

Solvent Properties of Dichloromethane. IV. Conductivity Studies of Fairly Concentrated Solutions of Tetraalkylammonium-, Tetraphenylarsonium- and Bis(triphenylphosphine)iminium Salts in Dichloromethane

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The variation of conductivity with concentration of some tetraalkylammonium salts, R_4NX , tetraphenylarsonium salts, Ph_4AsX , and bis(triphenylphosphine)iminium salts, $[(Ph_3P)_2N]X$, abbreviated $[PNP]X$, has been studied in the 2×10^{-3} – 2×10^{-1} M concentration range in dichloromethane at 25.00 °C. The molar conductivities of the more concentrated solutions of all the examined salts are considerably higher than expected from the association constants determined in the 10^{-5} M range. The molar conductivities, Λ , in the 5×10^{-3} – 2×10^{-1} M range are actually fairly constant, amounting to ~11, ~32 and ~40 % of the molar conductivities at infinite dilution, Λ° , for R_4NX , Ph_4AsX and $[PNP]X$, respectively.

For the Ph_4As^+ -salts and the R_4N^+ -salts with small R, except the BPh_4^- -salts, a minimum in the Λ -log c curves is observed which is fairly independent of the ions. Some of the salts show a maximum which is highly dependent of the cation but is independent of the anion. R_4N^+ -salts with large R, Ph_4B^- -salts and $[PNP]^+$ -salts display only an inflection in the Λ -log c curves. This inflection is observed at a concentration where the minimum in the Λ -log c curves for the other salts is observed. These observations lead to a discussion of the Walden empirical relationship, $\epsilon c_{min}^{-1/2} = \text{const}$.

The various factors being responsible for the considerable conductivity of fairly concentrated solutions of onium salts in dichloromethane and in other solvent of low dielectric constant are discussed. The conclusion is that the concept of conducting triple ions is doubtful and that a better explanation is that an increase in the dielectric constant of the solution causes a decrease of the association constant.

When solvents of low or fairly low dielectric constant, $\epsilon < 12$, are to be used as solvents for reactions involving ionic species, a number of difficulties arises which are generally not encountered in solvents of higher ϵ . The solubility problems can in most cases be circumvented by using large aliphatic or aromatic counterions. The low dielectric constant, however, causes a considerable fraction of the dissolved salts to exist as various ion-paired species¹ and probably also as higher aggregates.^{2,3} Characteristic for the extensive association which takes place in solvents of low ϵ is the low conductance of dilute solutions of salts as compared with the predictions based upon Onsager's limiting law. In recent years a number of highly sophisticated equations have appeared which have allowed accurate

determinations of association constants from conductivity data in dilute solutions. When ϵ is less than ~ 12 the sphere-in-continuum-theory appears valid and the FHFP equation⁴ based upon that theory seems to give the best fit to the conductance data.⁵ With association constants available, one may in principle interpret kinetic data for reactions involving ionic species in solvents of low dielectric constant.⁶⁻⁹

The possible involvement of free ions, ion-pairs and higher aggregates may often lead to ambiguities when interpreting the results from kinetic and sometimes product studies. The Bjerrum critical distance,¹⁰ q , is given by eqn. (1),

$$q = |z_1 z_2| e^2 / 2 \epsilon k T \quad (1)$$

in which z_1 and z_2 are the valence of the ions, e is the electronic charge, ϵ is the dielectric constant of the solvent, k is Boltzmann constant and T is the temperature. In solvents of low ϵ the Bjerrum critical distance as defined by eqn. (1) is large. In dichloromethane, ϵ is 8.90, this distance is ~ 32 Å which is several times the sum of the ionic radii of the most commonly employed salts. Consequently, several species with varying numbers of solvent molecules between the oppositely charged ions will satisfy the Bjerrum definition for ion-pairs. These species may differ in their reactivity toward the dissolved reactants and their relative abundance may vary with the concentration, the size of the solvent molecules and to what extent the solvent is associated.

The major uncertainty arises due to the fact that the association constants are derived from conductivity data in the 10^{-6} – 10^{-5} concentration range, well below the limit given by the Fuoss equation, $3.2 \times 10^{-7} \epsilon^3 \text{ M}$.¹¹ For dichloromethane Fuoss' limit is $2.3 \times 10^{-4} \text{ M}$.⁸ Obviously, few reactions can be examined in this concentration range and it is questionable whether the calculated association constants are reliable in the 10^{-3} – 10^{-1} M range, *i.e.* the concentration range in which most reactions are studied.

An improved description of more concentrated electrolytes in solvents of low ϵ seems therefore desirable. We report here on the conductivity of fairly concentrated solutions of some onium salts, mainly perchlorates, in dichloromethane at 25.00 °C. The perchlorates were primarily chosen since all the usual tetraalkylammonium perchlorates, R_4NClO_4 , and also other perchlorates, are most readily obtained in high purity. Dichloromethane is fundamentally a potential proton donor⁸ but the exceedingly weakly basic properties of the perchlorate ion^{12,13} justifies the assumption that this ion is essentially unsolvated in dichloromethane.⁸ The association constants of all the examined salts in dichloromethane at 25.00 °C have recently become available.⁸

The limited solubility of $\text{Ph}_4\text{AsClO}_4$, $\sim 1 \times 10^{-2} \text{ M}$, prevents this salt to be studied in concentrated solutions. Since $[\text{PNP}]\text{SCN}$ and $\text{Bu}_4\text{N}\text{SCN}$ were found to behave conductometrically similarly to $[\text{PNP}]\text{ClO}_4$ and $\text{Bu}_4\text{N}\text{ClO}_4$, respectively, the very soluble Ph_4AsSCN was considered as a valid alternative. Additionally, Ph_4AsCl was studied. The fairly soluble $\text{Bu}_4\text{N}\text{BPh}_4$ allowed a study of a BPh_4^- -salt without a cation with phenyl groups. None of the usual Me_4N^+ -salts were found to be sufficiently soluble to be included in the present study.

