The Solution Properties of Bis(triphenylphosphine)iminium Salts. I. Conductance and Surface Tension Studies

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The variation of conductance with concentration of bis(triphenylphosphine)iminium chloride, $[(Ph_3P)_2N]Cl$, abbreviated [PNP]Cl, has been studied in water at 25.00 and 45.00°C and in methanol together with [PNP]Br and [PNP]I at 25.00°C.

In methanol the [PNP]$^+$-halides behave as well-dissociated 1:1 electrolytes and $\lambda°$ for the [PNP]$^+$-cation is 31.1 ± 0.1 cm^2 mol^{-1} Ω^{-1} in this solvent at 25.00°C. In aqueous solution [PNP]Cl behaves normally for concentrations up to $\sim 5.0 \times 10^{-3}$ M and $\sim 7.0 \times 10^{-3}$ M at 25.00 and 45.00°C, respectively, whereupon a distinct reduction in conductivity is observed. From the linear part of the Λ vs. $c^{1/2}$ plots $\lambda°$-values for the [PNP]$^+$-cation of 15.9 ± 0.3 and 24.6 ± 0.3 cm^2 mol^{-1} Ω^{-1} were calculated at the two temperatures.

[PNP]Cl has been found to be surprisingly surface active in water and the results from surface tension studies at 25.0°C are presented together with data for the weakly active salt, Ph$_4$AsCl. A discontinuity in the surface pressure vs. log c plot for [PNP]Cl at a concentration of $\sim 5.0 \times 10^{-3}$ M is apparent.

The conductivity data and surface tension data are discussed and it is concluded that the [PNP]$^+$-cation due to its size and structure probably acts as a structure breaker in water. The discontinuities in conductivity and surface activity are suggested to be caused by the formation of aggregates which resemble micelles in their effect on surface tension and conductivity.

Various tetraorganoammonium, phosphonium and arsonium salts have been used successfully in recent years as sources for especially small anions in both organic and inorganic chemistry.[1-3] Salts of these large organic cations have been found to

be fairly soluble in a number of solvents, protic and aprotic ones, allowing reactions to be performed homogeneously and also to be followed kinetically. Furthermore, the weakly polarizing nature of these cations has allowed the synthesis of a number of salts of anions which otherwise would not be possible.[2,4,5]

Some twenty years ago, the bis(triphenylphosphine)iminium cation, $[(Ph_3P)_2N]^+$, abbreviated [PNP]$^+$,[6] was synthesized.[7] This cation has been utilized extensively in recent years, primarily in the preparation of crystalline salts of large inorganic anions;[7-9] for surveys of references, Refs. 6 and 10. Recently, [PNP]$^+$-salts have also been found to be a most valuable alternative to the usually employed tetraorganoammonium, arsonium and phosphonium salts as sources of anions in solution owing to their generally non-hygroscopic nature, their fairly cheap and facile preparation in high yield, the chemical and thermal stability of the [PNP]$^+$-cation and, above all, the exceptional solubility of [PNP]$^+$-salts in most organic dipolar solvents.[6,11,12]

The promising potential of [PNP]$^+$-salts as sources of several anions in various solvents requires some knowledge of the solution chemistry of these salts. However, no physicochemical data are presently available. Several X-ray studies have shown that the cation is bent with a PNP bond angle of $\sim 140°$.[9,10] In one salt, however, [PNP]$^+$V(CO)$_6^-$,[10] the cation is apparently linear which may suggest that the energy difference between the bent and the linear form is fairly small. Presently it is not known whether the linear or bent form is the favoured one in solution. ESCA-studies have shown that the positive charge of the cation

resides on the phosphorus atoms while the nitrogen atom is slightly negatively charged[13] which creates a $P^{\partial +}$ --- $N^{\partial\partial -}$ --- $P^{\partial +}$ center of the cation. The structure of the cation, regardless whether it is linear or bent, the distribution of charge on the three central atoms and the presence of six phenyl groups suggest that the solution chemistry of [PNP]$^+$-salts may be significantly different from that of salts derived from the usual tetrahedral organic cations such as R_4N^+, Ph_4As^+ and Ph_4P^+.

