

Solvent Properties of Dichloromethane. III. Conductivity Studies of some 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 10^{-5} M concentration range in dichloromethane at 25.00 °C. From the conductivity data the association constants, K_A , and the molar conductivities at infinite dilution, Λ^∞ , were calculated by means of the "FHFP" equation.

All salts behave as weakly dissociated 1:1 electrolytes in dichloromethane but the association constants are significantly dependent upon the cation, $R_4N^+ > Ph_4As^+ \geq [PNP]^+$; the tetraalkylammonium salts with the smallest alkyl groups having the largest association constants. While the association constants of the R_4N^+ -salts, particularly the Et_4N^+ -salts, increase with decreasing size of the anion, the association constants of the Ph_4As^+ - and the $[PNP]^+$ -salts seem to be determined by the cations only.

Based upon the assumption of equal mobility of Ph_4As^+ and of Ph_4B^- , the limiting molar conductivities of several cations and anions were calculated and compared with the corresponding values in various protic and aprotic solvents. The relatively low limiting molar conductivity of the smaller anions in dichloromethane suggests that this solvent acts as an acceptor solvent. From the Stokes' radii in dichloromethane the following "solvation numbers" for anions in this solvent have been calculated: $Cl^- \sim 2$; Br^- and $OCN^- \sim 1.5$; SCN^- and $I^- \sim 1$.

Halogenated alkanes is a group of solvents that is widely used, particularly as extraction agents, due to their excellent dissolving properties.

These solvents are also frequently used as solvents for Menschutkin¹⁻⁶ and Finkelstein⁷⁻¹⁰ reactions and for other types of reactions.^{11,12} The greatest potential for halogenated alkanes as solvents, however, may well be in inorganic chemistry for studies of coordination compounds.¹³⁻¹⁶ Their weakly coordinating properties, particularly their very weak ability to act as donors, have allowed studies of several complexes which would hardly be possible in the usual dipolar aprotic solvents.¹⁷⁻¹⁹ Dichloromethane seems presently to be the solvent of choice among the various halogenated alkanes when considering its price, its simple purification and its stability when properly stored.¹⁰

When reactions involving ionic species are to be examined in dichloromethane the low dielectric constant, 8.9 at 25.0 °C,²⁰ causes some severe restrictions on its general use as a solvent. Salts of small cations and anions like the alkali halides are virtually insoluble in this solvent and tetramethylammonium salts, Me_4NX , can generally not be used as sources for anions in homogeneous reactions.¹⁰ Salts with large aliphatic or aromatic cations, however, are readily soluble in dichloromethane¹⁰ but are known to be only weakly dissociated.^{15,20-28} Owing to the low degree of dissociation of salts in this solvent and also in related solvents,²⁹ a considerable fraction of the dissolved salts will exist as various ion-pair species³⁰ and possibly also higher aggregates.^{29,31} It is apparent that some measure of the reactivity of free ionic species in dichloromethane can only be obtained from kinetic studies when the association constants of the applied salts are known.

It should be emphasized, however, that the interpretation of kinetic data for reactions involving ions in solvents of low dielectric constant may still be complicated by the possible involvement of both free ions and various types of ion-pairs;^{10,32} cf. the complications produced by the equilibria between these species in the field of ionic polymerization.³³

In the present work we will report on the conductivity of several salts in dichloromethane at 25.00 °C. Since the reactivity of small anions in this solvent was of particular interest, salts of various cations were studied in order to examine to what extent the dissociation depends upon the cation present. As cations were chosen various tetraalkylammonium cations, mostly Et₄N⁺ and Bu₄N⁺, together with Ph₄As⁺ and [(Ph₃P)₂N]⁺, the latter abbreviated [PNP]⁺. Attempts to include some of the sparingly soluble tetramethylammonium salts, Me₄NX (X=I, SCN, ClO₄ and Ph₄B), in the present study failed, since reproducible results could not be obtained. By assuming equal mobilities of Ph₄As⁺ and of Ph₄B⁻ at infinite dilution, $\lambda^\circ(\text{Ph}_4\text{As}^+) = \lambda^\circ(\text{Ph}_4\text{B}^-)$,³⁴ the limiting molar conductivities of several ions, λ°_{\pm} , in dichloromethane at 25.00 °C could be calculated. A comparison with their limiting molar conductivities in other solvents, protic as well as aprotic ones, could thus be made in an attempt to obtain some information with regard to the solvation of the various ions in dichloromethane.

