the Falkenha-

gen-Vernon eqn.[10] The B coefficient, generally
termed the viscosity B coefficient, is a measure of
ion-solvent and solvent-solvent interactions, and
is by far the most significant coefficient in eqn.
(1). Most discussions of solvent-structural fea-
tures of solution viscosities have centered around
the B coefficient and its ionic contributions, B_+
and B_-.[11] Unfortunately, this coefficient cannot
be calculated a priori for the various solute-sol-
vent systems. The D coefficient, which in most
cases is small or negligible, is believed to depend
upon higher terms of ion-solvent and ion-ion in-
teractions, together with higher terms of the
hydrodynamic effect.[9] The significance of D is at
present not fully understood.[4]
   Tuan and Fuoss[12] pointed out that viscosity
data for solutions in non-aqueous solvents may
be simpler to interpret because complications due
to water structure can be excluded. In recent
years, the viscosity of solutions of a large number
of salts in several dipolar aprotic solvents and
alcohols, and in mixtures of these solvents, has
been studied.[11-21] For all the non-aqueous solvent
systems, the Jones-Dole eqn. [eqn. (1)], with or
without the Dc^2 term for higher concentrations,

has been found to be valid. A common feature for most systems studied has been that the combination of salt and solvent has allowed the presence of species other than dissociated ions to be neglected. Effects due to ion pairs have rarely been considered.[13, 22-24] For this type of solute-solvent systems the Jones-Dole eqn. has been restated by introducing the degree of dissociation, α, combined with separate B coefficients for dissociated ions, B_i, and for ion pairs, B_p [eqn. (2)].

$$\eta_{rel} = 1 + A(\alpha c)^{1/2} + B_i\alpha c + B_p(1 - \alpha)c \qquad (2)$$

For some solute-solvent systems, notably KIO_3 and $AgNO_3$ in water,[22] and $MgSO_4$ in water-ethanol mixtures,[24] B_p appears to be significantly smaller than B_i. For a number of other systems the effect of ion pair formation on the viscosity has been too small to measure. Ion pairing may therefore have little influence on the B coefficient, i.e. $B_p \sim B_i$.[24]

The latter conclusion, however, is based upon studies in water, and in mixtures of water and organic solvents in which the degree of association is not extensive. Furthermore, the uncertainties due to water structure will always exist for this class of electrolytes.[12] In a weakly structured solvent like dichloromethane one may assume that complications of this type will be absent. In this solvent, in which the fraction of ionic species in the $5 \times 10^{-3} - 2 \times 10^{-1}$ M concentration range is only ~ 0.1 for most R_4N^+ salts (~ 0.2 for Bu_4NBBu_4), ~ 0.3 for Ph_4As^+ salts and ~ 0.4 for $[PNP]^+$ salts,[1,2] the presence of species other than dissociated ions must necessarily be taken into account.

Experimental

Materials. The onium salts and dichloromethane were purified as described previously.[1,2,26,27] The salt solutions were generally studied up to ~ 0.2 M, exceptions being Et_4NClO_4 and Bu_4NBPh_4 owing to their limited solubility.[26] The solvents employed for calibration of the viscometer were purified according to standard procedures.[28]

Measurements. An Ubbelohde suspended-level viscometer with photoelectric timing and with a flow-time of 102.0 s for water at 25.00 °C was used. The viscometer was calibrated according to

$$\eta_o/d = Et - F/t \qquad (3)$$

eqn. (3). η_0 is the viscosity of the solvent, d is the density, t is the efflux time, while E and F are the viscometer constants. The following solvents were used for calibration: Water, $\eta_o = 0.8903$ cP;[29] benzene, $\eta_o = 0.5996$ cP;[30] dioxane, $\eta_o = 1.937$ cP;[31] hexane, $\eta_o = 0.2952$ cP;[31] decane, $\eta_o = 0.8555$ cP; methanol, $\eta_o = 0.5450$ cP.[33] The calibration was checked periodically and the viscometer constants, E and F, were found to be constant within experimental error during the study. The viscosity of pure dichloromethane was found to be 0.4120(5) cP at 25.00 °C.

All determinations of efflux times were repeated until five successive measurements agreed to within 0.01 s. A minimum of six concentrations were studied for each salt. The maximum overall uncertainty in each of the viscosities was estimated to be 0.1 %. The relative viscosity, η_{rel}, was calculated by eqn. (4), where t, t_o, d and d_o

$$\eta/\eta_o = \eta_{rel} = td/t_od_o \qquad (4)$$

are the efflux times and the densities of the solution and the solvent. The densities of the solutions were determined with a Paar DMA 601 density meter as described.[26]

Kay *et al.*[34] have suggested that certain corrections for kinetic energy and efflux time have to be made when viscosities of solutions of salts of large organic ions are determined. The origin of these corrections is adsorption of such ions on the walls of the capillary.[9] No such corrections were found to be necessary but some difficulties with regard to reproducibility were experienced for the most concentrated solutions of Bu_4NBBu_4, Dec_4NBr and Dec_4NClO_4.