EXPERIMENTAL

The purification of dichloromethane and the onium salts together with a description of the electrical equipment and the conductivity cell has been published.^{6,8} All measurements were

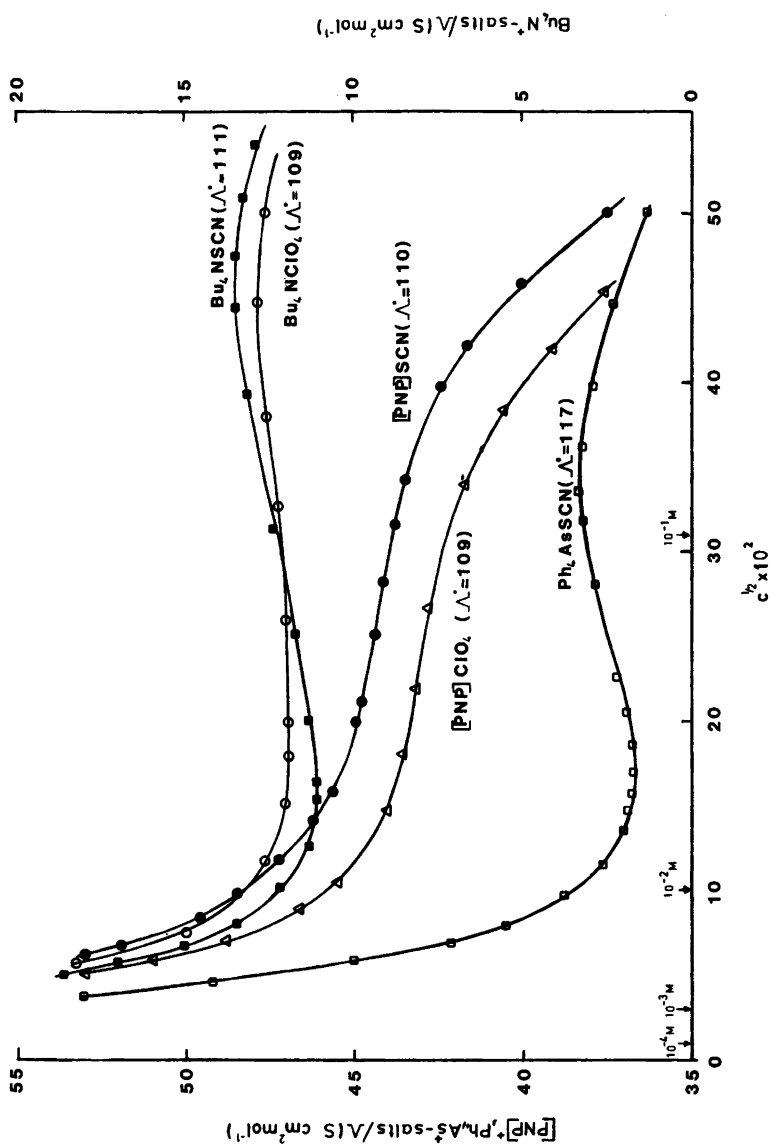


Fig. 1. The molar conductivity versus the square root of the molarity for $[PNP]SCN$, $[PNP]ClO_4$ and Ph_4AsSCN (left hand ordinate scale) and for Bu_4NSCN and Bu_4NClO_4 (right hand ordinate scale).

performed at 25.00(1) °C. A Wayne Kerr Co. Ltd. self-balancing bridge, Model B 331 Mk II, functioning at 1591.5 Hz, was applied throughout this study. The salts were generally studied from $\sim 2 \times 10^{-3}$ M and up to $\sim 2 \times 10^{-1}$ M when sufficiently soluble.

RESULTS

The conductance data for Bu_4NClO_4 , Bu_4NSCN , $[\text{PNP}]\text{ClO}_4$, $[\text{PNP}]\text{SCN}$ and Ph_4AsSCN in dichloromethane in the 10^{-3} – 10^{-1} M concentration range are shown graphically in Fig. 1 where Λ , the molar conductivity, is plotted versus $c^{1/2}$. The conductance curves appear in principle as expected for associated electrolytes up to a concentration of $\sim 5 \times 10^{-3}$ M. At higher concentrations the conductance curves are highly complex, particularly for the

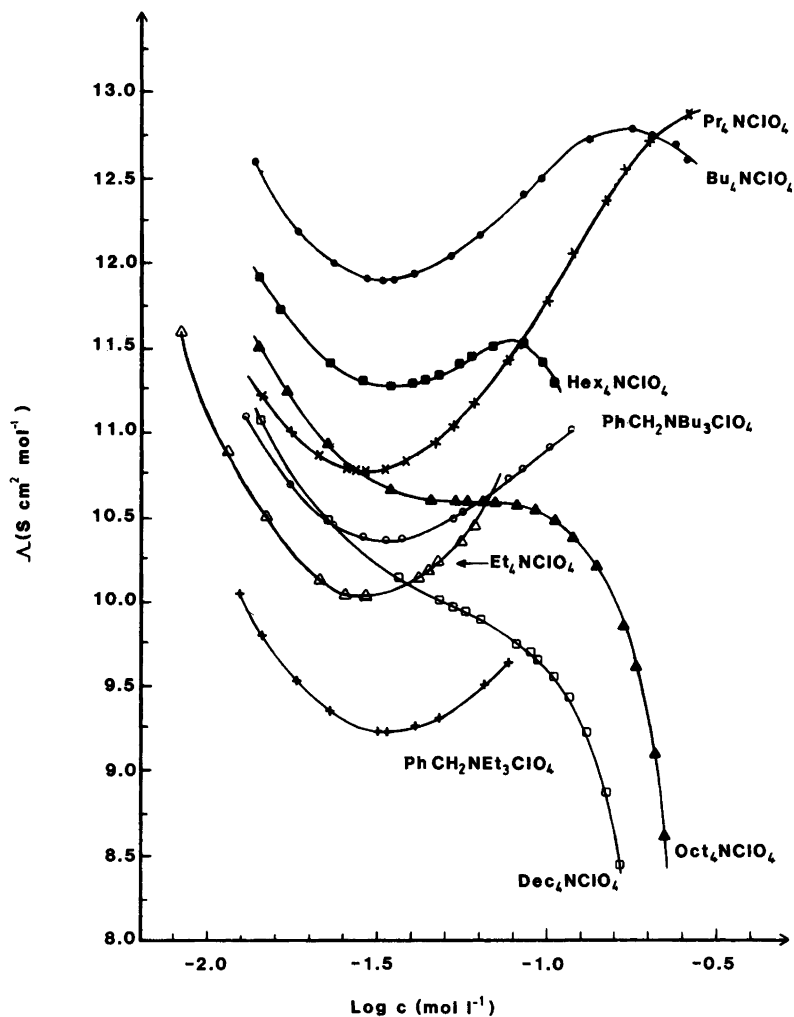


Fig. 2. The molar conductivity versus the logarithm of the molarity for tetraalkylammonium perchlorates.