EXPERIMENTAL

Materials. Tetraphenylarsonium tetraphenylborate, Ph₄AsBPh₄, was prepared from equivalent amounts of carefully purified samples of Ph₄AsCl and NaBPh₄ in dry ethanol. After removal of sodium chloride the salt was precipitated with a minimum amount of water. The product was carefully washed with warm water, benzene and finally diethyl ether, dried in vacuum and crystallized three times from acetonitrile, the latter solvent freshly distilled from calcium hydride. M.p. 293–295 °C.³⁵ Tetrabutylammonium hydrogen sulfate, Bu₄NHSO₄, Fluka *purum*, was first crystallized from ethanol–diethylether, then twice from acetone–diethylether; all solvents used were carefully freed from basic impurities. All other salts used in this study were first crystallized from water or washed with warm water when possible to remove traces of homoconjugated salts, HX₂⁻, and then purified accord-

ing to published methods.¹⁰ The iodides were finally crystallized from argon-flushed anhydrous ethanol to avoid any contamination from the corresponding I₃⁻ salts. Aqueous solutions of the water-soluble salts, except [PNP]CN, [PNP]OCN and Bu₄NHSO₄, were found to have a pH exactly like the water applied. Prior to use, the salts were dried to constant weight at ~50 °C at 0.2 mmHg. The hygroscopic salts, Ph₄AsCl, Et₄NBr, Bu₄NBr, Bu₄NHSO₄ and PhCH₂NEt₃Cl, were carefully shielded from atmospheric moisture.

Dichloromethane was purified as described¹⁰ and stored in darkness at ~-30 °C. The conductivity of the solvent was less than 8.4 × 10⁻¹⁰ S cm⁻¹ which was the lower limit of the conductivity equipment.

Conductivity cell and conductivity equipment. The conductivity cell was made from a 250 ml Erlenmeyer. The platinum electrodes were coated with platinum black as described by Janz and Ives.³⁶ The frequency variation in the 1000–5000 Hz region was found to be less than 0.2 % for a resistance of 430 Ω. The cell constant, determined with potassium chloride in the 1–20 × 10⁻³ M region and calculated according to standard procedure,^{37–39} was 0.497 cm⁻¹ with an estimated accuracy of 0.2 %. A test of the cell constant with sodium chloride in water at 25.00 °C resulted in a Λ° -value for this salt of 126.55(15) S cm² mol⁻¹, in excellent agreement with the accepted literature value, 126.45 S cm² mol⁻¹.³⁹ A Wayne Kerr Co. Ltd. selfbalancing bridge, Model B 331 Mk II functioning at 1591.5 Hz, was applied.

Procedure for conductivity measurements. The experiments were performed in the dark to prevent possible photochemical decomposition of the solvent and thus possible attack of the platinum electrodes. Solutions in the 1–10 × 10⁻⁵ M range were made up from stock solutions in the 2–5 × 10⁻³ M range, made in duplicate by separate weighing of the salts in different solvent batches. A complete series for each salt consisted of conductivity measurements of ten different solutions made from each one of the stock solutions. The results, both with regard to Λ° and K_A , were generally readily reproducible when taking the estimated uncertainties into account. In the case of the tetramethylammonium salts, Me₄NX (X=I, SCN, ClO₄ and BPh₄), however, of which stock solutions could only be made less than ~3 × 10⁻⁴ M owing to their highly limited solubility in dichloromethane, reproducible results could not be obtained, regardless in which way the salts were purified. Since the conductivity of the solutions appeared to decrease with time, no further attempts were made to determine Λ° and K_A for these salts.

Two of the salts, Ph₄AsSCN and [PNP]SCN, were also examined in the 10⁻⁴–10⁻² M range to look for any minima in the $\Lambda-c^{1/2}$ plots.²⁹

Temperature control. The conductance experiments were performed at 25.00(1) °C. Constant resistance of a solution was obtained after the cell had been immersed in the thermostat for *ca.* 30 min.