The temperature during the density and viscosity measurements was 25.00 °C, and was controlled to better than 0.01 °C with a Hewlett-Packard quartz thermometer.

Results and discussion

Determination of A, B and D. Results from viscosity studies are usually analyzed according to the extended Jones-Dole eqn., eqn. (5).[8,9] This

$$\eta_{rel} = 1 + Ac^{1/2} + Bc + Dc^2 \qquad (5)$$

$$(\eta_{rel} - 1)c^{-1/2} = A + Bc^{1/2} + Dc^{3/2} \qquad (6)$$

$$(\eta_{rel} - 1 - Ac^{1/2})c^{-1} = B + Dc \qquad (7)$$

eqn. can be rearranged to eqns. (6) and (7), which are more useful for the graphical determination of A, B and D. A for all solute-solvent systems is numerically small compared with B, and the $Ac^{1/2}$ term is quickly swamped by the much larger linear term, Bc.

Viscosity plots according to eqns. (5)–(7) are, for most solute-solvent systems, remarkably linear. The B coefficient, and in a few cases the A and the D coefficients, can therefore be determined with great accuracy. Crudden et al.,[23] however, have pointed out that the linearity of viscosity plots can be deceptive and may lead to consid-

erable uncertainty with regard to the B coefficient. The cause of this uncertainty seems to be the A coefficient, which can only be determined in very dilute solutions.[35] Theoretically, the A coefficient for a dilute and completely dissociated 1:1 electrolyte can be calculated by the Falkenhagen-Vernon eqn.[10] [eqn. (8)], on the basis of the

$$A = \frac{0.2577 \, \Lambda^\circ}{\eta_o(\varepsilon_o T)^{1/2}\lambda_+^\circ\lambda_-^\circ}\left[1-0.6863\left(\frac{\lambda_+^\circ - \lambda_-^\circ}{\Lambda^\circ}\right)^2\right] \qquad (8)$$

limiting equivalent conductivity of the salt, Λ°, the cation, λ_+°, and the anion, λ_-°. η_o and ε_o repre-
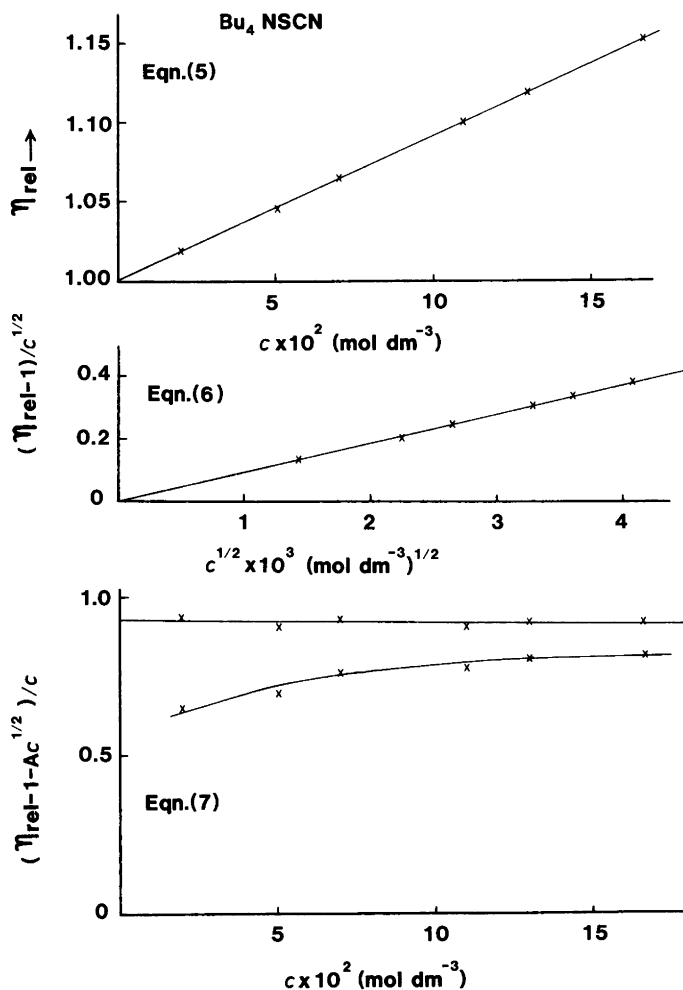

Fig. 1. Viscosity plots according to eqns. (5), (6) and (7) for Bu₄NSCN in dichloromethane at 25.00°C.

sent the viscosity and the permittivity of the solvent, respectively.