The solubility of [PNP]$^+$-salts of the most usual inorganic anions in water, methanol, ethanol and various dipolar aprotic solvents indicates the unique properties of the [PNP]$^+$-cation. In water, only the fluoride and the chloride are sufficiently soluble at room temperature to give 0.01 M solutions, see below. However, in most dipolar protic and aprotic solvents including dichloromethane, solutions up to 1 M may be obtained. Furthermore, even very dilute solutions of [PNP]Cl in water have been observed to be lathering suggesting that this cation exhibits some exceptional surface activity which apparently is not the case for the Ph_4As^+ and the Ph_4P^+ cations.[14]

As part of a study of the solution chemistry of [PNP]$^+$-salts in various solvents, we want to report the results from conductance studies in water and methanol and surface tension studies in water employing [PNP]$^+$-halides. Owing to the limited solubility of the bromide and the iodide in water and difficulties obtaining the fluoride free from traces of the HF_2^--salt, only the chloride could be studied in aqueous solution. For comparison, some surface tension studies with tetraphenylarsonium chloride, Ph_4AsCl, in water were performed.

EXPERIMENTAL

Materials. [PNP]$^+$-salts. The chloride was prepared as described by Ruff and Schlientz[15] and carefully washed with benzene and diethyl ether to remove coprecipitated triphenylphosphine oxide and triphenylphosphine prior to further purification. Since all attempts to remove traces of the HCl_2^--salt[16,17] by crystallization failed, the warm aqueous solution of the chloride was adjusted to a pH of 7 to 8 with a solution of sodium hydroxide to remove the acidic impurities. The crystalline product from the weakly basic solution was dried azeotropically and crystallized from acetone – diethyl ether and then from methanol –

diethyl ether. Finally the salt was ground and dried to constant weight at 80 °C in vacuum (0.1 mmHg). pH-Measurements and the subsequent conductivity studies in water did not indicate the presence of any acidic impurities. Attempts to free the sulfate and the fluoride entirely from acidic impurities, presumably traces of hetero-[18] and homoconjugates,[19,20] have so far not been successful. The bromide and the iodide and the remaining [PNP]$^+$-salts were precipitated from a solution of the purified chloride and excess potassium salts in water as described.[6] These salts were finally crystallized from acetone – diethyl ether and methanol – diethyl ether and dried as the chloride prior to use.

Tetraphenylarsonium chloride, Ph_4AsCl, Koch-Light Lab., was freed from traces of the HCl_2^--salt and repeatedly crystallized from ethanol and dried as the [PNP]$^+$-chloride. The purified salt was carefully shielded from atmospheric moisture.

Potassium chloride and sodium chloride, Baker Chemicals *p.a.*, were dried at 150 °C at 0.1 mmHg for 24 h prior to use.

Water was purified in an FI-STREM distillation apparatus. The electrolytic conductivity was $0.9 - 1.1 \times 10^{-6}$ and 2.0×10^{-6} Ω^{-1} cm^{-1} at 25.0 °C and at 45.0 °C, respectively.

Methanol, Merck *p.a.*, was treated with anhydrous $CuSO_4$ as described by Hartley and Raikes.[21] The electrolytic conductivity of the solvent was $6 - 11 \times 10^{-8}$ Ω^{-1} cm^{-1} as compared with 8×10^{-7} Ω^{-1} cm^{-1} for the unpurified sample. The density observed was 0.78640 g ml^{-1} at 25.0 °C.

Solubility studies in water. The salt-water mixtures were equilibrated at 25.0 °C for one week whereupon the concentration of the [PNP]$^+$-cation was determined by UV at 267.4 nm.[6] The solubility of [PNP]Cl was also determined by conductivity.