Calculations. The conductivity data were adjusted to the Fuoss-Hsia equation^{40,41} according to Fernandez-Prini,⁴² the "FHFP" equation:

$$\Lambda_c = \Lambda^\circ - S(ac)^{1/2} + Eac \log(ac) + J_1ac - J_2(ac)^{3/2} \quad (1)$$

The various coefficients in eqn. (1) are defined as outlined in Ref. 42. This equation has proved to be most successful for the calculation of the limiting molar conductivity, Λ° , and the association constant, K_A , of weakly dissociated salts.^{43,44} An iteration procedure described by Beronius⁴⁵ was used throughout this study. Λ° and K_A were calculated from measurements in the 1–10×10⁵ M range, well below the limit of 2.3×10⁻⁴ M as calculated by the Fuoss' equation, 3.2×10⁻⁷ D³ M.⁴⁶ The necessary physical constants of dichloromethane at 25.00 °C were taken from the recent study by Yamamoto.⁴⁷

RESULTS AND DISCUSSION

In Table 1 are summarized the limiting molar conductivities, Λ° , and the association constants, K_A , for the various salts in dichloromethane at 25.00 °C. Literature values for some of the studied salts and also for some other salts are listed in square brackets. The listed uncertainties in Table 1 represent deviations between calculated values⁴⁵ from parallel dilution runs. The uncertainties in Λ° and particularly in K_A are admittedly quite large and are considerably larger than the corresponding parameters as calculated from conductivity data in the usual protic and aprotic solvents. The large association constants in dichloromethane, however, cause the $\Lambda-c^{1/2}$ plots to be non-linear even in the 10⁻⁵ M concentration range. Furthermore, the Onsager slopes in dichloromethane are very high, 988 for a 1:1 electrolyte with a Λ° of 100 as compared with, *e.g.* 83.4 in water. Finally it ought to be mentioned that Λ° and K_A are interrelated by eqn. (1).

We have reason to believe that the limiting molar conductivities of the [PNP]⁺-salts, except [PNP]CN, are within 1 %. The Ph₄As⁺-salts and

the R₄N⁺-salts, except the Et₄N⁺-salts, are slightly less accurately determined, 1–2 %. The Λ° -values for the Et₄N⁺-salts are significantly less accurate, ~5 %, which is primarily due to the fairly high cell constant of the cell applied, 0.497 cm⁻¹. For accurate conductivity studies of salts with association constants approaching 10⁵, as experienced in the case of the Et₄N⁺-salts in dichloromethane, a conductivity cell with a cell constant less than 0.1 cm⁻¹ seems necessary.

The association constants K_A are significantly less accurate than the Λ° -values, which is generally the case in this type of study. As shown in Table 1 few of the calculated association constants pretend to be more accurately determined than 10 %.

The listed values for [PNP]CN are only estimates. The fairly high rate of the CH₂Cl₂–NC⁻ reaction with a half-life of only some 80 min¹⁰ prevents accurate conductivity data to be obtained. No attempt was made to include [PNP]N₃ or any other azide in the present study; the CH₂Cl₂–N₃⁻ reaction is known to proceed even more rapidly than the CH₂Cl₂–NC⁻ reaction.¹⁰ The remaining salts studied were all derived from anions which react only exceedingly slowly with the solvent.¹⁰

Ph₄AsBPh₄ was especially carefully studied since the conductivity data for this salt were the origin of the calculation of the limiting ionic conductivities of the various ions by assuming $\lambda^\circ(\text{Ph}_4\text{As}^+)$ to be equal to $\lambda^\circ(\text{Ph}_4\text{B}^-)$. The limiting molar conductivity of this salt was found to be 88(1) S cm² mol⁻¹ which is somewhat higher than the value reported by Balt and coworkers,¹⁶ 84.9 S cm² mol⁻¹. Since the cell constant of their applied cell, however, was determined with less than 2 % accuracy the discrepancy between the two values may not be significant.

The difficulties encountered in the case of the Me₄N⁺-salts, *cf.* Experimental, can hardly be due to impurities, since all these salts are most readily purified and several purification procedures were performed. Since solutions of other iodides, thiocyanates, perchlorates and tetraphenylborates appeared to be most stable for long periods as observed by their conductivities, one may assume the Me₄N⁺-ion to be somewhat unstable in dichloromethane. In the case of Me₄NI and Me₄NCSN, the salts of the fairly nucleophilic anions,¹⁰ this possible instability of the cation may be initiated by demethylation

Table 1. Limiting molar conductivities, Λ° , in $\text{S cm}^2 \text{ mol}^{-1}$, and association constants, K_A , of 1-1 electrolytes in dichloromethane at 25.00 °C. (Literature values in brackets).