Fig. 1 shows viscosity plots for Bu_4NSCN according to eqns. (5), (6) and (7). These plots are characteristic for all R_4N^+ salts examined. The upper plot, eqn. (5), indicates that A cannot be significantly different from zero. The value of B from this plot, 0.92(2) dm^3mol^{-1}, and the negligible value of A seem to be confirmed by the next plot, eqn. (6). The linearity in the latter plot suggests that the D coefficient cannot be significant. Thompson and co-workers,[17,18] in their studies on electrolytes in N-methylacetamide and ethylene carbonate, have found small positive D coefficients which tend to increase in an approximately linear manner with B^2. No such trend was evident from the present data on R_4N^+ salts. The lower curves in Fig. 1 show plots of $(\eta_{rel} - 1 - Ac^{1/2})/c$ [eqn. (7)] for $A = 0$ (upper curve) and for $A = 0.0453$ $dm^{3/2}$ $mol^{-1/2}$, the theoretical value at infinite dilution[10] (lower curve). When $A = 0$, D will be negligible and B attains the ex-

pected value. The shape of the lower curve indicates that the theoretical value of A, or a value of A less than the theoretical one, will lead to a decrease in the B coefficient and to a positive D coefficient which decreases with concentration. Apparently, viscosity data for R_4N^+ salts in dichloromethane seem to fit the Jones-Dole eqn. in which both A and D can be neglected, i.e. eqn. (9). Reliable values of B coefficients for this class

$$\eta_{rel} = 1 + Bc \qquad (9)$$

of salts can thus be obtained from simple $\eta_{rel} - c$ plots. Fig. 2 shows some representative plots according to eqn. (9). However, the uncertainty with regard to the A coefficient will not allow the B coefficients to be given with more than two digits. Table 1 gives a summary of the B coefficients with uncertainties evaluated from plots according to eqns. (5) and (6).

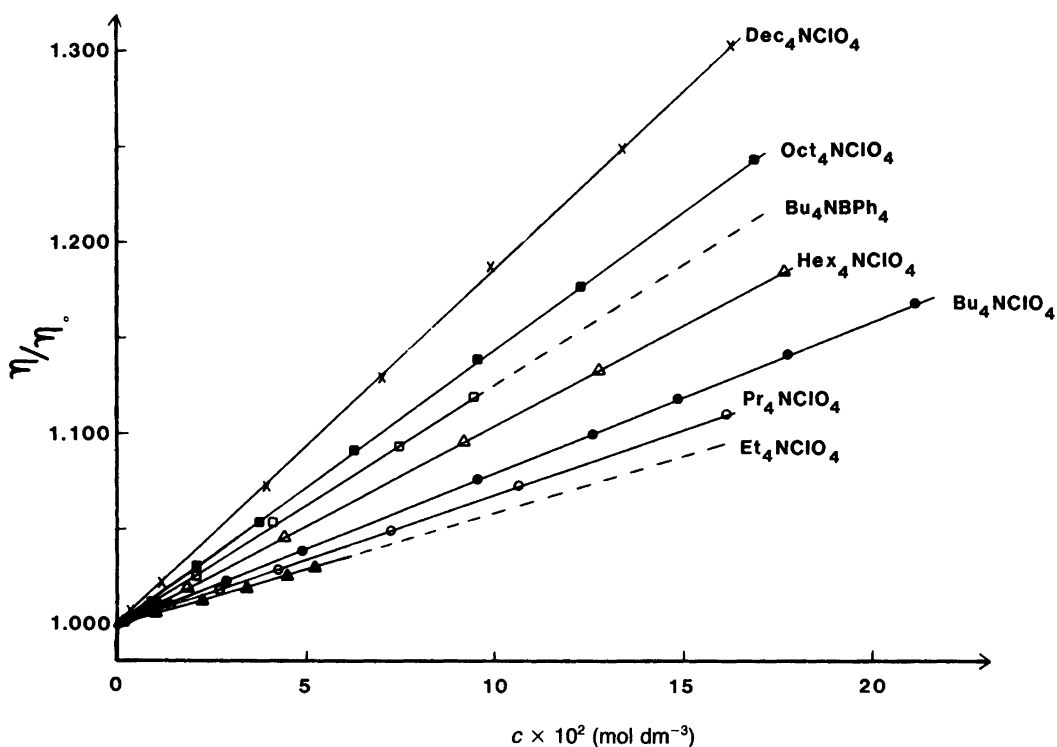The negligible A coefficients can probably be explained by the low degree of dissociation.[14]

Fig. 2. $\eta_{rel} - c$ plots for some R_4N^+ salts in dichloromethane.

Table 1. Viscosity *B* coefficients in dichloromethane at 25.00 °C.

Salt	$B/dm^3\ mol^{-1}$
Et_4NClO_4	0.53(3)
Pr_4NClO_4	0.63(5)
Bu_4NClO_4	0.82(2)
Hex_4NClO_4	1.11(8)
Oct_4NClO_4	1.48(12)
Dec_4NClO_4	1.83(17)
Bu_4NSCN	0.92(2)
Bu_4NBBu_4	1.38(6)
Bu_4NBPh_4	1.44(4)
Ph_4AsCl	1.08(8)
Ph_4AsBr	1.17(10)
Ph_4AsI	0.98(8)
Ph_4AsSCN	0.98(8)
[PNP]Cl	1.78(10)
[PNP]SCN	1.66(8)
[PNP]ClO_4	1.53(6)

From the conductivity studies it is known that only some 10 % of most R_4N^+ salts exist as dissociated species in the concentration range employed.[1,2] One may therefore assume that the *A* coefficients will not exceed 10 % of the theoretical values calculated by eqn. (8). These values are only from 3.3 % (Dec_4NClO_4) to 7.3 % (Et_4NClO_4) of the values of the corresponding *B* coefficients. The significant increase in the permittivity of the solutions, $d\varepsilon/dc$ being $\sim$50 M^{-1} for concentrations up to $\sim$0.07 M,[27] will further decrease the *A* coefficients as the concentration increases [cf. eqn. (8)].