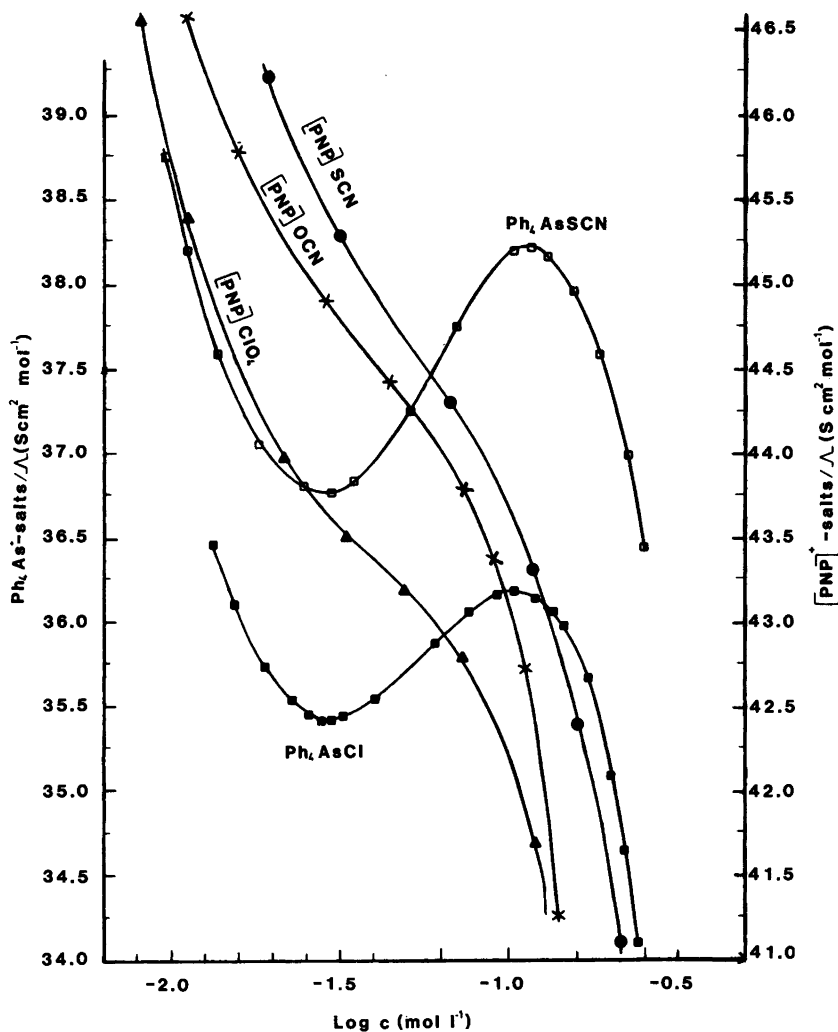


Fig. 3. The molar conductivity versus the logarithm of the molarity for Ph_4As^+ -salts (left hand ordinate scale) and for $[\text{PNP}]^+$ -salts (right hand ordinate scale).

Bu_4N^+ -salts and for Ph_4AsSCN . The molar conductivity seems to be fairly constant, $\sim 11\%$ and $\sim 32\%$ of Λ° , respectively. A minimum and a maximum, however, can be detected. In the case of the $[\text{PNP}]^+$ -salts the molar conductivity is less constant. No minimum and maximum can be observed, but an inflection in the $\Lambda-c^{\frac{1}{2}}$ curves where Λ is some 40% of Λ° is evident.

The peculiarities in the conductance curves at higher concentrations as indicated in Fig. 1 necessitate an improved graphical representation. Λ versus $\log c$ plots have often been used.¹⁴ Fig. 2 shows such plots for several tetraalkylammonium perchlorates; for the $[\text{PNP}]^+$ - and the Ph_4As^+ -salts, cf. Fig. 3. A distinct minimum at $\sim 3 \times 10^{-2}$ M is characteristic for all the studied ammonium perchlorates, except $\text{Oct}_4\text{NClO}_4$ and $\text{Dec}_4\text{NClO}_4$. The

concentration at which this minimum is observed increases only slightly with increasing size of the cation. For Bu_4NClO_4 and $\text{Hex}_4\text{NClO}_4$ a distinct maximum is also observed at $\sim 13 \times 10^{-2}$ and $\sim 8 \times 10^{-2}$ M, respectively. The Λ -log c curve for Pr_4NClO_4 seems to indicate a similar maximum at ~ 0.3 M but the solubility of this salt is not sufficient to allow an experimental verification. Et_4NClO_4 could only be examined up to a concentration of $\sim 8 \times 10^{-2}$ M allowing only a minimum to be detected. The molar conductivity, Λ , at this minimum ranges from 7.7 % of the molar conductivity at infinite solution, Λ° , for benzyltriethylammonium and tetraethylammonium perchlorate to ~ 11 % for the perchlorates of the largest cations. Presumably, this is due to the larger association constants of the perchlorates of the smaller cations.⁸ Λ° , c_{\min} , c_{\max} , Λ_{\min} , Λ_{\max} and various other derived data for the studied salts are summarized in Table 1.

While c_{\min} appears to be fairly independent of the cation, the concentration at which the maximum is observed, c_{\max} , and how pronounced this maximum is, seem to be highly dependent on the cation. With increasing size of the cation c_{\max} appears to approach c_{\min} and, finally, only an inflection in the Λ -log c curves can be observed, cf. curves for $\text{Oct}_4\text{NClO}_4$ and $\text{Dec}_4\text{NClO}_4$ in Fig. 2.

The most distinct minimum and maximum in the Λ -log c curves are observed for the two Ph_4As^+ -salts as illustrated in Fig. 3; for a direct comparison with Bu_4NClO_4 and Bu_4NCSN , cf. Fig. 1. The curves for the two Ph_4As^+ -salts are most similar and the minimum and maximum in the molar conductivity for these two salts, the chloride and the thiocyanate, are

Table 1. The concentration at which the molar conductivity, Λ , has a minimum, c_{\min} , a maximum, c_{\max} , or the Λ -log c curve has an inflection, c_{infl} , together with the corresponding values of Λ in % of Λ° . All values in dichloromethane at 25.00 °C.

Salt	Λ° ^a	c_{\min}		c_{\max}		c_{infl}	
	S cm ² mol ⁻¹	M × 10 ²	100 $\Lambda_{\min}/\Lambda^\circ$	M × 10 ²	100 $\Lambda_{\max}/\Lambda^\circ$	M × 10 ²	100 $\Lambda_{\text{infl}}/\Lambda^\circ$
Et_4NClO_4	130(5)	2.9	7.8	<i>c</i>			
Pr_4NI	110(2)	2.6	9.7	<i>c</i>			
Pr_4NClO_4	112(2)	2.8	9.6	~ 30	~ 11.6		
Bu_4NBr	106(2)	2.9	10.1	20	11.6		
Bu_4NI	108(2)	2.9	10.0	20	11.6		
Bu_4NNO_3	103(2)	2.5	10.0	20	11.9		
Bu_4NHSO_4	114(2)	5.6	2.4	17.4	2.6		
Bu_4NBPh_4	83(1)	<i>b</i>		<i>b</i>		~ 3.2	~ 14
Bu_4NCSN	111(2)	2.3	10.3	21	11.9		
Bu_4NClO_4	109(1)	3.1	10.9	19	11.7		
$\text{Hex}_4\text{NClO}_4$	103(1)	3.5	10.9	8	11.2		
$\text{Oct}_4\text{NClO}_4$	96(2)	<i>b</i>		<i>b</i>		~ 5.0	~ 11
$\text{Dec}_4\text{NClO}_4$	92(1)	<i>b</i>		<i>b</i>		~ 5.0	~ 11
$\text{PhCH}_2\text{NET}_3\text{ClO}_4$	120(4)	3.3	7.7	<i>c</i>			
$\text{PhCH}_2\text{NBu}_3\text{ClO}_4$	109(2)	3.3	8.5	<i>c</i>			
Ph_4AsCl	111(1)	2.8	31.8	10.5	32.6		
Ph_4AsSCN	117(2)	2.8	31.4	11.2	32.7		
[PNP]SCN	110(1)	<i>b</i>		<i>b</i>		~ 4.2	~ 41
[PNP]OCN	103(1)	<i>b</i>		<i>b</i>		~ 4.5	~ 43
[PNP]ClO ₄	109(1)	<i>b</i>		<i>b</i>		~ 4.0	~ 40

^a From Ref. 8. ^b Only inflection in Λ -log c curve. ^c Not sufficiently soluble.