	Λ°	$K_A \times 10^{-3}$
[PNP]Cl	101(1)[101.0] ¹⁶	1.7(3)[2.06] ¹⁶
[PNP]Br	104(1)	1.2(3)
[PNP]I	107(1)	1.9(3)
[PNP]CN	~95	~0.5
[PNP]OCN	103(1)	1.7(3)
[PNP]SCN	110(1)	1.8(3)
[PNP]SeCN	109(1)	1.2(3)
[PNP]ClO ₄	109(1)	1.4(3)
Ph ₄ AsCl	[111.3] ¹⁶	[3.6] ¹⁶
Ph ₄ AsBr	[116.0] ¹⁶	[3.9] ¹⁶
Ph ₄ AsNO ₃	110(2)	2.6(3)
Ph ₄ AsSCN	117(2)	3.3(3)
Ph ₄ AsClO ₄	117(1)[120.3] ¹⁶	2.1(3)[4.4] ¹⁶
Ph ₄ AsBPh ₄	88(1)[84.9] ¹⁶	2.3(3)[2.6] ¹⁶
Et ₄ NCl	[122.7] ¹⁶	[100] ¹⁶
Et ₄ NBr	118(5)[132(3)] ²⁰	66(10)[80(5)] ²⁰
Et ₄ NI	[118(5)] ²⁰	[42(5)] ²⁰
Et ₄ NNO ₂		[47] ¹⁵
Et ₄ NNO ₃		[96] ¹⁴
Et ₄ NClO ₄	130(5)[146(4)] ²⁰	46(10)[54(4)] ²⁰
Et ₄ NBPh ₄	99(5)	8(1)
Pr ₄ NI	110(2)	28(1)
Pr ₄ NClO ₄	112(2)	27(2)
Bu ₄ NCl	[104(2)] ²⁰	[41(3)] ²⁰
Bu ₄ NBr	106(2)	25(2)
Bu ₄ NI	108(2)	24(2)[38(4)] ³⁴
Bu ₄ NNO ₃	103(2)	25(3)
Bu ₄ NSCN	111(2)	27(5)
Bu ₄ NHSO ₄	114(2)	46(3)
Bu ₄ NClO ₄	109(1)	22(1)
Bu ₄ NBPh ₄	83(1)	3.3(1)
Hex ₄ NClO ₄	103(1)	20(1)
Oct ₄ NClO ₄	96(2)	17(1)
Dec ₄ NClO ₄	92(1)	14(1)
PhCH ₂ NEt ₃ Cl	110(4)	70(5)
PhCH ₂ NEt ₃ ClO ₄	120(4)	40(3)
PhCH ₂ NBu ₃ ClO ₄	109(2)	25(1)
Ph ₃ CSbCl ₆	[108] ²⁹	[19] ²⁹
Ph ₃ CAsF ₆	[127] ³¹	[14] ³¹

reactions. This suggestion, however, can hardly be upheld for Me₄NClO₄ and Me₄NBPh₄. Presently, we have therefore no convincing explanation to the irregularities observed for the Me₄N⁺-salts. The failure in obtaining reliable Λ° - and K_A -values for the Me₄N⁺-salts in dichloromethane does not appear to be a detriment to the

use of dichloromethane as a solvent. The limited solubility of the usual Me₄N⁺-salts, $<10^{-3}$ M at room-temperature, will prevent the use of these salts as sources of anions in this solvent. It is notable that even Me₄NBPh₄ has a highly limited solubility in dichloromethane; the previous suggestion, that salts with either anions or cations

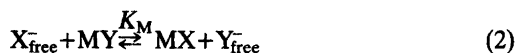
containing phenyl groups are highly soluble in this solvent due to interaction between the phenyl groups and the solvent molecules¹⁰ is apparently not valid for this salt.

