

# The Conductivity Behaviour of Bis[tri(4-methylphenyl)phosphine]iminium Chloride in Dilute Aqueous Solution

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Palmesen, T. and Songstad, J., 1989. The Conductivity Behaviour of Bis[tri(4-methylphenyl)phosphine]iminium Chloride in Dilute Aqueous Solution. – *Acta Chem. Scand.* 43: 763–770.

The conductivity of dilute aqueous solutions of bis[tri(4-methylphenyl)phosphine]iminium chloride,  $[(4\text{-McPh})_3\text{P}]_2\text{NCl}$ , has been investigated at 25, 45 and 60 °C. At 25 °C the molar conductivity increases with increasing concentration up to the saturation concentration, viz.  $\sim 1.9 \times 10^{-3} \text{ mol dm}^{-3}$ . At 45 and 60 °C the solubility of the salt is sufficient to allow distinct maxima in the conductivity plots to be detected at  $\sim 1.2 \times 10^{-3}$  and  $\sim 1.9 \times 10^{-3} \text{ mol dm}^{-3}$ , respectively. This conductivity behaviour is independent of pressure up to 1200 bar at 45 °C. A dimerization model due to Mukerjee *et al.* has been tested but an interpretation based upon a multi-step formation of small cation-cation aggregates is favoured.

Solubility studies of salts of cations containing several phenyl groups show that the free energy of transfer,  $\Delta G_{\text{trans}}^{\circ}$ , from  $\text{H}_2\text{O}$  to  $\text{D}_2\text{O}$  is positive. No obvious relations between solute-solvent interactions, as viewed by  $\Delta G_{\text{trans}}^{\circ}$ , and tendency of association, as based upon the conductivity plots, could be established.

The concept of ionic association provides a simple method of dealing with the situation which arises when ions of opposite sign are close together.<sup>1</sup> Due to electrostatic attraction between the cation,  $\text{A}^+$ , and the anion,  $\text{B}^-$ , ion pairs,  $\text{AB}$ , are formed.<sup>2</sup> At higher concentrations the ion pairs may further associate to quadrupoles,  $(\text{AB})_2$ , and to larger aggregates,  $(\text{AB})_n$ .<sup>3</sup> The various types of species and their individual concentrations will often influence the behaviour and the reactivity of an ionic reactant in a given solvent.<sup>4,5</sup>

It has become evident in recent years that other species may be present in electrolyte solutions. Apart from the disputed triple ions,  $\text{A}_2\text{B}^+$  and  $\text{AB}_2^-$ ,<sup>6,7</sup> dimeric species derived from ions of similar charge,  $\text{A}_2^{2+}$ , and  $\text{B}_2^{2-}$ , may also be present in finite concentrations. Lange and Herre<sup>8</sup> originally proposed the existence of picrate dimers,  $\text{Pi}_2^{2-}$ , in order to explain the results of cryoscopic and conductivity studies of aqueous solutions of  $\text{NaPi}$ . More recent measurements of transference numbers for solutions of  $\text{KPi}$  in water accord with this proposal.<sup>9</sup> Although pairing of anions may in principle be as feasible as pairing of cations,<sup>10,12</sup> it is the latter type of pairing which has received most attention. This is primarily due to the fact that cation pairing has been considered for a long time as a possible preaggregation step in the micelle formation of amphiphilic ions.<sup>13</sup> Cation-cation association of non-amphiphilic ions was first proposed by Wen and Saito<sup>14</sup> to explain the apparent molar volumes of  $\text{R}_4\text{N}^+$  bromides in concentrated aqueous solutions. The concept of attractive interaction between ions of like charge has since been supported by several studies.<sup>15–18</sup>

