

Conductometric and Dielectric Behaviour of Solutions of Tetrabutylammonium Perchlorate in Solvents of Low and Medium Permittivity

Tove Sigvartsen,^a Bo Gestblom,^b Erik Noreland^b and Jon Songstad^{a,*}

^aDepartment of Chemistry, University of Bergen, Allégt. 41, N-5007 Bergen, Norway and ^bDepartment of Physics, University of Uppsala, Box 530, S-75 127 Uppsala, Sweden

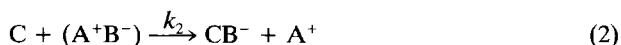
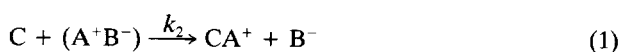
Sigvartsen, T., Gestblom, B., Noreland, E. and Songstad, J., 1989. Conductometric and Dielectric Behaviour of Solutions of Tetrabutylammonium Perchlorate in Solvents of Low and Medium Permittivity. – *Acta Chem. Scand.* 43: 103–115.

The conductometric and dielectric behaviour of solutions of Bu₄NClO₄ in several solvents of from low to medium static permittivity, from propionic acid ($\epsilon = 3.3$) to acetone ($\epsilon = 20.7$) have been studied at 25°C in the 10⁻³–10⁻¹ mol dm⁻³ range.

In dichloromethane and in solvents of ϵ less than 9 the Λ - c curves display a minimum in the 10⁻³–10⁻² mol dm⁻³ range and a maximum at ~ 0.1 mol dm⁻³. The concentration at which the minimum is observed, c_{\min} , is in accordance with Walden's empirical relationship, $\epsilon c_{\min}^{-1/3} = \text{const.}$ The value of c_{\max} decreases slightly with increasing ϵ . The ratio between Λ at c_{\max} and Λ at c_{\min} increases significantly with decreasing ϵ . In solvents of ϵ larger than 9 the Λ - c curves display only an inflection. This inflection is barely detectable in pyridine ($\epsilon = 12.3$) and in acetone.

The static permittivity of the solutions, ϵ_s , increases with the amount of dissolved salt in all solvents except in acetone. After a rapid increase at low concentrations, $d\epsilon_s/dc$ ranging from ~ 30 dm³ mol⁻¹ in propionic acid to ~ 70 dm³ mol⁻¹ in 1,2-dichloroethane, the ϵ_s - c curves level off to asymptotic values of ϵ_s , which are from 3 to 6 times larger than the permittivity of the pure solvents. The degree of dissociation, α , has been calculated by Ostwald's dilution function, $K_A^{-1} = \alpha^2 c(1-\alpha)$, based upon association constants corrected for the increase in the static permittivity of the solutions according to the Fuoss relation. The calculated values are in satisfactory agreement with α_{exp} , equal to Λ/Λ° , for concentrations up to c_{\max} , ~ 0.1 mol dm⁻³.

Many of the most efficient and powerful chemical synthetic routes are based upon the use of ionic reagents, (A⁺B⁻). The reacting part may be A⁺ or B⁻, depending upon the character of the reaction partner, C [eqns. (1) and (2)].



C may also be an ionic reagent, i.e. a carbenium salt, R₃C⁺X⁻, or a transition metal complex, ML_mⁿ⁺Xⁿ⁻. In most cases a solvent is used to homogenize the reaction mixture and to control the progress of the reaction. The choice of solvent is primarily determined by solubility and stability of reactants and products, the rate of the reaction, the structure of the transition state leading to the desired product, etc., but also by tradition, price and availability. Reactions of the type depicted by eqns. (1) and (2) are so common that they play a central role in chemistry.

For reactions according to eqn. (2), i.e. nucleophilic substitution reactions, the rate equation [eqn. (3)] is valid when opposing or consecutive reactions can be neglected.

$$d[CB^-]/dt = k_2 [C][B^-] \quad (3)$$

* To whom correspondence should be addressed.

[B⁻], the concentration of the reacting nucleophile, is set equal to the concentration of the ionic reagent. Likewise, if C is an ionic reagent, the concentration of the reacting part of C is set equal to [C]. Eqn. (3), which is the fundamental key to kinetic and mechanistic studies, will therefore only be valid when the reactants are completely dissociated, i.e. in water and in other solvents of high permittivity. However, a large number of reactions, both in organic and in inorganic chemistry, have to be performed in media in which the fraction of dissociated species originating from one or both reactants is small; cf. phase-transfer reactions in the organic solvent phase,¹ reduction reactions of LiAlH₄ in ethers² and substitution reactions involving transition metal complexes in halogenated alkanes.³ Lithium alkyls in hydrocarbons, which are the sources of R⁻ ions in a large number of reactions, show no evidence of a degree of association lower than four-fold.⁴

Numerous studies have shown that small alterations in the solvent, the concentration of the reagents, the counter ion, the temperature, etc., may seriously influence the rate, the mechanism, and the regio- and stereospecificity of a reaction.^{5,6} Apart from solvation phenomena, these complications seem to be due to variations in the concentration of dissociated ions and of other species, notably various types of ion pairs, and the rapid equilibria between these

species.⁷⁻¹⁵ Our understanding of the dynamic behaviour of reactive ions and ion pairs stems largely from the classical studies of Winstein⁹ and Eigen.¹⁵ Recently, the Winstein ion pair formulation was elegantly confirmed by Masnovi and Kochi.¹⁶ However, precise information concerning individual concentrations cannot presently be obtained for concentrations that are of synthetic and of mechanistic interest. It is apparent that mechanistic descriptions of a large number of reactions will remain obscure until these problems have been solved.

Much of our knowledge concerning electrolytes derives from static conductometric measurements.¹⁷⁻²⁰ The interpretation of this kind of studies, however, suffers from the lack of reliable relationships between conductance and concentration.²¹ Furthermore, the question of whether triple ions contribute to the conductivity causes an additional uncertainty.^{18,20,22-27} In the present study we report the results of a combined conductometric and dielectric study on solutions of Bu_4NClO_4 in several commonly used organic solvents up to $\sim 0.3 \text{ mol dm}^{-3}$. One of the basic conclusions that can be drawn from the fundamental studies of Bjerrum²⁸ and Fuoss²⁹ is that the association constant, K_A , is related to the permittivity of the solvent. Although a number of exceptions are known,³⁰ there is a wealth of data that confirm the basic idea embodied in the $\ln K_A - \epsilon^{-1}$ relationship.³¹ The permittivity of the solvent, in spite of being a macroscopic quantity (cf. the serious limitations in the Born model^{32,33}) is undoubtedly of profound importance when association phenomena are considered.

Bu_4NClO_4 was chosen as a model compound since this salt has been extensively studied and a large body of data exists in the literature. The size and structure of both ions are known from numerous volumetric, viscometric, conductometric and crystallographic studies.^{31,34,35} The ions can hardly be considered as "innocent" ions; cf. particularly the ability of the perchlorate ion to act as a ligand toward hard metal cations³⁶ and the facile reaction between ClO_4^- and

BF_3 .³⁷ A permittivity study of solutions of several onium salts in dichloromethane at 20°C has recently been published.^{25,38}

Experimental

Materials. Bu_4NClO_4 was prepared and purified as described.^{39,40} The solvents were of the highest available quality and were purified according to known procedures.⁴¹ Chloroform was used immediately after purification. Table 1 summarizes relevant properties of the solvents used in this study. The solutions of Bu_4NClO_4 were studied from $\sim 5 \times 10^{-3} \text{ mol dm}^{-3}$ and up to $\sim 3 \times 10^{-1} \text{ mol dm}^{-3}$ when experimentally possible. This concentration range embraced the minimum and the maximum in the Λ - c plots. Concentrations up to 0.3 mol dm^{-3} were readily obtained in all solvents except propionic acid ($\sim 0.2 \text{ mol dm}^{-3}$) and ethyl acetate ($\sim 0.07 \text{ mol dm}^{-3}$). Since the Λ - c plot in the available concentration range in ethyl acetate was comparable to that in ethyl benzoate, the dielectric behaviour of the dilute solutions of Bu_4NClO_4 in ethyl acetate was not studied.

Conductivity measurements. The conductivity equipment has been described previously.³⁹ The cell constant, $4.97 \times 10^{-3} \text{ m}$, with an estimated accuracy of 0.2%, was ideal for all concentrations in solvents of ϵ in the 5-13 range. The cell constant was too small in the case of the most dilute solutions in propionic acid and chloroform and too large in the case of the most concentrated solutions in acetone to give very accurate conductivity data. Since the results in acetone and chloroform agreed satisfactorily with published data,^{42,43} measurements in the uncertain concentration ranges in the three solvents were not repeated with more suitable cells. The conductivity experiments were performed at 25.00(1)°C.

Table 1. Survey of solvent properties at 25.0°C.^a

No.	Solvent	ϵ	η_0/cP	μ/D	τ_2/ps^b
1	Propionic acid	3.3	1.036	1.75	50
2	Chloroform	4.7	0.542	1.15	6
3	Ethyl benzoate	5.9	2.24	2.00	36
4	Acetic acid	6.2	1.155	1.68	90
5	1,2-Dimethoxyethane	7.2	0.413	1.71	7
6	Dibromomethane	7.2	0.980	1.43	3
7	Tetrahydrofuran	7.4	0.460	1.75	3
8	1,1,2,2-Tetrachloroethane	8.2	1.844 ^c	1.71	32
9	Dichloromethane	8.9	0.412	1.55	2
10	1,2-Dichlorobenzene	9.9	1.271	2.27	23
11	1,1-Dichloroethane	9.9	0.455	1.97	6
12	1,2-Dichloroethane	10.4	0.788	1.75	7
13	Pyridine	12.3	0.882	2.25	7
14	Acetone	20.7	0.316	2.69	3

^aMainly from Ref. 77. ^bThis study. ^c15°C.