The association constants. The association constants, K_A , are clearly highly dependent upon the cation; the order being $R_4N^+ > Ph_4As^+ \geq [PNP]^+$ for all salts and $Et_4N^+ > Pr_4N^+ > Bu_4N^+ \geq Hex_4N^+ \geq Oct_4N^+ \geq Dec_4N^+$ for the perchlorates. The available data, particularly together with the data by Balt and co-workers,^{15,20} leave no doubt that the tetraalkylammonium chlorides are more associated than the iodides; the bromides being intermediate. In this respect the R_4N^+ -halides in dichloromethane behave as if this solvent were neutral or basic. The difference in the association constants of the various R_4N^+ -halides, however, is far less distinct than observed in HMPA⁴⁸ and in acetone;^{49,50} for a comprehensive discussion, cf. Ref. 51. In protic or acidic solvents there seems to be no exception to the rule that the association constants follow the opposite sequence, i.e. $R_4NCl < R_4NBr < R_4NI < R_4NClO_4$; cf. association constants in 2,2,2-trifluoroethanol, hexafluoro-2-propanol, 2-propanol and ethanol.⁴⁹

The association constants of the $[PNP]^+$ -salts and the Ph_4As^+ -salts in dichloromethane seem to be independent upon the anions, K_A being $\sim 1.5 \times 10^3$ and $\sim 3 \times 10^3$, respectively. It is notable that the association constants of Ph_4As^+ -salts of the fairly large $FeCl_4^-$ and $FeBr_4^-$ anions have also K_A -values of $\sim 3 \times 10^3$.²⁰ Association constants of salts of large phenylic cations seem to be determined by the cations and are independent of the size of the anions.

For studies of the reactivities of anions in dichloromethane, salts with the large phenylic cations as counterions seem to be superior to the usual R_4N^+ -salts. The relatively small association constants of $[PNP]^+$ - and Ph_4As^+ -salts, cf. Table 1, will minimize the concentration of the various ion-pair species and thus also possible reactions induced by these species. Additionally, the considerable solubility of most salts of these cations in dichloromethane, their simple purification and their non-hygroscopic nature⁵² are in favour of these salts as compared with the R_4N^+ -salts. Since the association constants of the $[PNP]^+$ -salts and the Ph_4As^+ -salts are fairly independent of the anions, the reactivity of various anions in dichloromethane may be directly compared, pro-

vided the ion-pairs are non-reactive and constant ionic strength is maintained. Finally, these salts may be used for studies of element basicities, K_M , of anions in dichloromethane since the correction due to ion-pairing of the two competing anions will cancel, eqns. (2) and (3).



$$K_M = \frac{[MX][Y_{free}^-]}{[MY][X_{free}^-]} \approx \frac{[MX][Y_d^-]}{[MY][X_o^-]} \quad (3)$$

M is the element of which the basicity of X^- and Y^- is to be examined while X_o^- , Y_o^- , X_{free}^- and Y_{free}^- denote the molar concentration of the dissolved salts and the dissociated anions.

This procedure has recently been used successfully for the determination of element basicities of anions in dichloromethane toward elements as tetrahedral carbon, divalent selenium and Rh(I)-species.⁵³ Since the association constants of the tetraalkylammonium salts in dichloromethane are dependent upon the anions, the approximation as shown in eqn. (3) is not valid when R_4N^+ -salts are used.

The question arises, however, whether association data calculated from conductivity studies in dichloromethane in the 10^{-5} M concentration range are sufficiently reliable in the 10^{-3} – 10^{-1} M range, i.e. the concentration range in which most reactions are studied. Even the association pattern of $[PNP]^+$ - and Ph_4As^+ -salts may well be distinctly different in more concentrated solutions. However, the Λ - c^2 plots in the 10^{-4} – 10^{-2} M concentration range for $[PNP]SCN$ and for Ph_4AsSCN showed the anticipated form for associated salts and no minima could be detected. Such minima in the Λ - c^2 plots in solvents of low dielectric constants were originally observed by Walden⁵⁴ in the case of several tetraalkylammonium halides and nitrates. Fuoss and Kraus,²⁹ in their classical conductivity study on tetraisoamylammonium nitrate in dioxane-water mixtures, attributed the appearance of such minima to the presence of triple ions or other aggregates. In the case of tetraalkylammonium salts in dichloromethane, except the tetraphenylborates, this minimum in the Λ - c^2 plots is generally observed in the 0.02–0.05 M concentration range.^{54,55} The lack of any minima in dichloromethane, when

ions with several phenyl groups are present, may suggest that the unique interaction between these groups and the solvent molecules⁵⁶ is efficiently depressing the possible formation of triple ions or related species. Although the concept of triple ion has recently been seriously criticized,⁵⁷ the fairly regular behaviour of [PNP]⁺-salts and of Ph₄As⁺-salts in dichloromethane as viewed from the conductivity data, is an additional argument for the preferential use of these salts when reactions of small anions are to be examined in this solvent.