Fig. 3 shows $\eta_{rel} - c$ plots for some [PNP]$^+$ and Ph_4As^+ salts. In contrast to the plots for the R_4N^+ salts (Fig. 2) these plots are curved; only from $\sim$4 × 10^{-2} M upwards are the plots linear. This curvature leads to extrapolated values of η_{rel} at c = 0 which are less than unity. Previous studies on the density of this class of electrolytes have re-
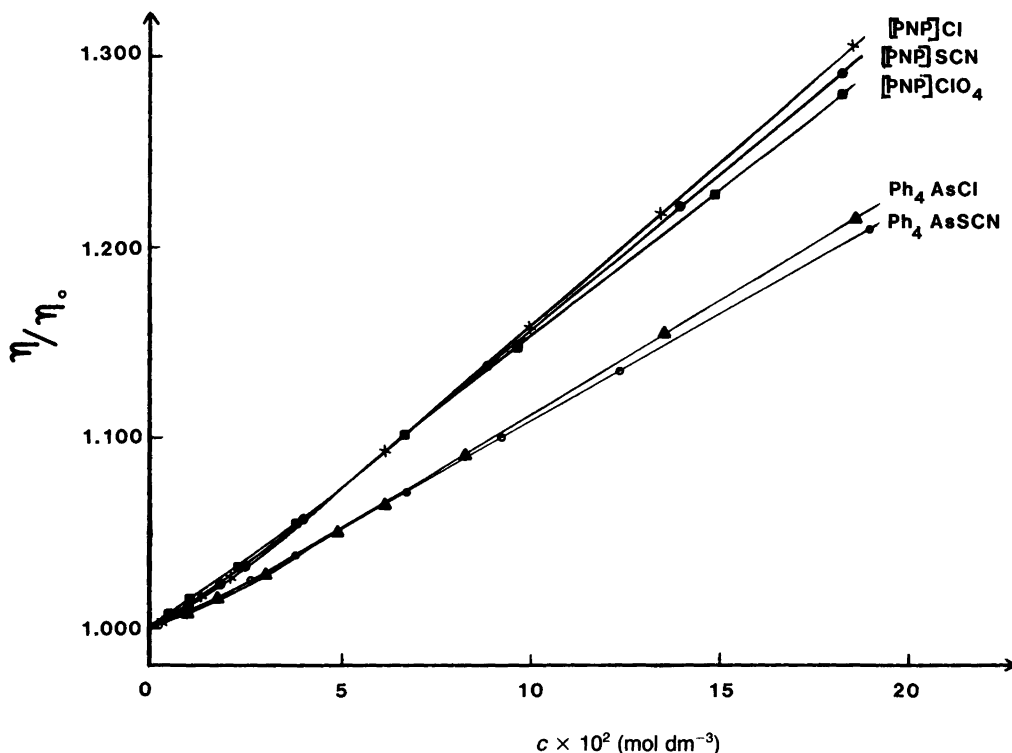
Fig. 3. $\eta_{rel} - c$ plots for [PNP]$^+$ and Ph_4As^+ salts in dichloromethane.

vealed that the $d - c$ plots are slightly curved, with decreasing slopes with increasing concentration.[26] This deviation from linearity in the $d - c$ plots, would, according to eqn. (4), lead to an opposite curvature in the $\eta_{rel} - c$ plots, and thus to extrapolated values of η_{rel} larger than unity. [PNP]$^+$ and Ph$_4$As$^+$ salts are known to be distinctly more dissociated than R$_4$N$^+$ salts.[1,2] One may therefore expect the former salts to have the larger A coefficients [cf. eqn. (8)]. A contribution by the $Ac^{1/2}$ term at low concentration, however, would also lead to extrapolated values of η_{rel} larger than unity. Concentration-dependent B coefficients can hardly be the cause of the nonlinear $\eta_{rel} - c$ plots. This would imply that solvent-separated ion pairs with a dipole moment of ~ 30 D,[27] the predominant species in dilute solution, were contributing less to the viscosity than contact ion pairs with a dipole moment of ~ 20 D and quadrupoles or larger species of negligible dipole moment.[36] The solute dipole moment is known to be a determining factor with regard to the size of the B coefficient.[37]

Seidel and co-workers[38] have argued that viscosity plots of the type shown in Fig. 3 are to be expected when the solvent is sufficiently perturbed by the solute species [eqn. (10)]. Eqn. (10) introduces a concentration-dependent con-

$$\eta_{rel} = 1 + Ac^{1/2} + Bc + \Delta\eta_{rel}c. \qquad (10)$$

tribution from the solvent, $\Delta\eta_{rel}c$. According to the domain theory of dilute electrolytes,[38] $\Delta\eta_{rel}$ may attain both positive and negative values, depending upon the efficacy of the ions to create small or large domains in the solution. Cations, particularly cations capable of interacting with the solvent, seem to favour the formation of larger domains with negative $\Delta\eta_{rel}$. Since Ph$_4$As$^+$ and [PNP]$^+$ ions, in contrast to R$_4$N$^+$ ions, interact with the solvent molecules, this effect alone may be the cause of the observed curvature in the $\eta_{rel} - c$ plots (Fig. 3). It is surprising, however, that this effect can be detected in a weakly associated and a weakly associating solvent like dichloromethane.