However, based on an intuitive understanding of the interaction between ions of similar charge, it is puzzling

that such a pair should show a net stabilization at short distance. Furthermore, since experiments leading to conclusive evidence are most difficult to design and perform, this type of pair formation has not gained general acceptance. Broadwater and Evans<sup>19</sup> studied aqueous solutions of the dibromide of the bolaform cation,  $[\text{Bu}_3\text{N}-(\text{CH}_2)_8\text{NBu}_3]^{2+}$ , a probable model for  $\text{Bu}_4\text{N}^+$  pairs. They concluded that all experimental results could be rationalized by the usual association model without invoking paired cations. Since cation-cation association of  $\text{R}_4\text{N}^+$  salts seems to take place only in highly concentrated aqueous solutions,<sup>15,18</sup> this class of solute-solvent systems will not be ideal for this kind of study. Hemmes<sup>12</sup> has concluded, from a simple sphere-in-continuum model, that dimerization of ions of like charge is favoured by large ions and by low permittivity of the solvent. Although viscosity studies may be a valuable approach in the search for dimeric species in solvents of low to medium permittivity,<sup>20</sup> it is most difficult to prove unequivocally the presence of aggregates of this kind in solutions which contain a considerable fraction of the usual cation-anion pairs. For conclusive evidence one thus has to examine systems in which other types of aggregates are absent, i.e. dilute solutions in solvents of high permittivity.

Previous studies on bis(triphenylphosphine)iminium chloride,  $[\text{PNP}]\text{Cl}$ , have revealed unexpected solution properties in aqueous solution.<sup>21</sup> From a structural point of view the cation does not resemble the usual associating solutes.<sup>22,23</sup> Nevertheless, a satisfactory interpretation of the various experimental results can apparently only be arrived at when some type of association is taken into account.<sup>24,25</sup> In contrast to  $\text{R}_4\text{N}^+$  salts,<sup>15,18</sup>  $[\text{PNP}]\text{Cl}$  seems to

start to associate in very dilute solutions, i.e.  $10^{-4} - 10^{-3}$  mol dm $^{-3}$ .<sup>21,24</sup> The rapid and most accurate conductivity technique can therefore be applied.<sup>24,26</sup> This class of solute-solvent system appears to be well suited for further studies to establish the association pattern and the forces responsible for the association.

In an attempt to increase the probability of cation-cation association, the six phenyl groups in the [PNP] $^{+}$  cation were exchanged with 4-methylphenyl groups. The methyl groups will increase the size of the ion and were hoped to enhance its hydrophobic character. As might be expected, the solubility of bis[tri(4-methylphenyl)phosphine]iminium chloride, abbreviated [(tol $_3$ P) $_2$ N]Cl, in water is significantly lower than that of [PNP]Cl. The poor solubility,  $\sim 1.9 \times 10^{-3}$  mol dm $^{-3}$  at 25.0°C, reduced the number of experimental methods available for the study of this salt. This paper reports on the conductivity of aqueous solutions of [(tol $_3$ P) $_2$ N]Cl at 25, 45 and 60°C, at 45°C at pressures up to 1200 bar. Studies of [PNP] $^{+}$  halides in methanol<sup>24,25</sup> have revealed that these salts behave as well-dissociated electrolytes in this solvent. Conductivity studies of [(tol $_3$ P) $_2$ N]Cl in methanol, in which the salt is very soluble, have therefore also been performed. To further elucidate the solvent effects upon the solution properties of salts of cations containing several phenyl groups, the solubility of several salts of this type has been measured in water and in heavy water in order to determine the free energy of transfer between the two solvents. Since D $_2$ O is usually considered to be more structured than H $_2$ O, effects arising from the structure of the solvent are expected to be enhanced in D $_2$ O.<sup>27,28</sup>

## Experimental

**Materials.** [(tol $_3$ P) $_2$ N]Cl was synthesized from tri(4-methylphenyl)phosphine (22 g) and the corresponding amounts of hydroxylamine hydrochloride and chlorine gas in 1,1,2,2-tetrachloroethane, as described by Ruff and Schlientz<sup>29</sup> for [PNP]Cl. After the solvent had been removed the residue was dissolved in hot benzene, from which the salt precipitated upon cooling (ethyl acetate, which is recommended for [PNP]Cl at this stage in the purification process,<sup>29</sup> could not be used owing to the considerable solubility of the product in this solvent). The salt was further crystallized from hot water of pH 7 to 8, from a methanol-diethyl ether mixture and from hot benzene. From methanol-diethyl ether mixtures a methanol solvate was obtained. The salt was dried to constant weight at 1 mmHg at  $\sim 40^\circ\text{C}$ . At higher temperatures the salt slowly acquired a yellowish colour, presumably due to some decomposition. The yield of purified product was only 3.3 g ( $\sim 20\%$ ), m.p. 199–203°C (dec.). Purification was continued until reproducible conductivity data were obtained for several samples purified differently.