Permittivity measurements. The time domain (TDS) technique was used for all measurements. Details of the measuring system including sample cell and computing procedures have been described.^{25,44,45} A time window of 20 ns was used. The temperature was kept at 25.0(1) °C by means of a thermostatted jacket surrounding the coaxial line. Throughout this study the static permittivity of a pure solvent is denoted by ϵ , while ϵ_s is used for the static permittivity of a solution.

In total transmission TDS, the transmission coefficient, $T(\omega) = R(\omega)/V(\omega)$, is obtained by Fourier transformation of the pulses transmitted through the sample, $r(t)$, and through the air-filled measurement cell, $v(t)$. The apparent total complex permittivity ϵ_t^* can then be calculated from the transmission line equation, eqn. (4),⁴⁵ where $\rho = (1 - \epsilon_t^{*1/2})/(1 + \epsilon_t^{*1/2})$ and c is the velocity of light in free space.

$$T(\omega) = \frac{(1 - \rho^2) \exp(-i\omega l/c) (\epsilon_t^{*1/2} - 1)}{1 - \rho^2 \exp(-2i\omega l/c) \epsilon_t^{*1/2}} \quad (4)$$

Measurement accuracy may be improved by measuring relative to a reference liquid with known dielectric parameters. The unknown spectrum can be obtained by solving eqn. (5) where $T_{\text{ref}}(\omega)$ is the transmission coefficient of the reference liquid as calculated from eqn. (4). In the study of the electrolyte solutions the pure solvents were used as reference liquids; cf. Table 1 for dielectric parameters.

$$\frac{R(\omega)}{R_{\text{ref}}(\omega)} = \frac{T(\omega)}{T_{\text{ref}}(\omega)} \quad (5)$$

The total permittivity is generally described by eqn. (6) where $\epsilon^*(\omega)$ and $-i\sigma/\omega\epsilon_0$ are the dielectric and ionic conductance contributions to ϵ_t^* . ϵ_0 is the permittivity of free space and σ is the conductivity of the solution. Owing to the conductivity of the solutions, no reliable TDS measurements could be performed for concentrations above ~ 0.05 mol dm⁻³ in acetone and above ~ 0.15 mol dm⁻³ in pyridine. In solvents of lower permittivity the solutions could be studied up to ~ 0.4 mol dm⁻³, but the accuracy declined rapidly above ~ 0.3 mol dm⁻³.

$$\epsilon_t^*(\omega) = \epsilon^*(\omega) - i\sigma/\omega\epsilon_0 = \epsilon' - \epsilon'' - i\sigma/\omega\epsilon_0 \quad (6)$$

The pure solvent data, as measured relative to the empty cell, were fitted to a Debye model function [eqn. (7)].

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon - \epsilon_\infty}{1 + i\omega\tau_2} \quad (7)$$

The experimentally determined relaxation times for the pure solvent, τ_2 , are listed in Table 1. ϵ_∞ ranged from 2.0 to 2.3, in reasonable agreement with the square of the refract-

ing index of the solvents, n_D^2 . When fitting the electrolyte solution spectra to a definite dielectric model function the concentration dependence of the solvent relaxation times causes an uncertainty; dissolution of a salt in associated liquids is known to have a distinct influence upon the solvent dielectric relaxation.⁴⁶ In the calculations, the solvent relaxation times were considered to be independent of the concentration of Bu₄NClO₄ in all solvents. The possible error in the solution permittivities and in the ion pair relaxation times due to this assumption is difficult to estimate, particularly in the associated solvents. However, when the ion pair relaxation time is much greater than that of the solvent, the ion pair dielectric parameters are not critically dependent on the solvent parameters.

The model function for the permittivity spectra of the solutions is given by eqn. (8), where $\epsilon_1 - \epsilon_\infty$ gives the dielectric increment for the solvent dispersion. The term $\epsilon_s - \epsilon_1$

$$\epsilon^* = \frac{\epsilon_s - \epsilon_1}{1 + (i\omega\tau_1)^{1-h}} + \frac{\epsilon_1 - \epsilon_\infty}{1 + i\omega\tau_2} + \epsilon_\infty \quad (8)$$

represents the dielectric increment resulting from salt addition, the increment being due to the presence of ion pairs with a mean relaxation time τ_1 . The h parameter in the Cole-Cole function is introduced to account for a possible distribution of relaxation times around τ_1 , generally recognized as a depression of the ϵ'' vs. ϵ' arc below the semicircle expected for only a single relaxation time. Since the ϵ'' vs. ϵ' arcs were generally observed to be depressed, the value of h for each data set was chosen from the best computer fit to the Cole-Cole function. The use of values of h up to ~ 0.3 , instead of $h = 0$, in eqn. (8) caused a significant increase in τ_1 but only a modest increase in ϵ_s , the permittivity of the solutions. The notable depression in the ϵ'' vs. ϵ' arc, however, seemed to justify the use of h values different from zero. Although a value of the conductivity, σ , can be obtained from the TDS data,⁴⁵ the conductivity was similarly used as a possible variable parameter in the fit. The solvent parameters, i.e. τ_2 (Table 1) and ϵ_∞ , were fixed as outlined above. Tables of conductivity and permittivity data together with derived parameters at different concentrations are available from the authors on request.

Results

Conductivity data. The results from the conductivity study are presented in Fig. 1, where the molar conductivity, Λ , in per cent of the limiting molar conductivity, Λ° , has been plotted vs. the logarithm of the concentration of Bu₄NClO₄. The numbering of the solvents is as in Table 1, i.e. according to their permittivity, from propionic acid (1) with $\epsilon = 3.3$, to acetone (14) with $\epsilon = 20.7$. By plotting $10^2 \Lambda/\Lambda^\circ$, instead of Λ , vs. the concentration, a more reliable comparison between the various solvents is obtained since the greatly different solvent viscosities are eliminated. The Λ° values were taken from accurate conductivity stud-

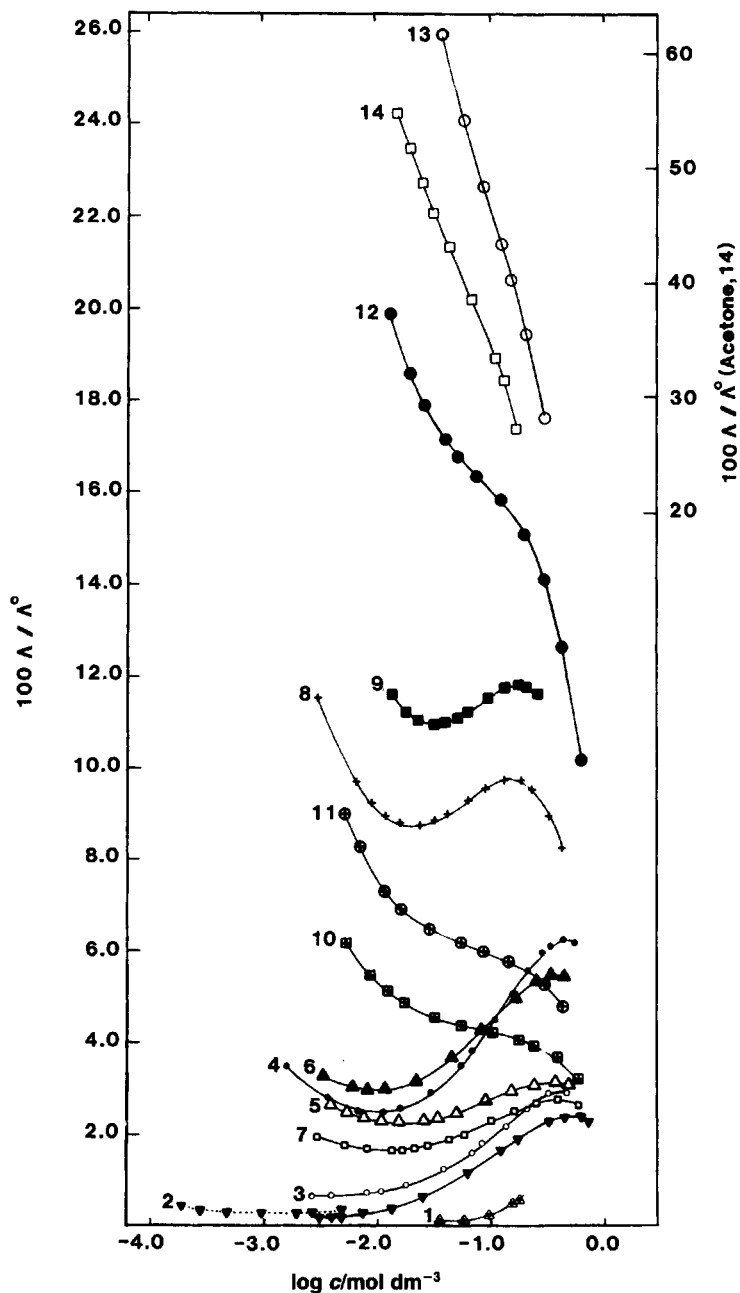


Fig. 1. The ratio, Λ/Λ° , between the molar conductivity and the limiting molar conductivity ($\times 100$) at 25.0°C vs. the logarithm of the concentration of Bu_4NClO_4 . For numbering of solvents, cf. Table 1 [dotted line for chloroform (2), $10^{-4} - 10^{-2}$ mol dm^{-3} , is from Ref. 42].

ies^{40,42,47,48} or were calculated by means of Walden's product using an average value of $\Lambda^\circ\eta_0 = 0.55 \text{ S cm}^2 \text{ mol}^{-1} \text{ P}$ for Bu_4NClO_4 at 25.0°C. Since this product is known to vary considerably,⁴⁹ viz. from ~ 0.4 to ~ 0.7 in organic solvents, an uncertainty in the ordinate values for some of the solvents will necessarily be introduced; this uncertainty, however, is small compared with the variations in the solvent viscosities. Table 2 gives a summary of relevant conductivity data.