Few dissociation studies of onium salts in other halogenated alkanes have been performed. Tetraphenylarsonium chloride has an association constant in 1,2-dichloroethane of 9.0×10^2 at 25.00 °C,⁵⁸ *i.e.* one fourth of the association constant in dichloromethane, *cf.* Table 1. The same ratio between the association constants in the two solvents for some R₄N⁺-salts can be arrived at from a comparison between the data in Table 1 and the association constants in 1,2-dichloroethane determined by Kraus and co-

workers. For a survey of references, see Ref. 59. Presumably, the larger dielectric constant of 1,2-dichloroethane, 10.23 at 25.00 °C,⁵⁹ is the cause of the association constants in this solvent being smaller than in dichloromethane. As pointed out by Denison and Ramsey,⁶⁰ however, the dielectric constant is not the only factor relevant to association constants of salts in this class of solvents; 1,1-dichloroethane, being isodielectric with 1,2-dichloroethane, is well known to be a far less dissociating medium than the latter solvent.⁶⁰

The limiting molar conductivities of cations and anions in dichloromethane at 25.00 °C. Since transference data in dichloromethane are not available, the individual ionic conductivities, λ_{\pm}° , were calculated by Kohlrausch's law, assuming the mobility of Ph₄As⁺ to equal that of Ph₄B⁻. The results are summarized in Table 2, first column.

The validity of the $\lambda^{\circ}(\text{Ph}_4\text{As}^+) = \lambda^{\circ}(\text{Ph}_4\text{B}^-)$ assumption is obviously questionable. In acetonitrile, *e.g.*, the limiting molar conductivities of

Table 2. The limiting molar conductivities of various ions in dichloromethane at 25.00 °C, λ (S cm² mol⁻¹), the Walden products, $\lambda^{\circ}\eta_0$, the Stokes' radii, r_s , the crystallographic radii, r_c , together with the r_s/r_c ratios.

Ion	$\lambda^{\circ a}$	$\lambda^{\circ}\eta_0$	$r_s(\text{Å})^b$	$r_c(\text{Å})^c$	r_s/r_c
Cl ⁻	64(1)	0.264	3.11	1.81	1.72
Br ⁻	67(1)	0.276	2.97	1.95	1.52
I ⁻	70(1)	0.288	2.85	2.16	1.32
CN ⁻	58 ^d	0.24	3.4	<i>f</i>	
OCN ⁻	66(1)	0.272	3.01	2.1	1.43
SCN ⁻	73(1)	0.301	2.72	2.27	1.20
SeCN ⁻	72(1)	0.297	2.76	2.4	1.15
ClO ₄ ⁻	72(1)	0.297	2.76	2.4	1.15
NO ₃ ⁻	65(2)	0.268	3.06	2.70	1.13
HSO ₄ ⁻	77(2)	0.317	2.59	<i>f</i>	
Ph ₄ B ⁻	44(1) ^e	0.181	4.53	4.25	1.1
Ph ₄ As ⁺	44(1) ^e	0.181	4.53	4.25	1.1
[PNP] ⁺	37(1)	0.152	5.39	<i>f</i>	
Et ₄ N ⁺	54(5)	0.22	3.69	4.00	~0.9
Pr ₄ N ⁺	40(2)	0.165	4.97	4.52	~1.1
Bu ₄ N ⁺	38(3)	0.157	5.22	4.94	~1.0
Hex ₄ N ⁺	31(2)	0.128	6.41	5.9	~1.1
Oct ₄ N ⁺	24(2)	0.099	8.28	<i>f</i>	
Dec ₄ N ⁺ ^g	20(2)	0.082	10.00	<i>f</i>	
PhCH ₂ N ⁺ Et ₃	48(4)	0.198	4.14	<i>f</i>	
PhCH ₂ N ⁺ Bu ₃	37(2)	0.152	5.39	<i>f</i>	