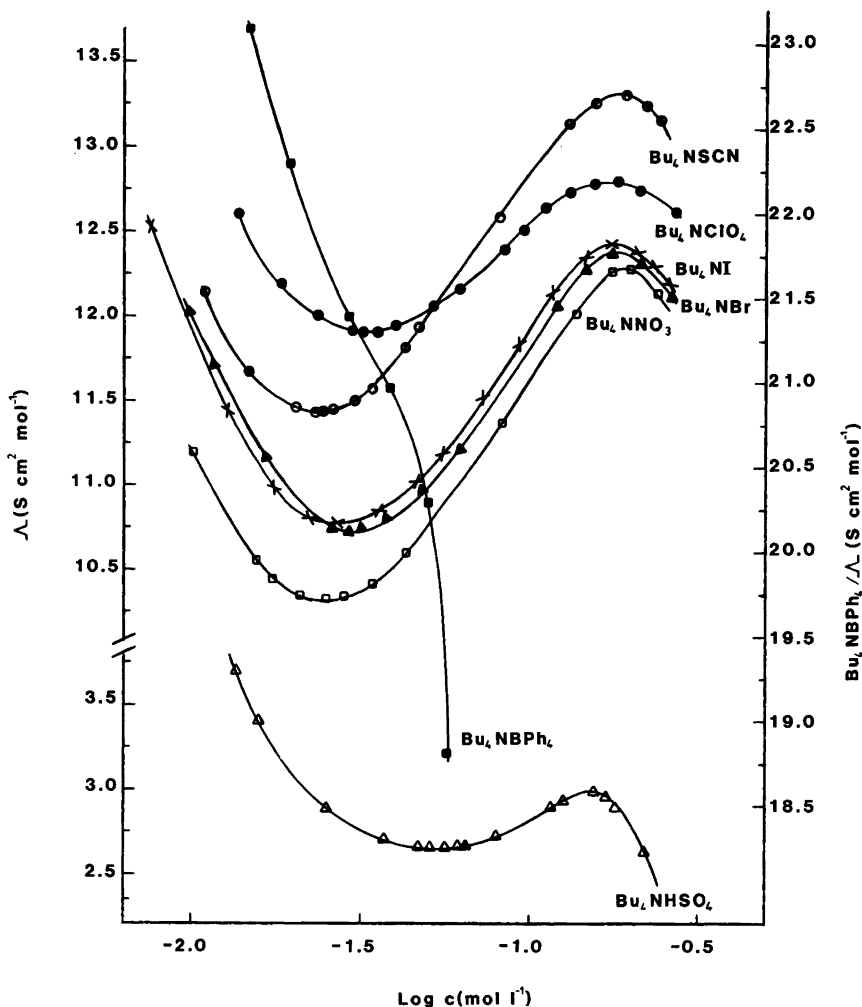


Fig. 4. The molar conductivity versus the logarithm of the molarity for Bu_4N^+ -salts. (Right hand ordinate scale for Bu_4NBPh_4).

found at $\sim 3.0 \times 10^{-2}$ M and at $\sim 11 \times 10^{-2}$ M. The lowering of the curve for Ph_4AsCl as compared with that for Ph_4AsSCN with some $1.5 \text{ S cm}^2 \text{ mol}^{-1}$ in Λ probably reflects that Λ° is lower for Ph_4AsCl than for Ph_4AsSCN , 111.3^{15} and $117(2) \text{ S cm}^2 \text{ mol}^{-1}$.⁸ It is notable that the concentration at which the minimum in Λ is found, c_{min} , is quite comparable with that observed for the ammonium perchlorates, *cf.* Fig. 2.

The Λ - $\log c$ curves for $[\text{PNP}]\text{SCN}$, $[\text{PNP}]\text{OCN}$ and $[\text{PNP}]\text{ClO}_4$, are all of the same form. This indicates that for salts of this cation the anions exert only a negligible influence. Similarly may be said for the Ph_4As^+ -salts. No distinct minima and maxima are evident and the Λ - $\log c$ curves for the $[\text{PNP}]^+$ -salts are quite similar to that of $\text{Dec}_4\text{NClO}_4$; *cf.* Fig. 2. At a concentration of $\sim 4 \times 10^{-2}$ M an inflection in the Λ - $\log c$ curves is observed where Λ for all

three [PNP]⁺-salts is approximately 40 % of Λ° . The [PNP]⁺-salts have previously been shown to be the least associated salts in dichloromethane.⁸

The Λ -log c curves for several Bu₄N⁺-salts are shown in Fig. 4. (The scale in the ordinate values is as in Figs. 2 and 3.) The curve for Bu₄NBPh₄ is comparable to those for Dec₄NClO₄, Fig. 2, and the [PNP]⁺-salts, Fig. 3, *i.e.* only an inflection can be detected. The remaining Bu₄N⁺-salts exhibit a distinct minimum and a maximum as observed for Bu₄NClO₄. It is notable that Bu₄NHSO₄ with its exceptionally low molar conductivity in the 10⁻³–10⁻¹ M concentration range, *cf.* the lower curve in Fig. 4, has a Λ -log c curve quite comparable to the other Bu₄N⁺-salts. Contrary to the Ph₄As⁺-salts, c_{\min} for the Bu₄N⁺-salts seems to be slightly dependent on the anion. No obvious relationships are apparent between c_{\min} and the size of the anion, the association constants of the salts, *etc.* While c_{\min} for the Bu₄N⁺-salts depends on the anion, c_{\max} seems to be independent on the anion and is for all Bu₄N⁺-salts observed at $\sim 1.8 \times 10^{-1}$ M.

DISCUSSION

In solvents of low dielectric constant plots of the molar conductivity, Λ , *versus* some function of the salt concentration, c , $c^{\frac{1}{2}}$ or $\log c$, are well known to exhibit a minimum in the 10⁻⁴–10⁻² M concentration range. The concentration by which this minimum is observed is known to depend on ϵ . This phenomenon was probably first detected by Walden more than 80 years ago in a study of potassium iodide in sulfur dioxide.^{16,17} Later on, Walden examined a number of salts in several solvents, among which was dichloromethane. He found an empirical relationship between the dielectric constant of the solvent, ϵ , and the concentration at which the minimum occurred, c_{\min} , eqn. 2;

$$\epsilon c_{\min}^{-\frac{1}{2}} = \text{const.} \quad (2)$$

for surveys of references, *cf.* Refs. 18 and 19. A similar relationship was also detected by cryoscopic and melting point depression studies in acetic acid, $\epsilon=6.2$, and in other solvents.²⁰ To the best of our knowledge no theoretical explanation of justification for eqn. (2) has been suggested and discussed.