Anomalous A coefficients, i.e. negative A coefficients, are generally considered to be without physical significance.[7] This conclusion is obviously correct when ion-ion interactions in the sense of the usual cation-anion interactions are considered [cf. eqn. (8)]. The question arises, however, as to whether aggregates from cations can be formed in dilute solutions. [PNP]$^+$ salts and salts of the [{(4-MePh)$_3$P}$_2$N]$^+$ cation undoubtedly exhibit some unique type of association in dilute aqueous solution.[39,40] Hemmes[41] has argued that cation-cation association is to be anticipated for salts of large cations, particularly in solvents of low permittivity. The conductivity studies in dichloromethane, however, have provided no evidence of cation-cation association.[1,2] Provided the curvature in the $\eta_{rel} - c$ plots (Fig. 3) is due to negative A coefficients, viscosity studies may be superior to conductivity studies in detecting association patterns different from the usual cation-anion type. It is interesting to note that studies of chlorides of multivalent metal cations in ethanol lead to $\eta_{rel} - c$ plots of the type shown in Fig. 3.[35]

Regardless of the origin of the curvature in the viscosity plots (Fig. 3), it is apparent that the accuracy of the B coefficients will suffer. We have chosen to consider the slopes of the linear part of the plots, i.e. the slopes for concentrations higher than ~ 0.04 M, as being equal to the B coefficients. These are listed in Table 1 together with the corresponding coefficients for the R$_4$N$^+$ salts. No reliable information could be obtained from plots of $(\eta_{rel} - 1)/c$ vs. c [eqn. (7)] (cf. the corresponding plot for Bu$_4$NSCN in Fig. 1). Since the right-hand side of eqn. (7), i.e. $B + Dc$, for [PNP]$^+$ and Ph$_4$As$^+$ salts seems to be independent of c for concentrations above $\sim 7 \times 10^{-2}$ M, the D coefficients will be negligible. Extrapolation to $c = 0$ of plots according to eqn. (7) is particularly unreliable but leads to B coefficients in very dilute solutions which are from 0.4 dm^{3}mol^{-1} (Ph$_4$AsCl) to 0.2 dm^{3}mol^{-1} ([PNP]ClO$_4$) less than the B coefficients listed in Table 1.

The B coefficients. The B coefficients increase with increasing size of the R$_4$N$^+$ cations. For salts of cations containing several phenyl groups, [PNP]$^+$ and Ph$_4$As$^+$, the B coefficients are significantly larger than those for salts of R$_4$N$^+$ cations of comparable size. The weak dependence upon the size of the anions suggests that the anionic contribution to B, B_-, is small compared with B_+. These observations are in general agreement with results from viscometric studies of onium salts in dipolar aprotic solvents. The B coefficients for the various salts are comparable to those observed in acetonitrile,[12,34] acetone,[13]

methanol,[13,34] nitrobenzene,[13] N-methylforma-mide,[42] sulfolane,[43,44] N,N-dimethylformamide[16] and dimethyl sulfoxide.[14,15,45,46] The B coefficients are slightly larger than in ethylene carbonate,[19,47] but are distinctly smaller than in N-methylprop-ionamide[48] and in hexamethylphosphoric tria-mide, HMPA.[15] This comparison seems to con-firm the suggestion that B coefficients in organic solvents are in some way related to the molar volume, V_φ^s, and the dipole moment, μ^s, of the solvent[15,18,47] [eqn. (11)]. The first term in eqn. (11), αV_φ^s, is the predominant one for salts of

$$B = \alpha V_\varphi^s + \beta \mu^s \qquad (11)$$

large organic ions. The $\beta\mu^s$ term, a measure of ion-dipole or solute-solvent interactions, is small or negligible for large organic ions with aliphatic substituents, but is considerable for salts of small anions in acceptor solvents and for salts of small cations in donor solvents. It is notable that the degree of self-association and the viscosity of the solvent do not contribute significantly to the B coefficients (cf. the rather similar viscosity B coefficients for most R_4N^+ salts in dimethylsul-foxide, $\eta_o = 2.000$ cP,[15] and in dichloromethane, $\eta_o = 0.4120$ cP). The molar volumes of the two solvents are rather similar, viz. 71.3 cm³mol⁻¹ for DMSO[15] and 64.5 cm³ mol⁻¹ for CH_2Cl_2.[49] Appar-ently, a fundamental difference exists between the two types of transport properties of electro-lytes, viscosity and conductivity (cf. Walden's product, $\eta_o\Lambda^\circ \sim$ constant).