Conductance studies. The conductance cell was made from a 250 ml Erlenmeyer and the platinum electrodes were platinated as described by Ives and Janz.[22] The frequency variation in the 1000 – 5000 Hz region was less than 0.2 % for a resistance of 430 Ω. The cell constant, determined with potassium chloride solution in the $1 - 20 \times 10^{-3}$ M region and calculated according to standard procedure,[23-25] was 0.596 with an estimated accuracy of 0.1 %. As test for the cell constant and the accuracy of the applied conductivity equipment Λ° for NaCl at 25.0 °C was determined from measurements in the $2 - 14 \times 10^{-3}$ M region. The observed value, 126.55 ± 0.15 cm^2 mol^{-1} Ω^{-1}, was in excellent agreement with the accepted literature value, 126.45.[25] A Wayne Kerr Co. Ltd. selfbalancing bridge, Model B 331 Mk II functioning at a frequency of 1591.5 Hz, was applied.

Surface tension studies. The surface tension measurements were performed according to the

Wilhelmy plate method.[26] As measuring plate a piece of platinum metal, $20 \times 10.45 \times 0.03$ mm, was used. The calculated perimeter was thus 20.96 ± 0.15 mm. The perimeter of the platinum blade was controlled with several solutions of sodium chloride which gave an average value of 20.90 ± 0.08 mm.[27] As a further test of the equipment the surface tension of water at 20.0 °C and 25.0 °C and of benzene at 20.0 °C were determined as 0.0723 (0.07275 [28]), 0.0718 (0.07197 [28]) and 0.0291 (0.02888 [29]) J m^{-2}, respectively. A Cahn Electrobalance, Model RG, was used. All surface tension measurements were performed in triplicate; the uncertaintly in the measurements was estimated to be less than 3×10^{-4} J m^{-2}. A slight aging effect was observed for the most dilute [PNP]$^+$-chloride solutions but not for the Ph$_4$As$^+$-chloride solutions.

Temperature controls. The conductance experiments were performed at 25.00 ± 0.01 °C and at 45.00 ± 0.03 °C; the surface tension studies at 20.0 and 25.0 ± 0.3 °C.

RESULTS

Solubility of [PNP]$^+$-salts. In Table 1 are listed the results from the solubility studies in water. Owing to traces of impurities in the fluoride and in the sulfate the listed solubilities for these two compounds are subject to some uncertainty. Since no attempts were made to correct for activities, the results are given in mol per liter.

All the salts listed in Table 1 are very soluble in methanol and ethanol and solutions up to 0.5 or 1 M are readily obtained at room temperature preventing these solvents alone being used as crystallization agents. Tetraphenylarsonium salts,
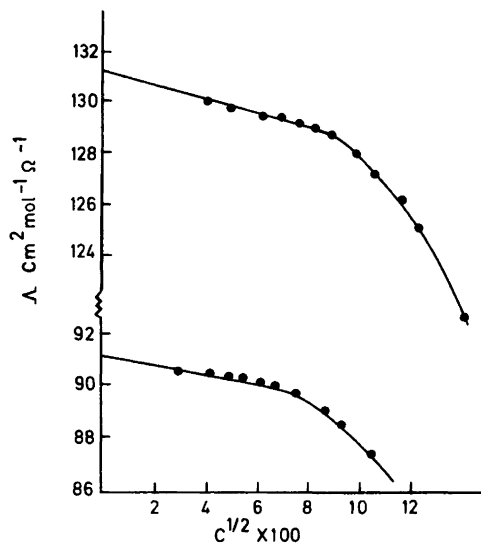

Fig. 1. The molar conductivity *versus* $c^{1/2}$ for [PNP]Cl in aqueous solution at 25 and 45 °C.

Ph$_4$AsX, for which extensive data are available in the literature with regard to solubility in methanol and water,[30,31] are also considerably more soluble in methanol than in water; the difference in pK_{sp} in methanol and water is generally 3 to 4 with the notable exception of the tetraphenylborate, Ph$_4$AsBPh$_4$, for which ΔpK_{sp} is 8.2.[30] Apparently the number of phenyl groups in this class of salts exhibits a profound influence upon the difference in solubility in the two solvents as experienced for the [PNP]$^+$-salts in the present study. Aryl-substituted onium salts show undoubtedly a significant preference for methanol compared with water.