In dichloromethane at 25 °C this minimum in the Λ -log c plots was observed by Walden at $\sim 2 \times 10^{-2}$ M for a number of R₄N⁺-salts and was found to be fairly independent upon both the size of the cation, Et₄N⁺ or Pen₄N⁺, and the anion, Cl⁻, Br⁻, I⁻ or NO₃⁻. The present results are in general agreement with Walden's original work. The exceptions are for the salts of Oct₄N⁺, Dec₄N⁺, [PNP]⁺ and BPh₄⁻, and the slight dependence of c_{\min} upon the anion in the case of the Bu₄N⁺-salts, *cf.* Fig. 4.

Kraus and Fuoss¹⁴ investigated several tetraisoamylammonium salts, particularly the nitrate, in various dioxane-water mixtures and observed a distinct minimum in the Λ -log c curves in solvent mixtures with ϵ less than ~ 12 , *cf.* Ref. 2. A similar upper limit in ϵ for the detection of a minimum was observed for lithium perchlorate in methanol-dioxane and in methanol-ethylacetate mixtures.^{21,22} In solvents of low ϵ like benzene, dioxane *etc.* this minimum is detected only in very dilute solutions, $\sim 10^{-4}$ M,^{2,23} in agreement with Walden's relationship. In the concentration range generally used for chemical reactions, 10⁻³–10⁻¹ M, many solvents with ϵ in the 5–12 range exhibit irregularities including a Λ -log c minimum.

Among these solvents commonly used are the aliphatic carboxylic acids, their esters and all the usual halogenated alkanes.

1,2-Dichloroethane seems to be a border-line case. The Λ -log c curves for tetraisoamylammonium salts in this solvent has an inflection but no minimum.¹⁴ This may partly be due to the size of this cation, *cf.* Fig. 2 which shows the plots for the various R₄N⁺-salts in dichloromethane. R₃NH⁺-salts display the usual minimum in 1,2-dichloroethane at a concentration of $\sim 7 \times 10^{-2}$ M.^{14,18,24} From c_{\min} for the R₃NH⁺-salts in 1,2-dichloroethane and in dichloromethane and using ϵ of dichloromethane as reference one may estimate the dielectric constant of 1,2-dichloroethane to be 11.6 by means of Walden's relationship, eqn. 2. This is in a surprisingly good agreement with the "effective" dielectric constant of 1,2-dichloroethane as calculated from association constants of several aryltrimethylammonium perchlorates in 1,2-dichloroethane.²⁵

The observed maxima in the Λ -log c curves have rarely been commented upon. This is perhaps due to the fact that these maxima occur at concentrations that for most salt-solvent combinations will not be attained for solubility reasons. In the case of Pr₄NI in dichloromethane Walden observed a maximum at $\sim 3 \times 10^{-1}$ M,¹⁸ a c_{\max} which is also indicated by the present data for Pr₄NClO₄, *cf.* Fig. 2. As for the two Pr₄N⁺-salts and all the Bu₄N⁺-salts examined, the concentration at which this maximum is observed is highly dependent on the cation but is fairly independent of the anion. Furthermore, while c_{\min} is dependent on ϵ , one may conclude from the extensive studies on LiClO₄ in various solvent mixtures^{21,23} that c_{\max} is fairly independent of ϵ when salts of only one cation are considered. The conclusion is that the smaller ϵ is, the more distant will c_{\min} and c_{\max} be, *cf.* Walden's study on tetraalkylammonium salts in chloroform, $\epsilon=4.95$, and in dichloromethane, $\epsilon=8.90$.¹⁸ In solvents with a dielectric constant of ~ 12 , c_{\min} and c_{\max} will nearly coincide and an inflection in the Λ -log c curves is observed, *cf.* the Λ -log c curves in 1,2-dichloroethane.¹⁴ Finally, in the usual protic and dipolar aprotic solvents with $\epsilon > 20$, the inflection will also disappear and Λ -log c curves without any peculiarities are observed.

Generally one may conclude that when Λ -log c curves display a distinct minimum, as for R₄N⁺-salts with fairly small alkyl groups and for Ph₄As⁺-salts, the Walden relationship, eqn. 2, seems quite reliable. In the case of the [PNP]⁺-salts, Oct₄NClO₄, Dec₄NClO₄ and Bu₄NBPh₄ in dichloromethane and the usual R₄N⁺-salts in solvents with slightly higher dielectric constant, this minimum is obscured due to the small separation of c_{\min} and c_{\max} . However, the inflection in the Λ -log c curves appears at a concentration in accordance with Walden's relationship.^{18,19}

Regardless of whether a c_{\min} and a c_{\max} or only an inflection is observed, the Λ -log c curves in solvents of low or moderate dielectric constant indicate that the molar conductivity is distinctly higher above a certain concentration than expected from a simple equilibrium between some type(s) of non-conducting ion-pairs and free ions. The magnitude of this discrepancy is considerable; *cf.* Table 2 for a comparison between observed and calculated molar conductivities, Λ_{obs} and Λ_{calc} , of 0.01 M and 0.1 M solutions of three representative salts, [PNP]ClO₄, Ph₄AsSCN and Bu₄NClO₄. The following possible causes for the significant difference between Λ_{obs} and Λ_{calc} have to be considered:

1. *The presence or formation of conducting ion-pairs.* Fuoss²⁶ has argued that solvent-separated ion-pairs in contrast to contact ion-pairs may contribute to the net transport of charge.^{27,28} The question arises whether the excess molar conductivity at higher concentrations is due to an increase in the fraction of ion-pairs, ion-pairs which may be weakly conducting, or the ion-pairs in a certain concentration range will change their

Table 2. Observed molar conductivities, Λ_{obs} , and calculated molar conductivities, Λ_{calc} , of 0.01 and 0.1 M solutions of [PNP]ClO₄, Ph₄AsSCN and Bu₄NClO₄. S cm² mol⁻¹.