Characteristic for all solvents mentioned above, with the exception of acetone, is that their permittivity, ε_o, is significantly greater than 20. The onium salts are therefore extensively dis-sociated, and the viscosity increments for the electrolyte solutions are due to cations and anions only. In dichloromethane, only small frac-tions of the dissolved salts exist as dissociated species; the rest, up to ~90% for most R_4N^+ salts,[1,2,26] exists in the form of various types of ion pairs, as quadrupoles and presumably also as larger aggregates in the most concentrated so-lutions. Nevertheless, the $\eta_{rel} - c$ plots are re-markably linear throughout the studied concen-tration range for the R_4N^+ salts and above ~4×10⁻² M for the [PNP]⁺ and the Ph_4As^+ salts (cf. Figs. 2 and 3). Although the fractions of the dissolved salts which exist as dissociated ions are rather independent of the concentration,[1,2] the

fractions of the ion pairs and also their structure are highly dependent upon the concentration. In the more concentrated solutions the fractions of quadrupoles and higher aggregates seems to in-crease while those of ion pairs level off to asymp-totic values.[27]

Apparently, each molecule of the dissolved salts, regardless of which form they exist in, con-tributes equally to the increase in the solution viscosity. As mentioned in the introduction, the effect of ion pairing upon viscosity B coefficients has rarely been commented upon. Vivo et al.,[24] in their study on Na_2SO_4 in water-ethanol mixtures, observed that the B coefficient decreases slightly with increasing content of ethanol, whereas the B values for the free ions and the ion pairs are not significantly different. In the case of $MgSO_4$ in the same solvent mixtures, the B coefficient for the ion pair is calculated to be less than that for the dissociated salt. Tominaga[13] has commented upon the linearity of viscosity plots for Bu_4NCl in acetone, K_A being 430(5) at 25.00°C, and con-cluded that ion pair formation does not, at least apparently, influence the B coefficient for this solute-solvent system. This conclusion, and the results obtained in the present study, suggest that a Jones-Dole eqn. with different B coefficients for ions and ion pairs [eqn. (2)][14] cannot be gene-rally applicable for onium salts in organic sol-vents.

The ionic contributions, B_+ and B_-. Since the viscosity B coefficients are independent of the type of species present in the solution, these co-

Table 2. Ionic viscosity coefficients, B_+ and B_-, in dichloromethane at 25.00°C.

Cation	$B_+/dm^3\ mol^{-1}$	Anion	$B_-/dm^3\ mol^{-1}$
Et_4N^+	0.40	Cl^-	0.33
Pr_4N^+	0.50	Br^-	0.29
Bu_4N^+	0.69[a]	I^-	0.23
Hex_4N^+	0.98	SCN^-	0.23
Oct_4N^+	1.35	ClO_4^-	0.13
Dec_4N^+	1.70	Bu_4B^-	0.69[a]
Ph_4As^+	0.75	Ph_4B^-	0.75[b]
[PNP]⁺	1.40		

[a]Based upon the $B_+(Bu_4N^+) = B_-(Bu_4B^-)$ assumption [eqn. (12)]. [b]Calculated from B coefficients for Bu_4NSCN, Ph_4AsSCN and Bu_4NBPh_4.

efficients may be regarded as coefficients for the dissociated ions. The B coefficients may therefore be split into their ionic contributions, B_+ and B_-. Numerous methods for carrying out this separation into the ionic contributions have been suggested[11,50,52] (for a recent critical survey, see Ref. 18). Recently, the $V_\varphi^\circ(Bu_4N^+) = V_\varphi^\circ(Bu_4B^-)$ and the $\lambda^\circ(Bu_4B^+) = \lambda^\circ(Bu_4N^-)$ assumptions have been used quite successfully to analyze volumetric and conductivity data for solutions in dichloromethane.[1,2,23] In this work we have therefore used the additional assumption that the Bu_4N^+ ion and the Bu_4B^- ion contribute equally to the B coefficient for Bu_4NBBu_4 [eqn. (12)].

$$B_+(Bu_4N^+) = B_-(Bu_4B^-) = \tfrac{1}{2}B(Bu_4NBBu_4) \quad (12)$$

This salt has previously been used as a reference salt by a number of authors.[15,16,18,53] An internal analysis of the B coefficients listed in Table 1 based upon eqn. (12) gave consistent values of B_+ for all ions within experimental error. It is of particular interest that the B coefficients for Ph_4AsSCN, Bu_4NSCN and Bu_4NBPh_4 lead to