In dichloromethane (9; $\epsilon = 8.9$), and in solvents of lower permittivity, the conductivity plots display a minimum and a maximum. In solvents of higher permittivity ($\epsilon > 9$) only an inflection is observed, which is barely detectable in pyridine and in acetone. The concentration at which the

minimum occurs, c_{min} , increases with increasing permittivity of the solvent and is in excellent agreement with Walden's empirical relationship, $\epsilon c_{\text{min}}^{-1/3} = \text{const.}$ ¹⁷ (cf. last column in Table 2). The value of c_{max} , the concentration at which the conductivity curves display a maximum, decreases slightly with increasing ϵ of the solvent. No obvious relationship between ϵ and c_{max} could be derived from the present data. The ratio between Λ/Λ° at c_{max} and at c_{min} decreases significantly with increasing ϵ .

The $\Lambda/\Lambda^\circ - c$ plots show the expected trend toward higher conductivity with increasing permittivity of the solvents. In three solvents, however, viz. tetrahydrofuran (7), 1,2-dichlorobenzene (10) and 1,1-dichloroethane (11), the solutions of Bu_4NClO_4 are distinctly less conductive than

Table 2. A summary of conductivity data and other derived data for Bu₄NClO₄ in organic solvents at 25.00 °C.

Solvent	$\Lambda^{\circ}/S\text{ cm}^2\text{ mol}^{-1}$	$\Lambda^{\circ}\eta_0/S\text{ cm}^2\text{ mol}^{-1}\text{ P}$	K_A	$10^2 c_{\text{min}}/M$	$10^2 \Lambda_{\text{min}}/\Lambda^{\circ}$	$10^2 c_{\text{max}}/M$	$10^2 \Lambda_{\text{max}}/\Lambda^{\circ}$	$\frac{\Lambda_{\text{max}}}{\Lambda_{\text{min}}}$	$10^2 c_{\text{inf}}/M$	$10^2 \Lambda_{\text{inf}}/\Lambda^{\circ}$	$\epsilon c_{\text{min}}^{-1/3}/M^{-1/3}$
1 ^a	53	~0.55	<i>i</i>								
2	110 ^c	0.60	2.9×10^8	~0.2	0.3	55	2.4	8			~35
3	27 ^b	~0.55	<i>i</i>	~0.4	0.7	45	2.9	4			~35
4	48 ^b	~0.55	<i>i</i>	0.9	2.5	45	6.2	2.5			30
5	133 ^b	~0.55	<i>i</i>	1.9	2.2	37	3.1	1.4			27
6	56 ^b	~0.55	<i>i</i>	1.1	2.9	41	5.0	1.7			32
7	127 ^d	0.58	1.7×10^6	1.4	1.7	42	2.8	1.5			31
8	33 ^b	~0.55	<i>i</i>	2.3	8.6	16	9.7	1.2			28
9	109 ^e	0.45	2.2×10^4	3.1	10.9	19	11.7	1.1			28
10	42 ^f	0.53	9.3×10^4						~7	6	~13 ^k
11	110 ^f	0.50	4.7×10^4						~9	4	~13 ^k
12	65 ^f	0.51	6.4×10^3						~10	16	~14 ^k
13	73 ^g	0.64	2.5×10^3						~10	22	~16 ^k
14	188 ^e	0.59	8.0×10^1								

^aNumbering of solvents as in Table 1. ^bFrom Walden's product, $\Lambda^{\circ}\eta_0 = \text{const.} \sim 0.55\text{ S cm}^2\text{ mol}^{-1}\text{ P}$. ^cRef. 42. ^dRef. 47. ^eRef. 40. ^fRef. 31. ^gRef. 48. ^hRef. 43. ⁱNot available. ^jWalden's empirical relationship, $\epsilon c_{\text{min}}^{-1/3} = \text{const.}$ ¹⁷ ^kAssuming c_{inf} to be equal to c_{min} ($M = \text{mol dm}^{-3}$).

Table 3. Calculated and experimental values for the degree of dissociation, α_{calc} , and α_{exp} , equal to Λ/Λ° , for 0.01 and 0.1 mol dm⁻³ solutions of Bu₄NClO₄ in some organic solvents.

Solvent	0.01 mol dm ⁻³			0.1 mol dm ⁻³		
	$10^2 \alpha_{\text{calc}}^a$	$10^2 \alpha_{\text{exp}}^b$	$\alpha_{\text{exp}}/\alpha_{\text{calc}}$	$10^2 \alpha_{\text{calc}}$	$10^2 \alpha_{\text{exp}}$	$\alpha_{\text{exp}}/\alpha_{\text{calc}}$
2 Chloroform	0.059	0.33	5.6	0.018	1.5	80
7 Tetrahydrofuran	0.76	1.6	2.1	0.24	2.4	10
9 Dichloromethane	6.5	12.3	1.9	2.1	11.6	5.5
Methyl formate	3.6	6.7 ^c	1.8			
10 1,2-Dichlorobenzene	3.2	5.3	1.7	1.0	4.2	4.2
11 1,1-Dichloroethane	4.5	7.6	1.7	1.5	5.8	4.0
12 1,2-Dichloroethane	11.7	21.3	1.8	3.9	16.1	4.1
13 Pyridine	18.1	34	1.9	6.1	22.2	3.6
14 Acetone	62	59	0.95	27	35.0	1.3

^a $\alpha_{\text{calc}} = [(4c K_A + 1)^{1/2} - 1]/2c K_A$ (K_A from Table 2). ^b $\alpha_{\text{exp}} = \Lambda/\Lambda^{\circ}$ (Fig. 1). ^cExtrapolated from data in Ref. 50.

anticipated. Recently, Bu₄NClO₄ was studied conductometrically in methyl formate,⁵⁰ a solvent which is isoelectric with dichloromethane ($\epsilon = 8.9$). The available conductivity data, up to $\sim 0.01\text{ mol dm}^{-3}$,⁵⁰ lead to a $\Lambda/\Lambda^{\circ} - c$ plot below that of 1,1-dichloroethane (11), and thus significantly below that of dichloromethane (9). Characteristic for tetrahydrofuran, 1,2-dichlorobenzene, 1,1-dichloroethane and methyl formate is that the association constant for Bu₄NClO₄ is larger than expected from a linear $\ln K_A - \epsilon^{-1}$ relationship (K_A in methyl formate is 7.3×10^4 , as compared with 2.2×10^4 in dichloromethane^{21,50}). Some of the $\Lambda/\Lambda^{\circ} - c$ plots intersect, but only at concentrations above $\sim 0.1\text{ mol dm}^{-3}$. Apparently, the association constant, K_A , in very dilute solution strongly determines the conductivity up to at least 0.1 mol dm^{-3} . The permittivity of the solvent, however, governs the form of the $\Lambda/\Lambda^{\circ} - c$ plots with regard to the presence of a minimum and a maximum or only an inflection; cf. the plots for 1,1-dichloroethane (11)

and for 1,2-dichlorobenzene (10), ϵ in both solvents being 9.9, and the plots for 1,1,2,2-tetrachloroethane (8) ($\epsilon = 8.2$) and for dichloromethane (9; $\epsilon = 8.9$).