	[PNP]ClO ₄		Ph ₄ AsSCN		Bu ₄ NClO ₄	
	Λ_{obs}	Λ_{calc}^a	Λ_{obs}	Λ_{calc}^a	Λ_{obs}	Λ_{calc}^a
0.01 M	47	24	38	19	13	7
0.1 M	43	8	38	6	12.5	2

^a $\Lambda_{\text{calc}} = a \Lambda^0$ in which a is given by $K_A^{-1} = a^2 c / (1 - a)$. (Λ^0 and K_A from Ref. 8).

character as to contribute to the conductivity. It is to be emphasized that the formal association constant, K_A , as defined in the usual way,⁸ may still remain constant over the entire concentration range. These questions require first of all an analysis of what type(s) of ion-pairs are present in very dilute solutions where no irregularities in the Λ -log c curves are observed.⁸

Although the Bjerrum theory¹⁰ is known to be inadequate describing experimental results from one solvent to another,^{29,30} this theory has proved to be of considerable value when predicting large-scale trends in a given solvent system and for estimating the distance of closest approach, a , in the ion-pair. Table 3 summarizes the a -values for a number of salts in dichloromethane as calculated by the Bjerrum equation¹⁰ using association constants in

Table 3. Association constants, K_A , of onium salts in very dilute solutions in dichloromethane at 25.00 °C together with a , the distance of closest approach, as calculated by the Bjerrum equation, and $r^+ + r^-$, the sum of the ionic radii of cation and anion.

	$K_A \times 10^{-3}^a$	a (Å) ^b	$r^+ + r^-$ (Å) ^c
Et ₄ NClO ₄	46(10)	4.9(3)	5.5
Pr ₄ NClO ₄	27(2)	5.2(2)	6.0
Bu ₄ NClO ₄	22(1)	5.4(2)	6.3
Hex ₄ NClO ₄	20(1)	5.5(2)	6.8
Oct ₄ NClO ₄	17(1)	5.6(2)	7.2
Dec ₄ NClO ₄	14(1)	5.8(2)	7.7
Ph ₄ AsClO ₄	2.1(3)	10.1(9)	6.7
[PNP]ClO ₄	1.4(3)	12.8(15)	7.9
Ph ₄ AsCl	3.6(3)	8.0(2)	6.1
Ph ₄ AsSCN	3.3(3)	8.3(3)	6.4
[PNP] Cl	1.7(3)	11.3(9)	7.2
[PNP] SCN	1.8(3)	11.0(9)	7.5
Bu ₄ NCl	41(3)	4.9(1)	5.6
Bu ₄ NBr	25(2)	5.3(2)	5.8
Bu ₄ NI	24(2)	5.3(2)	6.0
Bu ₄ NSCN	27(5)	5.2(3)	5.9
Et ₄ NBPh ₄	8(1)	6.4(2)	7.3
Bu ₄ NBPh ₄	3.3(1)	8.3(1)	8.1
Ph ₄ AsBPh ₄	2.3(3)	9.7(4)	8.5

^a From Ref. 8. ^b Limits of error in a derived from uncertainty in K_A and $Q(b)$; cf. Ref. 2 and Appendix 14.1 in Ref. 35, page 549. ^c The following radii for the R₄N⁺-cations were calculated by the Stearn-Eyring equation; cf. text: Et₄N⁺ 3.1 Å, Pr₄N⁺ 3.5 Å, Bu₄N⁺ 3.8 Å, Hex₄N⁺ 4.3 Å, Oct₄N⁺ 4.8 Å, Dec₄N⁺ 5.2 Å.

this solvent⁸ and the sum of the ionic radii of the cation and the anion, r^+ and r^- . The usual Pauling radii³¹ were used for the smaller anions while the van der Waals' ones, 4.25 Å,³² were used for Ph₄As⁺ and Ph₄B⁻; cf. Ref. 8 for a compilation. The ionic radii for the R₄N⁺-cations were derived from the recently estimated partial molar volumes in dichloromethane, V_ϕ° ,³³ by means of the Stearn-Eyring equation,³⁴ $r = (V_\phi^\circ/8N)^{\frac{1}{3}}$. The use of this equation yields somewhat smaller radii for the R₄N⁺-cations than the usual radii derived from studies in aqueous solutions^{35,36} and are also smaller than the generally less reliable Stokes' radii.⁸ The Stearn-Eyring equation,³⁴ however, seems to take into account the effect of the various possible conformations of the alkyl groups which will cause a decrease in the effective ionic radii of R₄N⁺-cations, particularly in a weakly coordinating and a weakly associated solvent like dichloromethane; cf. Refs. 37 and 38. The ionic radius of the ClO₄⁻ anion is likewise uncertain; from the crystal structures of KClO₄³⁹ and of HClO₄ and HClO₄·H₂O⁴⁰ one may calculate the radius to be 1.8 Å. Since the partial molar volume of the perchlorate ion is slightly but significantly larger than that of the iodide ion ($r=2.2$ Å) in all solvents,^{33,37} the ionic radius as determined by Bax and co-workers,⁴¹ 2.45 Å, was used.^{32,38} The ionic radius of the [PNP]⁺-cation is more difficult to estimate since it is not known whether this ion is bent or linear in solution. The Stokes' radius in water, 5.8 Å,⁸ in methanol, 4.8 Å,⁴² and in dichloromethane, 5.4 Å,⁸ may suggest the latter value to be a fair estimate.

Irrespective of the uncertainties in some of the ionic radii, the Bjerrum equation¹⁰ seems to yield a -values in dichloromethane in reasonable agreement with the sum of the ionic radii for the salts of the smaller R₄N⁺-cations. The discrepancy for the salts of the larger R₄N⁺-cations may actually indicate that even the Stearn-Eyring equation³⁴ leads to too large radii for these cations in dichloromethane. Since the distance of closest approach, a , does not exceed the sum of the ionic radii for any of the R₄N⁺-salts, one has to conclude that the contact ion-pairs are the most conceivable ion-pair species in dilute solution for this class of salts in dichloromethane. A similar conclusion has recently been arrived at from a conductivity study of several R₄N⁺-picrates in this solvent.⁵ The ion-pairs in dilute solutions of [PNP]⁺- and Ph₄As⁺-salts may rather be characterized as solvent-separated ion-pairs; for all these salts the calculated a -values are significantly larger, 2–5 Å, than calculated from the ionic radii. Presumably, the interaction between the phenyl groups of these two cations and the solvent molecules is sufficiently strong to allow some solvent molecules to be retained in the ion-pairs. It is notable that in the case of the Ph₄B⁻-salts the Bjerrum equation leads to reasonable estimates for the distance of closest approach, a ; cf. the last three entries in Table 3. The Ph₄As⁺-cation and the Ph₄B⁻-anion seem thus to behave differently toward dichloromethane in spite of the apparent validity of the assumption of equal mobility of these two ions in this solvent.⁸

This analysis of the structure of the ion-pairs in dichloromethane leads to the conclusion that there can be no relationships of any kind between the form of the Λ -log c curves, cf. Figs. 1 to 4, and thus the magnitude of the discrepancy between Λ_{obs} and Λ_{calc} , cf. Table 2, and the type of ion-pairs being present in dilute solutions, contact ion-pairs or solvent-separated ion-pairs. The arguments, as originally advocated by Fuoss,²⁶ with regard to the contribution to the transport of charge by the presence of solvent-separated ion-pairs seem therefore weakened. Furthermore, it is difficult to imagine how contact ion-pairs (R₄N⁺- and Ph₄B⁻-salts) or ion-pairs separated by a limited number of solvent molecules ([PNP]⁺- and Ph₄As⁺-salts) can possibly be transformed into ion-pairs with sufficient charge separation to assist in the transport of charge with an increase in the concentration from