$B_+(Ph_4As^+)$ equal to $B_-(Ph_4B^-)$. This observation supports the conclusion that the slopes of the linear parts of the viscosity plots for the Ph_4As^+ salts, and presumably also for the $[PNP]^+$ salts (Fig. 3) represent the true B coefficients for these salts in dichloromethane. Table 2 summarizes the calculated B_+ and B_- coefficients. Fig. 4 shows a plot of $B_\pm$ vs. the limiting equivalent conductivity, $\lambda_\pm$, from Ref. 2. The expected inverse relationship for the R_4N^+ ions is apparent, with the notable exception of Et_4N^+. Presumably, the structure of this cation is sufficiently open to allow some interaction between the positively charged nitrogen atom and the basic chlorine atoms of the solvent molecules. The ability of dichloromethane to act as a weak donor towards electropositive species has been observed previously.[54-56] Me_4N^+ salts cannot be studied viscometrically in dichloromethane due to the limited solubility of this class of salts. Since the limiting equivalent conductivity of the Me_4N^+ ion in CH_2Cl_2 is less than that of the Et_4N^+ ion,[57] the B_+ coefficient for Me_4N^+ will probably exceed that for the Et_4N^+ ion. The B_- coefficients for the
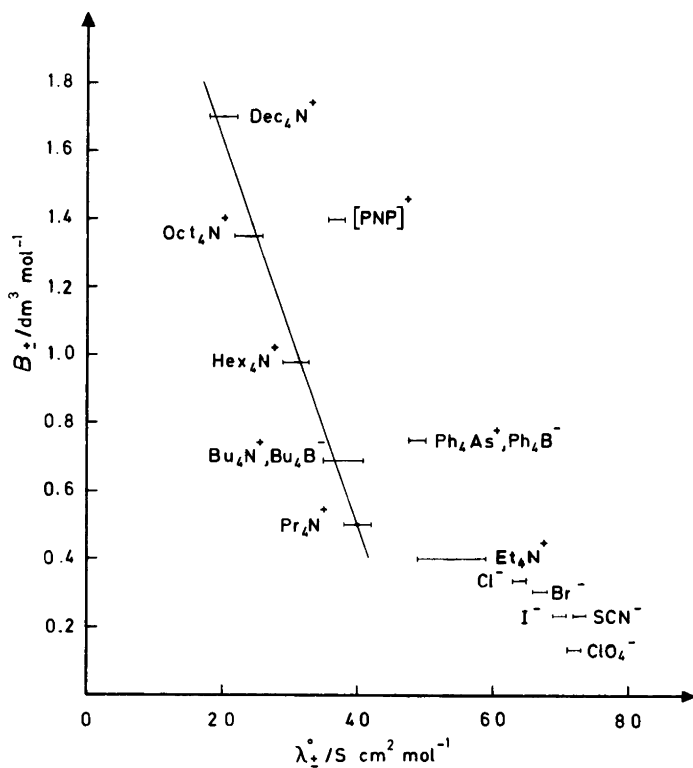

Fig. 4. Ionic B coefficients, $B_\pm$, vs. the limiting molar conductivity of the ions, $\lambda_\pm^\circ$, in dichloromethane.

inorganic anions are significantly larger than in several organic solvents of the donor type but are comparable to the coefficients observed in methanol.[18] The order of B_-, i.e. $Cl^- > Br^- > I^-(SCN^-) > ClO_4^-$, is as expected for a solvent which is predominantly of the acceptor type.

In the case of an idealized model of spheres in a continuum, the viscosity of the solution should increase according to the Einstein eqn., eqn. (13), where φ is the fraction of the total volume occupied by the spheres. If one assumes that this

$$\eta_{rel} - 1 = 2.5 \, \varphi \tag{13}$$

fraction of the total volume is equal to $V_\varphi^\circ c$, V_φ° being the partial molar volume of the solute, and that eqn. (12) is solely responsible for the B coefficient in the Jones-Dole eqn., one obtains:

$$B = 0.0025 \, V_\varphi^\circ \tag{14}$$

when B is in $dm^3 mol^{-1}$ and V_φ° is in $cm^3 mol^{-1}$.[26] Fig. 5 shows a test of this expectation. For the

R_4N^+ cations the agreement with eqn. (14) is excellent; only Et_4N^+ deviates positively, presumably owing to ion-dipole interaction with the solvent as outlined above. A similar deviation for this ion has been observed in methanol[13] and in some solvents of the donor type.[17,18] It is notable that the point for the perchlorate ion lies close to the theoretical Einstein line. It has previously been concluded that this ion is essentially unsolvated by dichloromethane.[2] The trend displayed by the halide ions is as expected. The points for the ions containing phenyl groups, i.e. Ph_4As^+, Ph_4B^- and $[PNP]^+$, lie significantly above the theoretical line. This is as observed with a number of solvents, water, however, being a notable exception.[13] Presumably, organic solvent molecules are able to enter the void space between the rigid phenyl groups.