Based upon Ostwald's dilution function one can calculate the degree of dissociation, α_{calc} [eqn. (9)]. Table 3 gives a comparison between α_{calc} and α_{exp} , the latter being equal to

$$K_A^{-1} = \alpha_{\text{calc}}^2 c(1 - \alpha_{\text{calc}}) \quad (9)$$

Λ/Λ° , at two arbitrary concentrations, viz. 0.01 and 0.1 mol dm⁻³, in some solvents for which accurate association constants for Bu₄NClO₄ are available. The results show clearly that α_{exp} is distinctly higher than expected, particularly in the solvents of lowest permittivity, i.e. chloroform and tetrahydrofuran. In the remaining solvents the ratio between α_{exp} and α_{calc} is essentially independent of ϵ at 0.01 mol dm⁻³, ~ 1.8 , but decreases from 5.5 to 3.6 with increasing ϵ at 0.1 mol dm⁻³. In acetone, in which Bu₄NClO₄

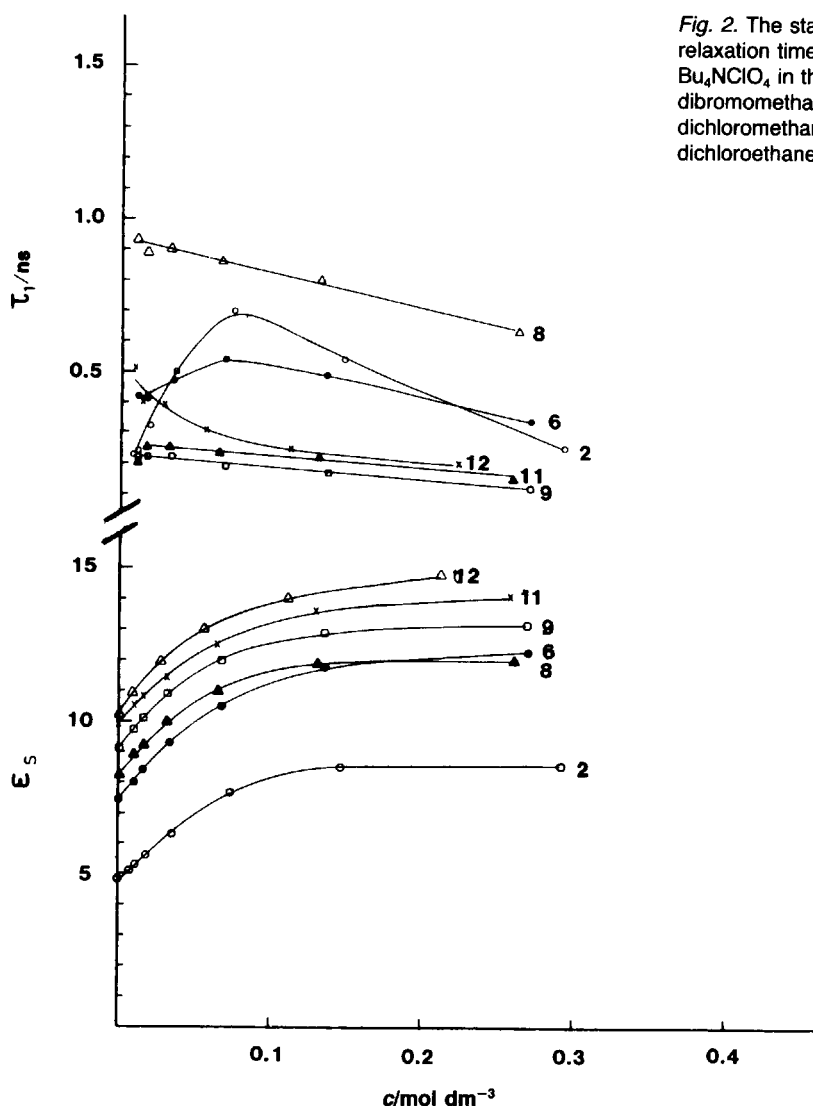


Fig. 2. The static permittivity, ϵ_s (lower plots), and the ion pair relaxation time, τ_1 (upper plots) vs. the concentration of Bu_4NClO_4 in the halogenated alkanes: chloroform (2), dibromomethane (6), 1,1,2,2-tetrachloroethane (8), dichloromethane (9), 1,1-dichloroethane (11) and 1,2-dichloroethane (12).

is significantly less associated, α_{calc} is in fair agreement with α_{exp} , even at 0.1 mol dm^{-3} .

Permittivity data. Figs. 2 and 3 show plots of the permittivity of the solutions, ϵ_s , and the ion pair relaxation time, τ_1 , vs. concentration; Fig. 2 for the halogenated alkanes and Fig. 3 for the remaining solvents. The numbering of the solvents is as in Table 1 and Fig. 1. The permittivity of the solutions of Bu_4NClO_4 in acetone was found to be independent of the concentration up to $\sim 0.05 \text{ mol dm}^{-3}$, the upper limit for reliable permittivity studies in this solvent. No relaxation phenomena in addition to the usual acetone relaxation could be detected in the dilute solutions. Acetone is therefore omitted in Fig. 3.

In all other solvents the permittivity of the solutions, ϵ_s , increases with the concentration of Bu_4NClO_4 . After an initial strong increase at low concentrations, $d\epsilon_s/dc$ ranging from $\sim 25 \text{ dm}^3 \text{ mol}^{-1}$ in propionic acid (1) (Fig. 3) to $\sim 70 \text{ dm}^3 \text{ mol}^{-1}$ in 1,2-dichloroethane (12) (Fig. 2), the $\epsilon_s - c$ plots level off to asymptotic values of ϵ_s . These values are

from ~ 3 [pyridine (13)] to ~ 6 [acetic acid (4)] larger than ϵ for the pure solvents. The levelling off in the $\epsilon_s - c$ plots is significantly slower for propionic acid (1), ethyl benzoate (3) and 1,2-dichlorobenzene (10) than for the other solvents. It is notable that the initial increase and the asymptotic value of ϵ_s for 1,2-dichloroethane (12) are larger than for 1,1-dichloroethane (11).

At low salt concentrations the small dielectric increment due to the ion pairs makes an accurate determination of the corresponding relaxation time difficult. In the $\tau_1 - c$ plots only τ_1 values for $c \geq 0.02 \text{ mol dm}^{-3}$ are therefore considered. These plots show a complex pattern. In the solvents of highest ϵ , i.e. pyridine (13) and 1,2-dichloroethane (12), the relaxation time due to the ionic solute initially decreases and then levels off to asymptotic values for higher concentrations. In some solvents of intermediate permittivity, viz. dichloromethane (9), 1,1,2,2-tetrachloroethane (8) and 1,1-dichloroethane (11), the relaxation time decreases slowly with increasing concentration. As ϵ for the solvent further decreases, a trend toward increasing τ_1 at low con-

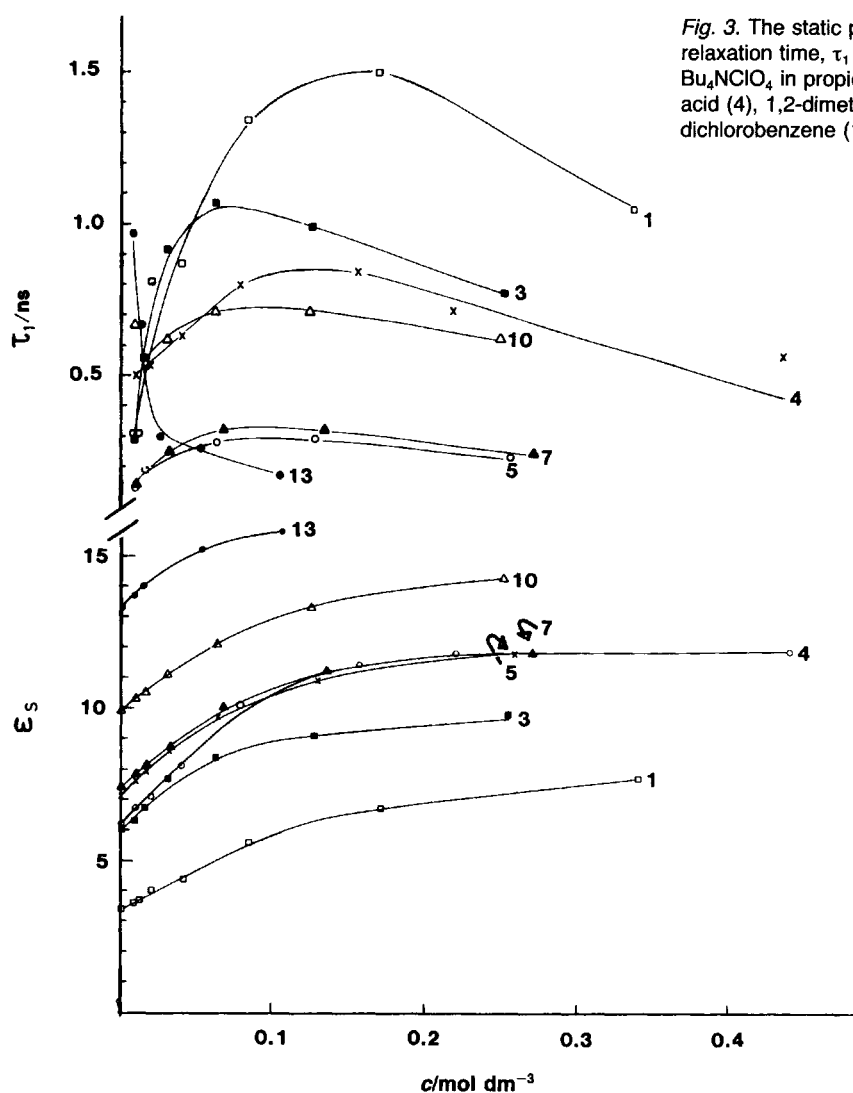


Fig. 3. The static permittivity, ϵ_s (lower plots), and the ion pair relaxation time, τ_1 (upper plots) vs. the concentration of Bu₄NClO₄ in propionic acid (1), ethyl benzoate (3), acetic acid (4), 1,2-dimethoxyethane (5), tetrahydrofuran (7), 1,2-dichlorobenzene (10) and pyridine (13).

centrations followed by a decrease at higher concentrations is apparent. Additional calculations of τ_1 based upon a Debye model function led to slightly different values for the ionic conductivity, σ , and the relaxation time, τ_1 , but did not alter the general trend as outlined above.