$\sim 10^{-5}$ to $\sim 10^{-2}$ M. Actually, from the usual expression for the ion atmosphere of an ion, $a + \kappa^{-1}$,³⁵ in which κ is given by eqn. (3) for a 1:1 electrolyte,

$$\kappa = (8\pi e^2 N / 1000 \epsilon k T)^{1/2} c \quad (3)$$

the opposite effect is to be anticipated; *i.e.* the distance between the ions in the ion-pairs is to decrease with increasing concentration. Additionally, the mere size of the ions has to be considered in concentrated solutions of salts of particularly large ions. The ions alone in a 1×10^{-2} M solution of [PNP]Cl will occupy a volume of no less than 1 % of the bulk solvent.⁴² The anticipated increase in the dielectric constant of the solutions with increasing concentration⁴³ owing to the large dipole moment of the ion-pairs,⁴⁴ can hardly alter the structure of the ion-pairs sufficiently to cause the conductivity to be increased; *cf.* the expression for κ as shown in eqn. (3). Recently it has been shown that the distance of closest approach, a , for Pr_4N^+ -picrate is independent of the dielectric constant in dichloromethane-acetone mixtures,⁵ *i.e.* with ϵ varying from 8.90 to 20.56. Thus, one has to conclude that the observed irregularities in the Λ -log c curves in dichloromethane cannot be due to the formation of conducting ion-pairs in concentrated solutions.

2. *Formation of triple ions.* Fuoss and Kraus² have suggested that conducting triple ions, $[\text{ABA}]^+$ and $[\text{BAB}]^-$, may be formed from non-conducting ion-pairs, $[\text{AB}]$. According to this theory the fraction of triple ions above a certain concentration will increase more rapidly than the fraction of free ions will decrease and give rise to a minimum in the Λ -log c curves; *cf.* Ref. 45 for a comprehensive discussion. Beronius and co-workers^{3,5,46,47} have in a series of papers analyzed the results from numerous conductivity studies in solvents of low dielectric constant based upon the triple ion assumption. Recent spectroscopic studies⁴⁸ and computer simulations⁴⁹ have yielded evidence for a higher degree of association than ion-pairs in these solvents. Further evidence for this class of species has been obtained from freezing-point measurements of solutions of several R_3NH^+ - and R_4N^+ -salts.⁵⁰ Grigo,⁵¹ however, has suggested that it may be possible to fit conductance data in solvents of low dielectric constant without the additional assumption of triple ion formation.

The similarity in the Λ -log c curves for the various Bu_4N^+ -salts as shown in Fig. 4, however, can only be considered as evidence against triple ion formation. Although the bromide ion, the iodide ion and the thiocyanate ion are weakly solvated by dichloromethane,⁸ it is hard to imagine how the stability of $[\text{R}_4\text{N}-\text{X}-\text{NR}_4]^+$ and $[\text{X}-\text{R}_4\text{N}-\text{X}]^-$, X being weakly coordinating anions like ClO_4^- and NO_3^- , can equal that of possible triple ions formed from Br^- , I^- and SCN^- . Furthermore, if triple ions were to be considered in solvents of low dielectric constant, these species may not be formed from only the non-conducting ion-pairs, but may equally well be formed from ion-pairs and free ions, *cf.* eqns. (4) and (5).



Eqns. (4) and (5) are in principle the same equations as for homoconjugation between Lewis and Brønsted acids and bases and their corresponding bases and acids;⁵² *cf.* the formation of species like HX_2^- , HF_2^- and I_3^- .

3. *Change in transport mechanism.* With reference to the high mobility of H⁺ and OH⁻ in aqueous solution one may suppose a similar mechanism for the transport of ions in dichloromethane; increasing total concentration implies increasing concentration of ion-pairs and of higher aggregates (clusters) and the net transport of the free ions may thus be increased. Reger *et al.*⁵³, in an attempt to explain the sharp increase in the conductivity of the Al₂Br₆-LiBr-toluene system with increasing concentration, proposed that the ions may jump from one cluster to another. By this mechanism an ion may reach a cluster at one end and another ion of the same type leaves the cluster at the other end. The coordinating ability of the ions seems to be of importance for the stability of higher aggregates as for possible triple ions. The similarity in the Λ -log *c* plots for the various Bu₄N⁺-salts, Fig. 4, may therefore be considered as evidence against this alternative transport mechanism.

4. *Decreasing association constant with increasing concentration.* The association constant of an electrolyte is known to be highly dependent on the dielectric constant of the solvent. This is well established by Bjerrum's original work¹⁰ and by later studies.^{25,29,54-56} Comprehensive discussions and various expressions for K_A as a function of ϵ are given in Refs. 35, 57 and 58. A recent investigation by Lindbäck⁵ illustrates this dependence. The association constant of Pr₄N⁺-picrate is found to decrease from 1.4×10^4 in dichloromethane ($\epsilon=8.90$) to 1.05×10^2 in acetone ($\epsilon=20.56$).⁵

Contrary to solvents of medium and high ϵ ,⁵⁹ the dielectric constant of solvents of low ϵ appears to be highly dependent on the concentration of dissolved salts. Cavell and Knight⁴³ have shown that the dielectric constant of 1,2-dichloroethane increases from 10.23 of the pure solvent to 17.2 for a concentration of 0.298 M of tributylammonium picrate. These authors derived the following equation from Bjerrum's original equation¹⁰ for the dependence of the association constant, K_A , on the dielectric constant of the solution, ϵ_s , eqn. (6),

$$K_A(\epsilon_s) = K_A^0 \exp(e^2/akT)(1/\epsilon_s - 1/\epsilon_0) \quad (6)$$

in which K_A^0 is the association constant in very dilute solutions. Eqn. (6) leads to a linear correlation between log K_A and ϵ^{-1} . This has been verified both for pure⁴³ and mixed^{2,5} solvents. Cachet and co-workers⁶⁰ have shown that ϵ of tetrahydrofuran increases from 7.24 when pure to 17.95 in a 0.8 M solution of Bu₄NBr. They argue convincingly that this increase in ϵ with concentration has to be taken into account when electrolytes in weakly dissociating media are to be described. It is generally assumed that the high dipole moment of the ion-pairs is the cause for this increase in ϵ .

Although no detailed studies of the concentration dependence of the dielectric constant of dichloromethane are presently available, preliminary investigations⁶¹ have indicated a dependence on the salt concentration of the same order of magnitude as observed in 1,2-dichloroethane⁴³ and in tetrahydrofuran.⁶⁰ This suggests that the fundamental cause for the special features in the Λ -log *c* curves, *cf.* Figs. 1 to 4, and hence the considerable discrepancy between the calculated and the observed molar conductivities for high concentrations in dichloromethane, *cf.* Table 2, is due to a decrease in the association constant leading to a larger fraction of conducting ions with increasing concentrations.