Conductivity studies. In Fig. 1 is plotted the molar conductivity *versus* the square root of the concentration of [PNP]Cl in water at 25.00 °C and 45.00 °C. In Fig. 2 are presented the similar plots from the conductance studies of [PNP]Cl, [PNP]Br and [PNP]I in methanol at 25.00 °C. In methanol the curves are as anticipated for well – dissociated 1:1 electrolytes; in water, however, a distinct discontinuity is displayed at $\sim 5.0 \times 10^{-3}$ M and at $\sim 7.0 \times 10^{-3}$ M at 25.00 °C and 45.00 °C, respectively. It should be emphasized that the concentrations by which the departure from the regular behaviour takes place are approximately 40 and 10 % of the saturation concentrations

Table 1. Solubility in mol per liter, M, of some [PNP]-salts in water at 25.0 °C.

Salt	Solubility M ^{a}
[PNP]F	$\sim 1.4 \times 10^{-2}$
[PNP]Cl	1.3×10^{-2} ^{b}
[PNP]Br	1.7×10^{-3}
[PNP]I	7.5×10^{-5}
[PNP]NO$_3$	6.3×10^{-4}
[PNP]SCN	2.5×10^{-4}
[PNP]ClO$_4$	$<1 \times 10^{-5}$
[PNP]$_2$SO$_4$	$\sim 4.1 \times 10^{-3}$

^{a} Determined by UV at 267.4 nm. ^{b} 1.27×10^{-2} M as determined by conductivity.
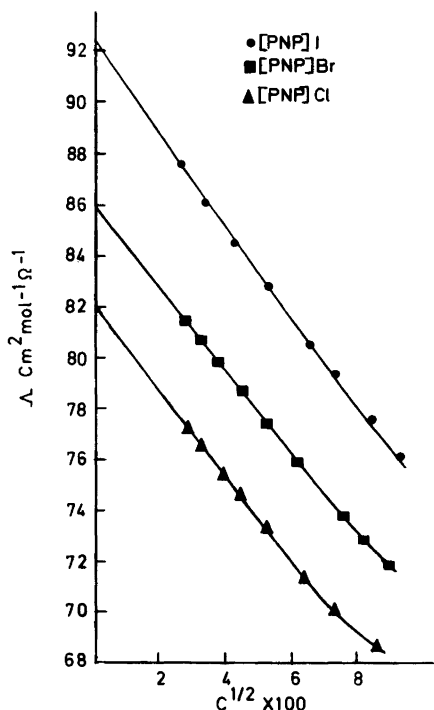
Fig. 2. The molar conductivities of [PNP]-halides versus $c^{1/2}$ in methanol at 25 °C.

at the two given temperatures and are thus apparently independent upon saturation phenomena.

In Table 2 are listed the empirical slopes from the Kohlrausch plots (the linear part at low concentrations of [PNP]Cl in water), the calculated Onsager slopes and $\Lambda°$ as calculated from the Kohlrausch plots. It is notable that the ratios

between the empirical slopes and the Onsager slopes in the two solvents differ significantly, being ~0.2 in water and ~0.8 in methanol. For Ph$_4$PCl, Ph$_4$AsCl and Ph$_4$SbCl in water ratios of 0.8–0.9 have been observed.[34]

This discrepancy between empirical slopes and Onsager slopes, especially in water, cf. Table 2, suggests that the Kohlrausch equation could not with confidence be applied for the determination of molar conductivities at infinite dilution. The data were therefore analyzed in terms of the Fuoss-Onsager theory[35] according to which the following expression applies to non-associated electrolytes, eqn. 1.

$$\Lambda = \Lambda° - Sc^{1/2} + Ec\log c + (J - B\Lambda°)c \qquad (1)$$

The first approximative $\Lambda°$-values were determined by the Shedlovsky method. $\Lambda°$ and $J(a)$ were finally determined from the Λ' vs. c plots according to eqn. 2.

$$\Lambda' = \Lambda + Sc^{1/2} - Ec\log c = \Lambda° + J(a)c \qquad (2)$$

The plots for the [PNP]$^+$-halides in methanol and for [PNP]Cl in water at 25.0 °C are shown in Fig. 3. For the sake of brevity the corresponding plot for [PNP]Cl in water at 45.0 °C is omitted in Fig. 3.