From the Debye model for a rotating spherical dipole of radius a the relationship between the macroscopic relaxation time, τ_1 , and the bulk solvent viscosity, η_0 , given by eqn. (10) is valid. Based upon the Powles-Glarum relation⁵¹

$$\tau_1 = \frac{4\pi a^3}{kT} \eta_0 \quad (10)$$

between the microscopic and the macroscopic relaxation time one obtains the following expression for τ_1 in a dilute solution of ion pairs [eqn. (11)]:^{25,52}

$$\tau_1 = \frac{3V_\phi^\circ}{N_A k T} \eta_0 \quad (11)$$

Here, V_ϕ° is the partial molar volume of a salt in a solvent of viscosity η_0 , while N_A , k and T represent Avogadro's number, Boltzmann's constant and the absolute temperature, respectively. Eqn. (11) can be expected to be valid for dilute solutions only.⁵² The form of the $\tau_1 - c$ plots, particularly in the solvents of low ϵ , and the experimental uncertainty in τ_1 for concentrations less than $\sim 0.02 \text{ mol dm}^{-3}$ prevented reliable values for τ_1 ($c \rightarrow 0$) from being obtained. We have therefore chosen to test eqn. (11) at two arbitrary concentrations, viz. 0.03 and 0.1 mol dm^{-3} . A separate study has shown that the partial molar volume of Bu₄NClO₄ in several organic solvents is in the range $0.300 - 0.325 \text{ dm}^3 \text{ mol}^{-1}$.⁵³ The value for V_ϕ° (Bu₄NClO₄) in dichloromethane, viz. $0.3045 \text{ dm}^3 \text{ mol}^{-1}$,³⁵ was therefore used for all solvents. The change in viscosity up to 0.1 mol dm^{-3} , usually less than $\sim 10\%$,⁵³ was sufficiently small to allow the viscosity of the pure solvents to be used. Fig. 4 shows the $\tau_1 - \eta_0$ plots according to eqn. (11). Although a clear correlation between τ_1 and η_0 can be observed, it is also apparent that this equation is poorly obeyed in some of the solvents, particularly at 0.1 mol dm^{-3} .

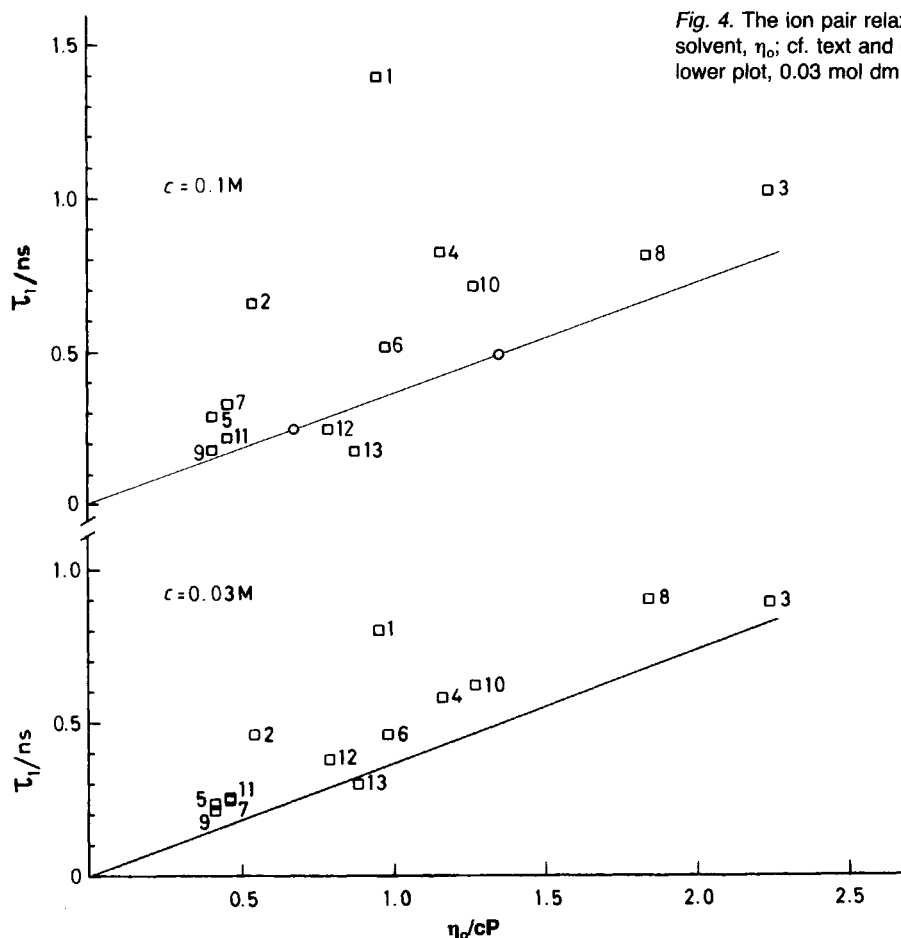


Fig. 4. The ion pair relaxation time, τ_1 , vs. the viscosity of the solvent, η_0 ; cf. text and eqn. (11) (upper plot, 0.1 mol dm^{-3} ; lower plot, 0.03 mol dm^{-3}).

Discussion

Comments on the solvents and their properties. The choice of solvents for the present study was primarily determined by their static permittivity, ϵ . Additionally, solvents which are frequently employed in chemical reactions owing to their price and availability were preferred. Bu_4NClO_4 had to be sufficiently soluble, preferably up to $\sim 0.4 \text{ mol dm}^{-3}$, and sufficiently associated to allow effects due to ion pairing upon conductivity and permittivity of the solutions to be detected. Due to the limitations in the TDS technique when applied to samples with too high a conductivity only solvents with ϵ less than ~ 15 could be examined. Acetone ($\epsilon = 20.7$) was attempted, but the association constant, viz. $\sim 10^2$, was too small to allow reliable permittivity studies to be performed. The limited solubility of Bu_4NClO_4 in all alcohols of sufficiently low permittivity prevented the examination of this class of solvents. The lower end of the permittivity scale, i.e. propionic acid ($\epsilon = 3.3$), was similarly determined by the solubility of Bu_4NClO_4 . Some of the chosen solvents are fairly strong acids or bases, both in the Brønsted and the Lewis sense. In Bu_4NClO_4 the cationic charge is well screened by the alkyl groups, and the anionic charge is dispersed over several atoms. One may

therefore hope that the results obtained are not seriously affected by solvation in the various solvents.

Admittedly, ϵ , being a macroscopic parameter, is a poor measure for a microscopic description of a solvent. Nevertheless, when association phenomena are considered, the $\ln K_A - \epsilon^{-1}$ relationship, as can be deduced³¹ from the Bjerrum²⁸ and the Fuoss²⁹ equations, leaves no doubt about the importance of this parameter. However, the large association constant and thus the low conductivity of Bu_4NClO_4 in some of the solvents (Fig. 1) indicate that other factors play an important role. A reasonable assumption is that the intrinsic dipole moment of the solvent molecules will have to be considered. A high dipole moment will presumably favour ion pairs with large interionic distance. Since less energy will be required to dissociate a "loose" solvent-separated ion pair than a "tight" contact pair, one may expect that the dipole moment will influence the association constant. The intrinsic dipole moment, however, will depend upon the degree and the type of association of the solvent molecules, and may differ from the usually quoted gas-phase moment (Table 1). The presence of an ionic solute may further alter the association pattern.

It has become customary to consider the Kirkwood correlation factor, g , as a measure of the degree of association

$$\frac{(\epsilon - \epsilon_\infty)(2\epsilon - \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} = \frac{N_1}{9\epsilon_0 k T} g \mu^2 \quad (12)$$

of a solvent. This factor is defined by eqn. (12), where ϵ is the static permittivity of the pure liquid and μ is the gas-phase dipole moment (Table 1).⁵⁴ N_1 is the number of molecules per unit volume and ϵ_0 is the permittivity of free space. A deviation from $g = 1$ is a measure of local ordering due to short-range intermolecular forces. Whereas g factors significantly larger than unity, ~ 2.5 for most protic solvents, are explained by chain-wise association through hydrogen bonds, small g factors, i.e. less than ~ 0.9 , indicate "contra-association" of the dipoles as opposed to the head-to-tail or "co-association" in water and alcohols.⁵⁵ The absolute magnitude of the g factor is not of great significance because of the uncertainty in the value of ϵ_∞ . In the case of dichloromethane (9) a 15% increment in n_D^2 due to atomic polarization, i.e. $\epsilon_\infty = 2.3$, will reduce the g factor from 1.25 to 1.0.²⁵ Thus, g factors slightly different from unity may not indicate some particular type of association. The variation of the g factor within a series of measurements, however, is often of structural value.⁵⁶

Table 4 gives a summary of the calculated g factors. ϵ_∞ in eqn. (12) was set equal to n_D^2 , a convention which will necessarily lead to some doubt with regard to the g factors. The small g factor for the two acids studied, (1) and (4), is as expected; the association of this class of compounds to "contra-associated" dimers is well documented. The high dimerization constant for propionic acid⁵⁷ is presumably due to the stability of the *cis* conformation.⁵⁸ Less well known is the apparent association of the carboxylic acid

Table 4. Kirkwood's correlation factor, g , for the various solvents, together with the interionic distance in the ion pair, a , and the preexponential factor, $K_A^\circ = 4\pi N_A a^3/3$, from the best fit to $K_A = K_A^\circ \exp(q/a^2 k T \epsilon)$ (K_A from Table 2).