The Einstein line [eqn. (13)] will necessarily pass through the origin. The fact that the points for all R_4N^+ ions, except Et_4N^+, and ClO_4^- lie on this line is in marked contrast to what is observed with a number of organic solvents. Generally, the
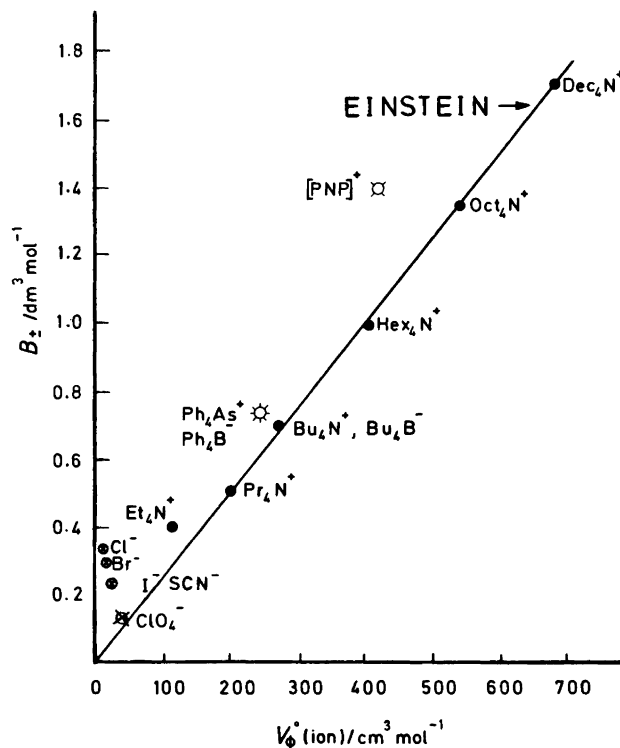

Fig. 5. Ionic B coefficients, $B_\pm$, vs. the partial molar volume of the ions, V_φ°. The solid line is calculated from the Einstein viscosity eqn. [eqn. (13)].

points for R_4N^+ ions lie along a line below, but parallel to, the Einstein line. This has been explained by considering a solvent molecule as a solute in the solvent causing the Einstein line to cross the V_φ^o axis at V_φ^s, the molar volume of the solvent. It has therefore been suggested that eqn. (15) is a more appropriate form for the relation

$$B = 0.0025 \, (V_\varphi^o - V_\varphi^s) \qquad (15)$$

between the viscosity B coefficients and the molar volumes of the solutes.[13,17,18] Provided eqn. (15) is correct, the use of eqn. (14) will necessarily lead to underestimation of ion-dipole interactions, particularly for ions of small size. Some idea of the average number of solvent molecules, n_s, that comprise the solvation shell of an ion may be obtained from a combination of the Einstein viscosity equation[58] and the Jones-Dole equation,[8] eqn. (16):[45]

$$B = (4/3N_A r_\pm^3 - n_s V_\varphi^s)/400 \qquad (16)$$

where N_A is Avogadro's number and $r_\pm$ is the ionic radius. This eqn. assumes that the ion-solvent complexes are spherical. On replacing $4/3N_A r_\pm^3$ by the partial molar volumes of the ions, V_φ^o,[23] one obtains the following values for n_s (solvation numbers from the conductivity study in parentheses):[1,2] $Cl^- \sim 2.0(2)$, $Br^- \sim 1.6(1.5)$, $I^- \sim 1.0(1.1)$, $SCN^- \sim 1.0(1)$, $ClO_4^- \; 0.23(0)$. The excellent agreement between the two sets of results, the one based upon viscosity data in the $10^{-3} - 10^{-1}$ M region and the other on conductivity data in the 10^{-5} M region,[1,2] seems to indicate that an Einstein line through the origin, [eqn. (14)] is a proper choice when viscosity data are to be interpreted with regard to solvation of small ions. Furthermore, if the larger R_4N^+ ions were solvated by dichloromethane by some type of hydrophobic interaction, one would anticipate non-charged aliphatic compounds to exhibit a similar effect. B coefficients for this class of compounds, however, are negligible and even negative in organic solvents;[17,18,59] only non-charged aromatic compounds have distinctly positive B coefficients in a solvent like dichloromethane.[49] Generally, the viscometric behaviour of Et_4C, Bu_4C and Ph_4Si is completely different from that of Et_4N^+, Bu_4N^+ and Ph_4As^+ in organic solvents.[14,49]

Conclusion

The most significant finding of this study based on the viscosity behaviour of solutions of onium salts in dichloromethane is that no conclusions of any kind can be drawn with regard to the nature of the various dissolved species (dissociated ions, ion pairs, quadrupoles etc.) and their individual concentrations. In fact, with the possible exception of dilute solutions of Ph_4As^+ and $[PNP]^+$ salts, the viscosity data do not even indicate that onium salts are extensively associated in dichloromethane. It is apparent that viscosity studies in organic solvents without concomitant conductivity studies are of limited value. The viscosity B coefficients for the various salts are governed by the size of the ions and are as observed in a number of organic solvents of comparable molar volume and of comparable donor and acceptor strength. B coefficients for salts in organic solvents are essentially independent of the solvent viscosity and the solvent permittivity (and thus the association constant), but seem to increase with the molar volume of the solvent.

The linearity of the Einstein plot for the larger R_4N^+ ions, with the expected positive deviation for Ph_4As^+, Ph_4B^- and $[PNP]^+$, may suggest that all species present in the solutions are approximately spherical. Although all ions, except the bent or cylindrical $[PNP]^+$ cation, can undoubtedly be considered as spheres, this conclusion can only be correct provided the salts are completely dissociated. The various types of ion pairs and larger aggregates, these species being the predominant ones in dichloromethane, can hardly assume forms of the spherical type. Since viscosity increments for prolate and oblate particles seem to be less different from those for spherical species than is generally recognized,[60-62] linear Einstein plots may be deceptive and should not form the basis for extensive conclusions with regard to the form of the dissolved species.

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