As shown in Fig. 3, the data in methanol for the [PNP]$^+$-halides are nicely accommodated by the Fuoss-Onsager theory, eqn. 1; a slight curvature is observed for all three salts for concentrations higher than ~3.5×10^{-3} M which is to be expected since κa exceeds 0.2 at this concentration.[36] Data for concentrations higher than 3.5×10^{-3} M were therefore neglected in

Table 2. A comparison between the empirical slope k from the Kohlrausch plot and the slope from the Onsager equation, together with $\Lambda°$ from the Kohlrausch plot for [PNP]$^+$-salts in water and methanol.

Salt	Solvent	Temp. °C	Empirical slope $k \pm 5$	Onsager slope [a]	$\Lambda°$ from Kohlrausch plot
[PNP]Cl	H$_2$O	25.00	16	81.6	91.1
[PNP]Cl	H$_2$O	45.00	25	121.6	131.1
[PNP]Cl	MeOH	25.00	168	224	82.0
[PNP]Br	MeOH	25.00	169	227	86.0
[PNP]I	MeOH	25.00	189	233	92.5

[a] The following dielectric constants and viscosities were used: 78.40 and 0.8903 cP for H$_2$O at 25.0 °C,[32] 71.51 and 0.5963 cP for H$_2$O at 45.0 °C[32] and 32.62 and 0.5428 cP for CH$_3$OH at 25.0 °C.[33]
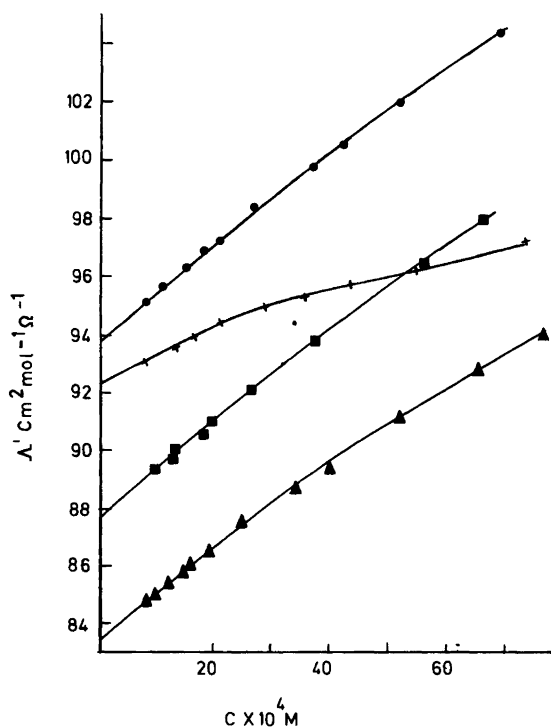
Fig. 3. Fuoss-Onsager plots at 25 °C: ● [PNP]I, ■ [PNP]Br, and ▲[PNP]Cl in methanol, +[PNP]Cl in water.

the calculation of $\Lambda°$ and $J(a)$ in methanol according to eqn. 2.

In water, however, the situation appears far more complex. A distinct change in slope is observed already at concentrations of $\sim 2.5 \times 10^{-3}$ M at 25.0 °C, $\sim 4.5 \times 10^{-3}$ M at 45.0 °C, not shown in Fig. 3, even though deviations from the Fuoss-Onsager theory were to be anticipated at higher concentrations in water than in methanol. $\Lambda°$

and $J(a)$ were therefore calculated from measurements at concentration lower than 2.5×10^{-3} and 4.5×10^{-3} M at 25.0 and 45.0 °C, respectively. The conductance parameters in water and methanol are summarized in Table 3. The excellent agreement for the limiting ionic conductance for the [PNP]$^+$-cation from the three halides studied in methanol may also serve as a reliable criterion of the purity of the studied [PNP]$^+$-salts. In Table 4 a compari-

Table 3. Conductance parameters for [PNP]$^+$-salts in water and methanol.