Solvent ^a	g^b	a/nm	K_A°
1	0.23		
2	0.95	0.60	0.54
3	0.45 ^c	^d	^d
4	0.67		
5	0.79		
6	1.13		
7	0.78	0.48	0.29
8	0.93		
9	1.25	0.59	0.52
10	0.66	0.44	0.22
11	0.88	0.47	0.26
12	1.17	0.57	0.47
13	0.86	0.51	0.33
14	1.06	0.48	0.28
Water	2.45 ^e		

^aNumbering of solvents as in Table 1. ^bCalculated from eqn. (12) using $\epsilon_\infty = n_D^2 = 2.0$ and μ from Table 1. ^c0.58 in ethylacetate and 0.54 in methyl formate.⁵⁰ ^d0.51 nm and 0.33 in methyl formate. ^eRef. 55.

esters, cf. the small g factors for this class of compounds (0.4–0.6). Gramstad and Snarud⁵⁹ have concluded from an IR study that the more polar phosphorus (V) esters are associated. The two ethers, (5) and (7), and 1,2-dichlorobenzene (10) also have g factors significantly smaller than unity. Acetone (14) and chloroform (2), which are believed to be unassociated liquids,⁵⁴ give $g \sim 1.0$, as do the halogenated alkanes. The g factors for the two dichloroethanes are different, viz. 0.9 (11) and 1.2 (12), probably due to the presence of the more polar *gauche* conformation in (12). Ionic compounds are generally significantly less associated in 1,2-dichloroethane than in 1,1-dichloroethane.^{60,61} The difference in the dissociating ability of the two solvents is far greater than expected from their permittivity [10.4(12) and 9.9(11)]. A similar equilibrium between *gauche* and *trans* conformations is known to exist in 1,2-dimethoxyethane (5).⁶²

According to Fuoss²⁹ the association constant K_A should be a continuous function of the permittivity. For a 1:1 electrolyte K_A is given by eqn. (13), in which K_A° includes

$$K_A = K_A^\circ \exp(q^2/a k T \epsilon) \quad (13)$$

the effect of interaction between solvent and solute and the free volume of solute. q is the electronic charge and a is the interionic distance. k and T have the usual definition. In the so-called "new" equation of Fuoss,⁶³ K_A° is equal to $4\pi N_A a^3/3$ (a in nm). From this equation and eqn. (13), a and K_A° can be calculated when K_A is known. The results are summarized in Table 4 together with Kirkwood's g factors. While K_A° does not appear to be related to ϵ and g , the interionic distance in the ion pair, a , seems to decrease with decreasing g . Since no obvious relation between a and ϵ can be extracted from the present data, one may conclude that the structure of the ion pair in very dilute solutions is not seriously influenced by the static permittivity of the solvent. The shape of the τ_1 - c curves (Figs. 2 and 3) indicates that solvents of low and of intermediate ϵ respond differently to the presence of an ionic solute with regard to the interionic distance in the ion pair; only at concentrations above 0.1–0.15 mol dm⁻³ do the solvents behave similarly. This unique effect of the ionic solute upon the ion pair relaxation time in solvents of low ϵ is further demonstrated by the $\tau_1 - \eta_0$ plots in Fig. 4.

The interionic distance in acetone (14), 0.48 nm, is remarkably small when it is taken into account that this solvent is essentially unassociated. It is known, however, that K_A for Bu₄NClO₄ in this solvent, as in alcohols and in other solvents with ϵ higher than ~ 15 , is distinctly larger than expected from a linear $\ln K_A - \epsilon^{-1}$ relation. This apparent inadequacy in the Fuoss equation [eqn. (13)] for solvents of intermediate permittivity can partly be removed by introducing the Gilkerson constant⁶⁴ in eqn. (12). This constant, based upon Kirkwood's theory of free volume, takes into account the changes in the solvation through the process of association.⁶⁵

The static permittivity of the solutions. Figs. 2 and 3 show that the static permittivity of the solutions, ϵ_s , increases with concentration. This is as observed in similar studies in solvents of low permittivity.^{25,66} This increase in ϵ_s with concentration is generally considered to be due to incomplete dissociation. The ions will be associated to pairs which, due to their large dipole moments, will increase the permittivity of the solutions. The initial increase in static permittivity with dipole solute concentration is given by eqn. (14),⁶⁷ in which μ_2 is the dipole moment of the solute

$$\frac{d\epsilon_s}{dc} = \frac{N_A (\epsilon_\infty + 2)^2 \epsilon^2 \times 10^3}{9\epsilon_0 k T (2\epsilon^2 + \epsilon_\infty^2)} \mu_2^2 \quad (14)$$

species. Assuming μ_2 to be independent of the solvent and using $\epsilon_\infty \sim 2$, eqn. (14) can be simplified to eqn. (15), in which D includes all the constants in eqn. (14). Eqn. (15)

$$\frac{d\epsilon_s}{dc} = D \frac{\epsilon^2}{\epsilon^2 + 2} \quad (15)$$

states that the initial increase in ϵ_s will increase slightly with increasing permittivity of the solvent. Apart from some notable exceptions such as pyridine (13) and acetone (14), the expected trend is confirmed by the present data. For the haloalkanes, $d\epsilon_s/dc$ increases from $\sim 45 \text{ dm}^3 \text{ mol}^{-1}$ for chloroform (2) to $\sim 70 \text{ dm}^3 \text{ mol}^{-1}$ for 1,2-dichloroethane (13) (Fig. 2). For acetic acid (4), $d\epsilon_s/dc$ is ~ 60 as compared with only $\sim 25 \text{ dm}^3 \text{ mol}^{-1}$ for propionic acid (1) (Fig. 3).

A number of other factors are known to contribute to the initial slopes in the $\epsilon_s - c$ plots. First of all, eqn. (14) will only be valid when the dissolved salt exists entirely as ion pairs. This will obviously not be the case in the solvents of highest permittivity. Furthermore, eqn. (14) is simplified to eqn. (15) by assuming that μ_2 is independent of the solvent. The calculated interionic distances, a (Table 3), indicate that solvents with low Kirkwood g factors have to be considered separately. The Hubbard-Onsager kinetic depolarizing effect⁶⁸ [eqn. (16)], which will cause a decrease in ϵ_s , is

$$\Delta\epsilon_s = -24 \times 10^9 \pi \tau_2 \sigma (\epsilon_s - \epsilon_\infty) / \epsilon_s \quad (16)$$

essentially proportional to the relaxation time of the solvent. With τ_2 equal to 2 ps, as in dichloromethane (9) and in several other solvents, this term will be negligible. In the two acids (1 and 4), and in ethyl benzoate (3), 1,1,2,2-tetrachloroethane (8) and 1,2-dichlorobenzene (10), the solvent relaxation time (Table 1) is too large to justify this approximation.

Of more importance to $d\epsilon_s/dc$ and to the form of the $\epsilon_s - c$ plots is the contribution by the solvent molecules. The dispersion $\epsilon_1 - \epsilon_\infty$ in eqn. (8) is interpreted as being due to the solvent molecules. On salt addition the number of solvent molecules per unit volume, N_1 , will be lowered. Thus, the permittivity of the solvent itself will be lowered [cf. eqn. (12)]. The partial molar volume of Bu_4NClO_4 at infinite dilution, V_ϕ^∞ , and the slope, S_v , in the Masson

equation⁷⁰ are fairly independent of the solvent.⁵³ This reduction in N_1 will therefore be of the same magnitude for all solvents. For a 0.1 mol dm^{-3} solution this reduction amounts to approximately 4%, in fair agreement with the experimental data. Since this reduction in ϵ_1 is essentially proportional to the reduction in N_1 , a plot of ϵ_1 vs. $c^{1/2}$ should be linear.²⁵ When taking the considerable uncertainty in ϵ_1 into account, this expectation was confirmed for all solvents except propionic acid (1). In this latter solvent ϵ_1 was found to be essentially independent of the concentration, viz. from 3.4 to 3.6.

Finally, when $\epsilon_s - c$ curves are to be discussed, one has to consider the average intrinsic dipole moment of the solvent molecules. It is known that when an ionic compound is dissolved in a solvent of low static permittivity, the "polarity" of the solvent will be increased.⁷⁰⁻⁷³ A plot of the Kosower Z value vs. the concentration of Bu_4NClO_4 in dichloromethane⁷¹ shows a remarkable similarity to the corresponding $\epsilon_s - c$ curve (Fig. 2). Thus, solvent species of higher dipole moment will be favoured upon addition of an ionic solute, cf. the $\epsilon_s - c$ plots for 1,2-dichloroethane (12) and 1,1-dichloroethane (11). Of particular interest is the $\epsilon_s - c$ curve for acetic acid (4), cf. the large initial slope and the large asymptotic value of ϵ_s , ~ 12 , which is twice as large as that for the pure solvent. Presumably, the "contra-associated" dimeric structure is readily broken down by the ionic solute, whereby the fraction of solvent monomers of high dipole moment is increased.