It must, however, be emphasized that this concentration dependence of the association constant in solvents of low dielectric constant is not alone responsible for the levelling off in the Λ -*c*^{1/2} slopes as shown in Fig. 1. Since the slope, *A*, in the Onsager limiting law, $\Lambda = \Lambda^0 - Ac^{1/2}$, is a function of the dielectric constant,³⁵ in dichloromethane it is essentially

proportional to $\varepsilon^{-\frac{1}{2}}$, this slope will necessarily decrease with increasing concentration. For low concentrations, 10^{-6} – 10^{-4} M, in solvents of low ε , as for fairly concentrated solutions in solvents of high ε ,⁵⁹ this change in the dielectric constant from that of the pure solvent is negligible and can be disregarded.⁴ For concentrations in the 10^{-2} – 10^{-1} M range in solvents of low dielectric constant a 100 % increase in ε from that in the pure solvent may be experienced^{43,60,61} and will cause a considerable reduction in the Onsager slope. In pure dichloromethane, $\varepsilon=8.9$, this slope is $988 \text{ Scm}^2 \text{ mol}^{-\frac{1}{2}}$ for a 1:1 electrolyte with a Λ^0 of $100 \text{ Scm}^2 \text{ mol}^{-1}$ at 25.0 °C but only $487 \text{ S cm}^2 \text{ mol}^{-\frac{1}{2}}$ when $\varepsilon=17.8$. The increase in viscosity with increasing concentration, amounting to form 10 % and up to 30 % for 2×10^{-1} M solutions of the various salts in dichloromethane,⁶¹ will further decrease the Onsager slope.³⁵

Apart from the special features in the Λ - $c^{\frac{1}{2}}$ plots, involving a minimum and a maximum or only an inflection, the most interesting result from the present study is the observation that the equivalent molar conductivities, Λ , are essentially constant for a concentration range of close to two powers of ten, *i.e.* from $\sim 5 \times 10^{-3}$ to $\sim 2 \times 10^{-1}$ M, *cf.* Fig. 1. This concentration range is of particular interest both in synthesis and in kinetics. The concentration range is more narrow for the [PNP]⁺-salts, the Ph₄B⁻-salts and for the perchlorates of the larger R₄N⁺-cations as these salts exhibit an inflection in the Λ - $c^{\frac{1}{2}}$ plots. This is presumably due to the large size of these ions combined with the high viscosity of fairly concentrated solutions of these salts.⁶¹ This apparent constancy of Λ in dichloromethane, as in several other solvents with a dielectric constant in the 5–12 range,^{16–20} suggests that in this class of solvents the degree of dissociation, α , given by $\alpha = \Lambda/\Lambda^0$, is fairly independent on the concentration for the usually employed salts.

Recently several Finkelstein reactions, $\text{CH}_3\text{I} + \text{X}^-$ and $\text{CH}_2\text{Cl}_2 + \text{X}^-$, X⁻ being various pseudohalide ions, were studied kinetically at various concentrations in dichloromethane as solvent.⁶ The second order rate constants, uncorrected for association, were found to be fairly independent on the concentration range in which the reactions took place but were strongly dependent on the cation. It was concluded that one or several assumptions made when evaluating the rate equations were not valid. The results from the present study clearly reveal that when rate equations for reactions involving ionic reactants in a solvent like dichloromethane are to be evaluated, the basic assumption that the association constant is independent on the concentration is wrong. However, when the degree of dissociation, α , is considered constant, reasonable kinetic results may be obtained.⁶

It is worth noticing that the various constants in the Debye-Hückel limiting law, and in extended forms of this law, are dependent on the dielectric constant of the solution. All attempts to calculate activity coefficients in solvents of low ε by means of these equations, in case these equations are valid, have therefore to be postponed until accurate data for the dielectric constant of the salt solutions have been made available.

CONCLUSION

The various mathematical treatments published in recent years seem to give a fairly good description of the dependence of the molar conductivity on electrolyte concentration for 1:1 electrolytes which are subject to ion-pair formation for concentrations less than $\sim 1 \times 10^{-4}$ M. These equations provide a most valuable basis for conductivity studies at higher concentrations since association constants, K_A , molar conductivities at infinite dilution, Λ^0 , and various other important parameters may be calculated with fairly high accuracy from conductivity studies in the 10^{-6} – 10^{-5} M range. Furthermore, the apparent success of the

Bjerrum equation¹⁰ in most solvents of low dielectric constant allows one to obtain a measure for the structure of the ion-pairs. One may in principle estimate the "effective" dielectric constant of the various solvents.²⁵

For higher concentrations in weakly dissociating solvents, *i.e.* the 10⁻³–10⁻¹ M range, the concentration range of interest for most practical chemists, there are no mathematical equations of any reliability available. The Λ -log *c* curves in this concentration range display a number of features which seem to be a complex function of the structure and the dielectric constant of the solvent, the association constant of the dissolved salt, the size and structure of the ions, *etc.* Generally, the molar conductivity of fairly concentrated solutions of salts in solvents of low dielectric constant is far higher than expected and a fairly constant value of the degree of dissociation, α , as given by $\alpha = \Lambda/\Lambda^0$, is observed for a considerable concentration range, $\sim 5 \times 10^{-3}$ to $\sim 2 \times 10^{-1}$ M. The high conductivity of concentrated solutions seems to be due to an increase in the dielectric constant of the solution causing the association constant, K_A , to decrease.

Each solvent-salt combination has to be treated separately when attempting to find a relationship between the molar conductivity and the concentration in concentrated solutions in solvents of low ϵ . Still, some general conclusions may be made. The similarity in the Λ -log *c* curves for all Bu₄N⁺-salts (except Bu₄NBPh₄), for the Ph₄As⁺-salts and the [PNP]⁺-salts in dichloromethane suggests that in this solvent it is the cation that is the governing factor. Some information on only one salt of each of these cations may thus be partly valid for other salts provided the cation is not changed. Furthermore, the apparent reliability of the Walden empirical relationship, $\epsilon c_{\min}^{-1/3} = \text{const.}$, suggests this relationship to be a good starting point for further experimental and theoretical work.

The present lack of information on concentrated salt solutions in solvents of low ϵ causes the concentration of the various conceivable species, *i.e.* free ions, ion-pairs, triple ions (if such exist) to be unknown. Consequently, calculations of free ion activity coefficients by the Debye-Hückel limiting law become highly dubious. The relative reactivity of free ions and ion-pairs toward a given substrate will necessarily remain uncertain. An increase in the rate constant with increasing concentration has been considered as evidence for the ion-pairs to be reactive since the fraction of these species will necessarily increase at the expense of the free ions when K_A is assumed to be constant. If the association constant is decreasing with increasing concentration, however, it is the fraction of the free ions which increases at the expense of the ion-pairs. Thus, the application of the Acree equation⁶² and a discussion of salt effects in solvents of low ϵ seem fruitless until better descriptions of electrolytes in this class of solvents become available.

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