^a All values based upon the assumption that $\lambda^{\circ}(\text{Ph}_4\text{As}^+) = \lambda^{\circ}(\text{Ph}_4\text{B}^-)$. ^b Calculated by the Stokes-Einstein equation. ^c Mainly from Refs. 62 and 74. ^d Unknown accuracy, *cf.* text. ^e Assumed values. ^f No estimate available. ^g (C₁₀H₂₁)₄N⁺.

these two ions are slightly but significantly different, 55.8 and 58.3 S cm²mol⁻¹, respectively.⁶¹ The calculated limiting molar conductivities of the various ions were therefore the subject of an internal consistency analysis by means of Kohlrausch's law. When taking the estimated uncertainties into account, this analysis showed no anomalies or discrepancies. Apparently, the $\lambda^\circ(\text{Ph}_4\text{As}^+) = \lambda^\circ(\text{Ph}_4\text{B}^-)$ assumption in dichloromethane cannot be seriously wrong. Furthermore, the calculated uncertainties in the limiting molar conductivities of the various ions, as listed in Table 2, seem realistic.

It is notable that the smaller anions have the smaller limiting molar conductivities, *i.e.* $\lambda^\circ(\text{Cl}^-) < \lambda^\circ(\text{Br}^-) < \lambda^\circ(\text{I}^-) \sim \lambda^\circ(\text{ClO}_4^-)$ and $\lambda^\circ(\text{OCN}^-) < \lambda^\circ(\text{SCN}^-)$ and $\lambda^\circ(\text{SeCN}^-)$. This is quite a general observation in solvents being of the acceptor type like the usual protic solvents; *cf.* Refs. 51 and 59 for surveys of references, but also in ketonic solvents capable of acting as enols toward anions.⁶² In solvents of the donor type as DMSO,⁶³ HMPT,⁶⁴ and DMF⁶⁵ the limiting molar conductivities of the smaller anions are generally observed to be significantly larger than those of the greater anions. Acetonitrile may appear to be an exception to this rule.⁶¹ This solvent, however, is known to have considerable acceptor properties in addition to its donor properties.⁶⁶

Single-ion conductivities alone may not be a reliable measure for ion-solvent interactions; *cf.* Ref. 51 for a critical discussion. However, the data in Table 2 and a comparison with the limiting molar conductivities in various solvents of the acceptor and of the donor type suggest that solvation of anions in dichloromethane follows a pattern characteristic for protic solvent, *i.e.* $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^-$.⁶⁷ The perchlorate ion is acting as a reference ion since it is only weakly coordinated to hydrogen donors.⁶⁷ The same trend has recently been observed in 1,2-dichloroethane from partition data⁶⁸ and from calorimetric studies.^{69,70} Selective solvation by dichloromethane of even the iodide ion has been suggested in order to explain various results from extraction studies on tetraalkylammonium iodides in dichloromethane-water mixtures.²⁸ Dichloromethane is well known to act as an acceptor, the acceptor number of this solvent as derived from ³¹P-NMR measurements of triethylphosphine oxide is 20.4 and thus comparable with

that of acetonitrile.⁶⁶ Furthermore, dichloromethane is known to be only weakly associated due to the weak donor properties of this solvent.^{71,72} Taft and coworkers⁷³ have recently shown that weakly self-associating acidic solvents may participate more effectively in a hydrogen-bonding interaction with donors than a stronger but self-associated acidic solvent.

In Table 2 the Walden products are also listed, $\lambda^\circ\eta_0$, the Stokes' radii, r_s , as calculated by the Stokes-Einstein equation,⁵⁹ together with the corresponding crystallographic radii, r_c , from various literature sources. Further evidence of the specific solvation of the smaller anions in dichloromethane comes from a comparison between the r_s -values and r_c -values of these ions. The Stokes' radii, r_s , are for the larger anions comparable with the crystallographic ones but are significantly larger than r_c in the case of OCN^- , Br^- and particularly Cl^- . The available data may allow the calculation of the number of solvated dichloromethane molecules to these anions. Since the agreement between r_c and r_s for the weakly coordinating anions is fair, no correction factor as for R_4N^+ -cations in water appears necessary.⁵⁹ With a volume of 64.5 Å³ for dichloromethane, the following "solvation numbers" may be calculated: $\text{Cl}^- \sim 2$; Br^- and $\text{OCN}^- \sim 1.5$; SCN^- and $\text{I}^- \sim 1$. These values are admittedly speculative but appear in principle quite reasonable.

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