Dissociation of Bu_4NClO_4 in solvents of low ϵ . In a solution of a salt AB in a solvent of low permittivity one may assume that the following species are present: Single ions A^+ and B^- (with a fraction equal to f_1), ion pairs $[\text{AB}]$ of various types (f_2), triple ions $[\text{ABA}]^+$ and $[\text{BAB}]^-$ (f_3), quadrupoles $[\text{ABAB}]$ and larger aggregates $[\text{AB}]_n$ (f_4). Provided the activity coefficient of all suggested species is unity, the following equations are valid:^{25,74}

$$f_1 + f_2 + 3f_3 + 2f_4 = 1 \quad (17)$$

$$f_2/f_1^2 = K_A c \quad (18)$$

$$f_3/f_2 = K_T c \quad (19)$$

$$f_4/f_2^2 = K_{AA} c \quad (20)$$

Here, K_A , K_T and K_{AA} represent the association constant for the ion pairs, the triple ions and the quadrupoles, respectively. At present, two distinctly different theories are available that can be used to explain conductivity plots of the type shown in Fig. 1. According to the Fuoss-Kraus triple ion hypothesis,¹⁵ conducting triple ions, formed from non-conducting ion pairs, will cause an increase in the conductivity at higher concentrations. The Cavell-Knight approach²⁴ is based upon the assumption that f_3 and K_T are small or negligible. The decrease in K_A due to the increase

Table 5. Static permittivity, ϵ_s , association constants corrected for the increase in the permittivity, K_A^s , and the ratio between experimental and calculated values of α for 0.01 and 0.1 mol dm⁻³ solutions of Bu₄NClO₄.

Solvent	0.01 mol dm ⁻³			0.1 mol dm ⁻³		
	ϵ_s^a	$K_A^s^b$	$\alpha_{\text{exp}}^c/\alpha_{\text{calc}}^d$	ϵ_s^a	$K_A^s^b$	$\alpha_{\text{exp}}^c/\alpha_{\text{calc}}^d$
2 Chloroform	5.3	2.5×10^7	1.7	8.1	5.5×10^4	1.2
7 Tetrahydrofuran	7.8	7.9×10^5	1.8	10.6	1.6×10^4	1.0
9 Dichloromethane	9.7	9.4×10^3	1.3	12.5	1.0×10^3	1.2
10 1,2-Dichlorobenzene	10.3	5.2×10^4	1.2	12.9	4.3×10^3	0.9
11 1,1-Dichloroethane	10.5	2.2×10^4	1.2	13.2	2.2×10^3	0.9
12 1,2-Dichloroethane	10.9	3.9×10^3	1.4	13.8	5.9×10^2	1.3
13 Pyridine	13.7	1.0×10^3	1.3	15.8	3.5×10^2	1.4

^aFrom Figs. 2 and 3. ^b $K_A^s = K_A^0 \exp(q^2/a k T \epsilon_s)$; a and K_A^0 from Table 4. ^c $\alpha_{\text{exp}} = \Lambda/\Lambda_0$ from Fig. 1. ^d $\alpha_{\text{calc}} = [(4c K_A^s + 1)^{1/2} - 1]/2 c K_A^s$.

in the permittivity of the solutions with increasing concentration of the ionic solute (Figs. 2 and 3) will supposedly generate a sufficient increase in the fraction of ions to cause an increase in Λ at high concentration.

Provided the latter approach is correct, it is necessary to be able to show that the considerable discrepancy between α_{calc} and α_{exp} (Table 3) can be eliminated on taking into account the dependence of K_A upon ϵ_s according to eqn. (12). Table 5 gives a summary of recalculated association constants, K_A^s , at 0.01 and 0.1 mol dm⁻³, together with the corresponding $\alpha_{\text{exp}}/\alpha_{\text{calc}}$ ratios. Indeed, the Cavell-Knight approach²⁴ leads to a highly satisfactory result, particularly at 0.1 mol dm⁻³. It is notable that this procedure correctly predicts that α_{exp} will attain higher values for Bu₄NClO₄ at 0.1 mol dm⁻³ than at 0.01 mol dm⁻³ when the permittivity of the solvent is less than ~ 9.5 (cf. Fig. 1). The ratios in 1,2-dichloroethane are significantly larger than in 1,1-dichloroethane. This observation strengthens the suggestion that solvents capable of increasing their intrinsic dipole moment due to the ionic solute will cause an increase in the degree of dissociation. This probable effect upon the association constant is not accounted for by the Cavell-Knight approach,²⁴ in which only the increase in ϵ_s is considered. It should be emphasized, however, that α_{calc} , and thus the $\alpha_{\text{exp}}/\alpha_{\text{calc}}$ ratios, are dependent upon the activity coefficients of the various species [cf. eqns. (17) to (20)]. A significant difference in the concentration dependence of the activity coefficient of particularly the dissociated ions in the various solvents may invalidate conclusions based upon minor changes in $\alpha_{\text{exp}}/\alpha_{\text{calc}}$ from one solvent to another.⁷⁵

Formation of larger aggregates. From the linearity in the $\epsilon_s - c$ plots at low concentrations one may conclude that the fraction existing as ion pairs, f_2 , is rather constant, i.e. $df_2/dc = 0$. At higher concentrations the $\epsilon_s - c$ plots level off to asymptotic values. Presumably, the ion pairs are consumed as larger aggregates. Owing to their small or negligible dipole moments these species will not contribute to the permittivity of the solutions. Above a certain concentration, characteristic for each solvent, the values of f_2c , ϵ_s and K_A will remain constant. Since f_1 will start to

decrease, the $\Lambda/\Lambda^0 - c$ plots will go through a maximum.²⁵ According to Petrucci and co-workers,²³ the quadrupole formation constant, K_{AA} [eqn. (20)], will be the determining factor with regard to the shape of $\epsilon_s - c$ and $\Lambda - c$ plots for concentrations beyond c_{min} .

Following a procedure devised by Chabanel and co-workers⁷⁶ one may obtain an estimate of the quadrupole formation constants, K_{AA} , by assuming that the deviation from linearity in the $\epsilon_s - c$ plots is entirely due to the formation of quadrupoles.²⁵ Table 6 summarizes the results at two arbitrary concentrations, viz. 0.1 mol dm⁻³ and 0.2 mol dm⁻³. The necessary corrections in ϵ_s due to ϵ_1 were extrapolated from the permittivity data. The term $f_2 + 2f_4$ was set equal to $1 - f_1 = 1 - \alpha_{\text{exp}}$.

Due to the numerous assumptions involved in the calculations, the K_{AA} values should only be considered as approximate. The data indicate that K_{AA} increases with concentration, which is as expected if further association to species larger than quadrupoles takes place. It is notable that the two acids (1 and 4), the two ethers (5 and 7), chloroform (2) and 1,2-dichlorobenzene (10) do not seem

Table 6. Approximate quadrupole formation constants, K_{AA} , for Bu₄NClO₄ at 25.0°C.

Solvent	K_{AA}	
	0.1 mol dm ⁻³	0.2 mol dm ⁻³
1 Propionic acid	0.4	2
2 Chloroform	1.7	4
3 Ethyl benzoate	3	10
4 Acetic acid	0.7	3
5 1,2-Dimethoxyethane	2	6
6 Dibromomethane	4	17
7 Tetrahydrofuran	2	5
8 1,1,2,2-Tetrachloroethane	9	16
9 Dichloromethane	2.5	15
10 1,2-Dichlorobenzene	2	4
11 1,1-Dichloroethane	4	11
12 1,2-Dichloroethane	8	13
13 Pyridine	4	

to favour quadrupole formation. It was expected that the quadrupole formation constants would tend to increase with decreasing dipole moment of the solvents. The data in Table 6 do not confirm this expectation, presumably due to the increase in the polarity of the solutions due to the dissolved salt. Irrespective of the uncertainties in the calculated values it is clear that the K_{AA} values in most solvents are several orders of magnitude smaller than the association constants, K_A , for ion pairs. This is as expected from Coulombic considerations. The triple ion hypothesis with sizable K_T will invariably lead to much larger K_{AA} to be able to account for a maximum in $\Lambda/\Lambda^\circ - c$ plots.

Conclusion

Conductivity and permittivity studies of Bu_4NClO_4 in several organic solvents of from low to intermediate permittivity lead to the conclusion that the Cavell-Knight approach²⁴ with strongly concentration dependent association constants is valid. On the basis of this approach and the Ostwald dilution law, the calculated degree of dissociation, α_{calc} , is in fair agreement with α_{exp} , equal to Λ/Λ° , for concentrations up to $\sim 0.1 \text{ mol dm}^{-3}$. Since α_{calc} can only be obtained when the association constant in very dilute solution is available, accurate conductivity studies are required.

At higher concentrations the formation of quadrupoles and higher aggregates causes a distinct decrease in the fraction of dissociated ions. Quadrupole formation constants, K_{AA} , have been roughly estimated from the $\epsilon_s - c$ plots and are several powers of ten smaller than K_A in most solvents.

On the basis of Kirkwood's g factors, the interionic distance, a , of the ion pairs, and the form of the $\epsilon_s - c$ plots it is concluded that solvents with the ability to form solvent species of increased polarity will have a higher dissociating ability than anticipated from the value of the static permittivity. In this class of solvents the ion pair relaxation time and the interionic distance in the ion pair seem to increase with increasing concentration. Acetic acid is particularly capable of dissociating Bu_4NClO_4 at high concentrations.