Temp. °C	Salt	$\Lambda°$ cm^2 mol^{-1} Ω^{-1}	$J(a)$	$\lambda°$[PNP]$^+$ cm^2 mol^{-1} Ω^{-1}
Water				
25.00	[PNP]Cl	92.2(3)	997(32)	15.9
45.00	[PNP]Cl	135.5(3)	1062(22)	24.6
Methanol				
25.00	[PNP]Cl	83.50(20)	1610(50)	31.12
25.00	[PNP]Br	87.73(15)	1628(30)	31.18
25.00	[PNP]I	93.82(15)	1630(36)	31.07

Table 4. Ionic molar conductivities, Walden products and Stokes' radii for some large organic cations in water, methanol and acetonitrile.

Solvent	Temp. °C	Cation	$\lambda°$ cm^2 mol^{-1} Ω^{-1}	Walden product $\lambda°\eta$	r_s Å	Ref.
H$_2$O	25.00	[PNP]$^+$	15.9(3)	0.142(3)	5.8	This study
	45.00	[PNP]$^+$	24.6(3)	0.147(3)	5.6	This study
	25.00	Ph$_4$As$^+$	19.4	0.173	4.8	34
	25.00	n-Pen$_4$N$^+$	17.5	0.156	5.2	37
MeOH	25.00	[PNP]$^+$	31.1(1)	0.169	4.8	This study
	25.00	n-Pen$_4$N$^+$	34.8	0.189	4.3	37
MeCN	25.00	Ph$_4$As$^+$	55.8	0.192	4.2	38
	25.00	n-Pen$_4$N$^+$	56.0	0.193	4.2	37

son is made between ionic molar conductivities and Walden products in various solvents together with calculated Stokes' radii.

Surface tension studies. From Gibbs' adsorption isotherm and the surface pressure π, one obtains the following expression for the surface concentration Γ_2 at low concentrations when activity coefficients are neglected:

$$\Gamma_2 = \frac{d\pi}{RT \, d \ln c_2} = \frac{1}{2.303 \, RT} \frac{d\pi}{d \log c_2} \quad (3)$$

In Fig. 4 the surface pressure π is plotted *vs.* the logarithm of the concentration of [PNP]Cl and of Ph$_4$AsCl in water; for comparison the figure includes data for n-Pen$_4$NBr and for n-Bu$_4$NCl from Ref. 39. The exceptional surface activity of [PNP]Cl is readily evident from the figure; most notable is a fairly linear dependence of the surface pressure on the logarithm of the concentration of [PNP]Cl up to a concentration of approximately 5.0×10^{-3} M, whereupon a distinct reduction in the slope is observed. Ph$_4$AsCl, as can be seen from the figure, behaves as a usual non-micellar electrolyte as do numerous symmetrical tetra-organoammonium halides, R$_4$NX.[39]

DISCUSSION

The results from the conductivity studies in water reveal some interesting features with regard to the solution chemistry of [PNP]Cl in this solvent. As shown in Fig. 1 a sharp decrease in conductance is observed at $\sim 5.0 \times 10^{-3}$ M at 25.0 °C ($\sim 7.0 \times 10^{-3}$ M at 45.0 °C). This discontinuity in the conductivity *vs.* concentration

plot can only be caused by a decrease in the number of charges capable of transport under the action of an external field. A fairly abrupt change in the slope of the Λ *vs.* $c^{1/2}$ plot as observed in the present study is generally assumed to be due to some sort of aggregation and resemble salts of the micelle forming type [40,43] and differ significantly from Ph$_4$As$^+$-salts [34,44] and salts of symmetrical [45,46] and fairly symmetrical [37] R$_4$N$^+$-ions. A slight but distinct change in the slope of the π *vs.* log c plot, Fig. 4, seems to substantiate the conclusion that some sort of micellar aggregate is formed at a concentration of $\sim 5.0 \times 10^{-3}$ of [PNP]Cl in water.[43]

For concentrations considerably lower than the "cmc"- value, the conductance of [PNP]Cl in water also shows a peculiar behaviour. As shown in Table 2 the empirical slopes of the Kohlrausch plots, Fig. 1, are only some 20 % of the theoretical slopes as calculated by the Onsager equation. The experimental conductivites are therefore higher than the theoretical predictions which may be explained by interactions between simple ions by which highly conducting ions are formed.[42]

However, several pieces of evidence may actually indicate that the Fuoss-Onsager theory [35] cannot be applied to describe the conductivity of [PNP]$^+$-salts in water. The slopes in the Λ *vs.* c plots, equal to $J(a) - B\Lambda°$, are ~ 1000 and ~ 1050 at 25.0 and 45.0 °C, respectively. Viscosity data for [PNP]$^+$-salts are presently not available, but if the B-value of the [PNP]$^+$-cation is comparable with that of Ph$_4$As$^+$ and of n-Bu$_4$N^{+}[47] or the Einstein relation [48,49] is valid, a B-value not very different from unity is to be anticipated. The $B\Lambda°$ term should thus be negligible compared

with $J(a)$. However, a $J(a)$-value of ~ 1000 in water cannot be accounted for by the Fuoss-Onsager equation.[50] Owing to the apparent discrepancy between the Fuoss-Onsager theory[35] and the experimental results, no attempts were made to determine association constants in water according to the extended Fuoss equation.[50,51]

Part of this discrepancy can presumably be traced to the size of the [PNP]$^+$-cation. Its length, as measured from one parahydrogen to another parahydrogen of a phenyl group linked to the other phosphorus atom, is 16.3 Å.[10,52] If one for simplicity considers the cation as a cylinder with radius equal to 6.58 Å $\times \sin 71°$,[52] one obtains a volume of no less than ~ 2000 Å.^{3} It is probably not justifiable to treat ions of this size as spheres.[35]

The figure arrived at for the size of the [PNP]$^+$-cation is admittedly in excess of the actual size of the cation since space is vacant for solvent molecules between the phosphorus atoms and presumably also between the phenyl groups.[49] For comparison, $\bar{V}°$ for the [PNP]$^+$-cation is 450.5 and 426 cm^3 mol^{-1} in water and methanol, respectively.[53] However, the former figure for the volume of the cation may act as a better estimate of the true size of the ion, especially during transportation in a solvent.

By simple algebra, the ions alone in, e.g., a 1×10^{-2} M solution of [PNP]Cl will occupy a volume of more than 1 % of the bulk volume. The number of solvent molecules between the ions even in dilute solutions will therefore necessarily be highly limited and the question arises whether zone C, "bulk solvent", as defined by Frank and Wen,[54] will be present in solutions of [PNP]$^+$-salts above a certain concentration. The "bulk solvent" may well consist of only zone A around the small chloride ions and of zone B around the [PNP]$^+$-cation; zone B is assumed to increase with increasing size.[55] In sufficiently dilute solutions, however, the bulk solvent may change its character owing to the presence of water with undisturbed structure, zone C. Since the various physical parameters like viscosity, dielectric constant etc. may change gradually with concentration of large ions even in fairly dilute solution, it is questionable whether the usual extrapolation procedures toward infinite dilution are valid for salts of this class of ions. It should be emphasized that a distinct reduction in the local dielectric constant of water in solutions

of [PNP]Cl may be the cause for the exceptional large value of J(a) as observed in the present study.

The conductance data in methanol are highly different from those obtained in water. All the [PNP]$^+$-halides were found to obey the Fuoss-Onsager theory[50] satisfactorily for concentrations lower than $\sim 3.5 \times 10^{-3}$ M, cf. Fig. 3. By applying the extended Fuoss equation,[50,51] the association constants for all three halides were found to be less than 5; the accuracy of the conductance data did not allow a more accurate determination.