Acknowledgement. One of the authors (T.S.) is indebted to the Norwegian Council of Science and Humanities, NAVF, for financial support and to *Nordiska Forskarstipendier* for a travel grant.

References

- Brändstrom, A. *Adv. Phys. Org. Chem.* **13** (1975) 483.
- Finholt, A. E., Bond, A. C. and Schlesinger, H. I. *J. Am. Chem. Soc.* **69** (1947) 1199.
- Boorman, P. M., Garner, C. D. and Mabbs, F. E. *J. Chem. Soc., Dalton Trans.* (1975) 1299.
- Lewis, H. L. and Brown, T. L. *J. Am. Chem. Soc.* **92** (1970) 4664.
- Hogen-Esch, T. F. *Adv. Phys. Org. Chem.* **15** (1977) 153.
- Gompper, R. and Wagner, H.-U. *Angew. Chem. Int. Ed. Engl.* **15** (1976) 32.
- Szwarc, M., Ed., *Ions and Ion Pairs in Organic Reactions*, Wiley-Interscience, New York 1972, Vol. 1; *Ibid.* Vol. 2, 1974.
- Pearson, R. G. and Ellgen, P. *Inorg. Chem.* **6** (1967) 1379.
- Winstein, S., Kleindienst, P. E., Jr. and Robinson, G. C. *J. Am. Chem. Soc.* **83** (1961) 885.
- Harris, J. M. *Prog. Phys. Org. Chem.* **11** (1974) 89.
- Jenkins, W. L., Tien, C.-F. and Hogen-Esch, T. E. *Pure Appl. Chem.* **51** (1979) 139.
- Van Even, V. and Hanlait-Pirson, M. C. *J. Solution Chem.* **6** (1977) 757.
- Acasio, I. J. and Sullivan, P. D. *J. Phys. Chem.* **84** (1980) 3028.
- Prue, J. E. *J. Chem. Educ.* **46** (1969) 12.
- Eigen, M. and DeMaeyer, L. In: Weissberger, A., Ed., *Investigation of Rates and Mechanism of Reactions*, Wiley, New York 1963, Vol. 8, Part II.
- Masnovi, J. M. and Kochi, J. K. *J. Am. Chem. Soc.* **107** (1985) 788.
- Walden, P. Z. *Phys. Chem.* **30** (1902) 513; *Ibid.* **100** (1922) 512; *Ibid.* **147** (1930) 1.
- Fuoss, R. M. and Kraus, C. A. *J. Am. Chem. Soc.* **55** (1933) 2387.
- Kraus, C. A. *J. Chem. Educ.* **35** (1958) 324.
- Fuoss, R. M. and Accascina, F. *Electrolytic Conducance*, Wiley Interscience, New York 1959.
- Fuoss, R. M. and Onsager, L. *J. Phys. Chem.* **61** (1957) 668.
- Grigo, M. *J. Solution Chem.* **11** (1982) 529.
- Delsignore, M., Farber, H. and Petrucci, S. *J. Phys. Chem.* **89** (1985) 4968.
- Cavell, E. A. S. and Knight, P. C. *Z. Phys. Chem. (Neue Folge)* **57** (1968) 331.
- Gestblom, B. and Songstad, J. *Acta Chem. Scand., Ser. B* **41** (1987) 396.
- Ebeling, W. and Grigo, M. *J. Solution Chem.* **11** (1982) 151.
- Reger, A., Peled, E. and Gileadi, E. *J. Phys. Chem.* **83** (1979) 873.
- Bjerrum, N. *Kgl. Dan. Vidensk. Selsk. Skr., Naturvidensk. Mat. Afd.* (1926) 7.
- Fuoss, R. M. *J. Am. Chem. Soc.* **80** (1958) 5059.
- Fuoss, R. M. *J. Solution Chem.* **15** (1986) 231.
- Inami, Y. H., Bodenseh, H. K. and Ramsey, J. B. *J. Am. Chem. Soc.* **83** (1961) 4745.
- Abe, T. *J. Phys. Chem.* **90** (1986) 713.
- Bucher, M. and Porter, T. L. *J. Phys. Chem.* **90** (1986) 3406.
- Barthel, J. and Buchner, R. *Pure Appl. Chem.* **58** (1986) 1077.
- Svorstøl, I., Sigvartsen, T. and Songstad, J. *Acta Chem. Scand., Ser. B* **41** (1987) 318.
- Wickramasinghe, W. A., Bird, P. H. and Serpone, N. *Inorg. Chem.* **21** (1982) 2694.
- Titova, K. V., Kolmakova, E. I. and Rosolovskii, V. Y. *Izv. Akad. Nauk SSSR, Ser. Khim.* (1975) 2821.
- Gestblom, B., Svorstøl, I. and Songstad, J. *J. Phys. Chem.* **90** (1986) 4684.
- Bekkevold, S., Svorstøl, I., Høiland, H. and Songstad, J. *Acta Chem. Scand., Ser. B* **37** (1983) 935.
- Svorstøl, I., Høiland, H. and Songstad, J. *Acta Chem. Scand., Ser. B* **39** (1985) 639.
- Perrin, D. D., Armarego, W. L. F. and Perrin, D. R. *Purification of Laboratory Chemicals*, Pergamon Press, Oxford 1966.
- Islam, M. N. and Leffek, K. T. *J. Chem. Soc., Perkin Trans. 2* (1977) 952.
- Evans, D. F. and McIlroy, M. I. *J. Solution Chem.* **4** (1975) 413.
- Gestblom, B. and Jonsson, B. *J. Phys. E.* **13** (1980) 1067.
- Gestblom, B. and Elmgren, H. *Chem. Phys. Lett.* **90** (1982) 412.

46. Gestblom, B. and Sjöblom, J. *J. Chem. Phys.* 90 (1986) 4175.
47. Werblan, L., Suzdorf, A. and Lesinski, J. *Bull. Acad. Pol., Ser. Sci. Chem.* 28 (1980) 627.
48. Lüder, W. F. and Kraus, C. A. *J. Am. Chem. Soc.* 69 (1974) 2481.
49. Nakahara, M. and Ibuki, K. *J. Phys. Chem.* 90 (1986) 3026.
50. Plichta, E., Salomon, M., Slane, S. and Uchiyama, M. *J. Solution Chem.* 16 (1987) 225.
51. Powles, J. G. *J. Chem. Phys.* 21 (1953) 633.
52. Nelson, R. D. and Smyth, C. P. *J. Phys. Chem.* 68 (1964) 2704.
53. Sigvartsen, T. and Songstad, J. *To be published.*
54. Fröhlich, H. *Theory of Dielectrics*, Clarendon Press, Oxford 1958.
55. Harris, F. E. and Alder, B. J. *J. Chem. Phys.* 21 (1953) 1031.
56. Hill, N. E., Vaughan, W. E., Price, A. H. and Davies, M. *Dielectric Properties and Molecular Behaviour*, Van Nostrand, London 1969, p. 275.
57. Barcza, L. and Mihalyi, K. *Z. Phys. Chem. (Neue Folge)* 104 (1977) 199.
58. Umemura, J. *J. Mol. Struct.* 36 (1977) 35.
59. Gramstad, T. and Snaprud, S. I. *Acta Chem. Scand.* 16 (1962) 999.
60. Denison, J. T. and Ramsey, J. B. *J. Am. Chem. Soc.* 77 (1955) 2615.
61. Gan, T. H., Peel, J. B. and Willett, G. D. *Trans. Faraday Soc.* 2, 73 (1977) 965.
62. Viti, V. and Zampetti, P. *Chem. Phys. Lett.* 2 (1973) 233.
63. Fuoss, R. M. *J. Phys. Chem.* 79 (1975) 525.
64. Gilkerson, W. R. *J. Chem. Phys.* 25 (1956) 1199.
65. Barthel, J., Wachter, R. and Knerr, M. *Electrochim. Acta* 16 (1971) 723.
66. Delsignore, M., Farber, H. and Petrucci, S. *J. Phys. Chem.* 90 (1986) 66.
67. Hill, N. E., Vaughan, W. E., Price, A. H. and Davies, M. *Dielectric Properties and Molecular Behaviour*, Van Nostrand, London 1969, p. 198.
68. Hubbard, J., Colonomos, P. and Wolynes, G. P. *J. Chem. Phys.* 71 (1979) 2652.
69. Masson, D. O. *Philos. Mag.* 8 (1929) 218.
70. Ekclin, K. and Sillén, L. G. *Acta Chem. Scand.* 7 (1953) 9887.
71. Mohammad, M. and Kosower, E. M. *J. Phys. Chem.* 74 (1970) 1153.
72. Braun, R. and Sauer, J. *Chem. Ber.* 119 (1986) 1269.
73. Rezende, M. C. and Dal Sasso, L. I. *Rev. Roum. Chim.* 31 (1986) 323.
74. Cachet, H., Cyrot, A., Fekir, M. and Lestrade, J. C. *J. Phys. Chem.* 83 (1979) 2419.
75. Sigvartsen, T., Gestblom, B., Noreland, E. and Songstad, J. *Work in progress.*
76. Menard, D. and Chabanel, M. *J. Phys. Chem.* 79 (1975) 1081.
77. *Handbook of Chemistry and Physics*, 56th ed., CRC Press, Boca Raton 1976.

Received February 1, 1988.