The empirical slopes from the Kohlrausch plots were comparable with the calculated Onsager slopes, cf. Table 2. Furthermore, the slopes in the Λ vs. c plots, Fig. 3, were of the anticipated order of magnitude for halides of large organic cations in methanol, ~ 1600.[37] From the $J(a)$-values for the three halides, an interionic distance of 5.3 ± 0.2 Å was calculated, in fair agreement with the calculated Stokes' radii for the [PNP]$^+$-cation, 4.8 Å, cf. Table 4. It is notable that the Λ vs. c plots, Fig. 3, are linear over a larger concentration range in methanol than in water; the opposite was actually to be anticipated. In short, the [PNP]$^+$-halides behave as well-dissociated 1:1 electrolytes in methanol over a fairly large concentration range in contrast to [PNP]Cl in water. The trend toward increasing dissociation in methanol relative to water with increasing size of the cation has previously been observed.[45,46]

The different behaviour of the [PNP]$^+$-salts in the two solvents may be due to differences in the interaction between the two types of solvent molecules and the cation. Kalfoglou and Bowen[34] have suggested that tetraarylonium cations are structure breakers in water owing to interactions between the water molecules and the π-electrons of the phenyl groups.[56] The magnitude of this interaction, however, has been disputed.[57,58] Provided the suggested structure breaking ability of aryl-substitued cations is due to interaction between phenyl groups and water molecules, one may propose the [PNP]$^+$-cation with its six phenyl groups to be a structure breaker also.

The Walden products for the [PNP]$^+$-cation in water and methanol are not compatible with this cation being a structure breaker, cf. Table 4. The ratio between the Walden products in the two solvents is 0.82 which is comparable with that for R_4N^+-cations with large alkyl groups,[59] cations which are generally accepted to act as structure makers. However, this ratio may not be a reliable
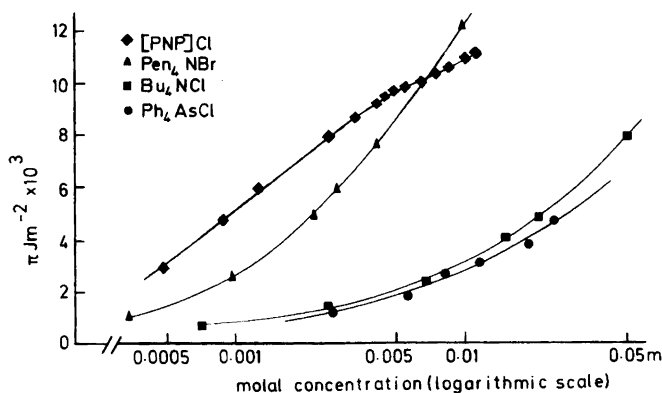
Fig. 4. Surface pressure *versus* concentration (logarithmic scale).

criterium for the $[PNP]^+$-cation which due to its size and structure may only with difficulty be transported in a highly structured solvent as water. The temperature effect on the Walden product in water, Table 4, is negligible; a distinct negative effect was to be anticipated for a structure breaking ion.[59]

The surface activity of $[PNP]Cl$ in water, *cf.* Fig. 4, indicates clearly that the $[PNP]^+$-cation and the Ph_4As^+-cation behave differently toward this solvent. Apparently, the interaction between the water molecules and the $[PNP]^+$-cation is not of sufficient energy to keep the $[PNP]^+$-salts solvated in the bulk solvent and, as a result, $[PNP]Cl$, even in very dilute solutions, $<1 \times 10^{-3}$ M, prefers to escape from the bulk solvent to the surface. The linearity in the π *vs.* log c plot for low concentrations, $\sim 1 \times 10^{-3}$ M, suggests that the excess surface concentration, Γ_2, is fairly constant and equal to 1.2×10^{-6} mol m^{-2}. This value is comparable with the one determined by Tamaki[39] for the very soluble salt n-Bu$_4$NCl, but for a concentration of ~ 0.1 M. In methanol, in which all $[PNP]^+$-salts are very soluble, no lathering effect of $[PNP]Cl$ could be observed.

Finally some comments on the discontinuities observed both in the conductivity and the surface tension studies at $\sim 5 \times 10^{-3}$ M of $[PNP]Cl$ in water at 25.0 °C. This type of behaviour is atypical for usual electrolytes and strongly resembles what is observed for systems in which micellar aggregates are formed. Presumably, the weakly solvating properties of water toward the $[PNP]^+$-cation and the presence of both neg-

atively and positively charged atoms in the cation[13] may cause dimers or higher aggregates to be formed.

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