The identity of the compound was confirmed by an X-ray diffraction study.<sup>30</sup> The P–N–P bond angle, 139.1°, and the P–N bond lengths, 0.1585 nm, are as observed in numerous [PNP] $^{+}$  salts.<sup>31–33</sup> The equivalence of the phosphorus atoms

was confirmed by  $^{31}\text{P}$  NMR; their chemical shift was 20.2 ppm relative to H $_3$ PO $_4$  dissolved in methanol.

[(tol $_3$ P) $_2$ N]Br, m.p. 207–211°C, and the bromides, iodides and perchlorates of [PNP] $^{+}$ , Ph $_4$ As $^{+}$ , Ph $_4$ P $^{+}$  and Ph $_3$ PMe were prepared from aqueous solutions of the chlorides and a large excess of the corresponding potassium salts.<sup>34</sup> The salts were carefully washed with warm water to remove traces of chlorides, crystallized several times from organic solvents and dried in vacuum to constant weight prior to use.<sup>35</sup>

Conductivity water was supplied from a Fi-stream distillation apparatus. Special care was taken to reduce and stabilize its conductivity ( $1.1 \times 10^{-6}$  S cm $^{-1}$  at 25°C and  $1.9 \times 10^{-6}$  S cm $^{-1}$  at 60°C). At 45°C the conductivity was determined up to 1200 bar, and the conductivity of water ranged from  $2 \times 10^{-6}$  S cm $^{-1}$  at normal pressure to  $10 \times 10^{-6}$  S cm $^{-1}$  at 1200 bar. Methanol (Merck *p.a.*) was used as received and had a conductivity of  $0.9 \times 10^{-6}$  S cm $^{-1}$ . D $_2$ O (99.8%; Norsk Hydro A/S) was used without further purification.

**Conductivity measurements.** The conductivity cell for the measurements at normal pressure was made from a 250 ml Erlenmeyer flask. The platinum electrodes were coated with platinum black as described by Ives and Janz.<sup>36</sup> The cell, tested and calibrated as previously described,<sup>24</sup> had a cell constant of 1.187 cm $^{-1}$  and was accurate to 0.1%.

The high-pressure conductivity equipment has been described by Høiland.<sup>37</sup> The conductivity cells for this part of the study had cell constants of  $\sim 20$  cm $^{-1}$ , determined to an accuracy of within 0.2%. The density of water at 45°C at various pressures was taken or was extrapolated from the work of Chen *et al.*<sup>38</sup> Tables of conductivity data together with derived parameters at different concentrations and pressures are available from the authors on request.

**Solubility measurements.** The molar solubilities in H $_2$ O and D $_2$ O were determined by U.V. spectrophotometry. A Perkin Elmer 555 spectrophotometer was used. Saturated solutions were prepared from slightly overheated solutions, equilibrated under constant shaking for one week at 25.00 (2)°C and then left for two days prior to separation and measurement. When necessary, the saturated solutions were diluted by weight. The molar absorptivities were determined for methanolic solutions. A small shift, up to  $\sim 2$  nm, of the absorption peaks on going from methanol to water for some of the cations was neglected. Concentrations, on the molar scale, were calculated using the following densities of the solvents: Methanol, 0.7900 kg dm $^{-3}$ ; H $_2$ O, 0.988 kg dm $^{-3}$ ; and D $_2$ O, 1.105 kg dm $^{-3}$ .<sup>39</sup>

## Results

**Conductivity data.** Fig. 1, lower curve, shows the molar conductivity of [(tol $_3$ P) $_2$ N]Cl in water at 25.00°C plotted vs. the square root of the concentration. The upper curves in Fig. 1 show the corresponding conductivity plots at 60.00°C

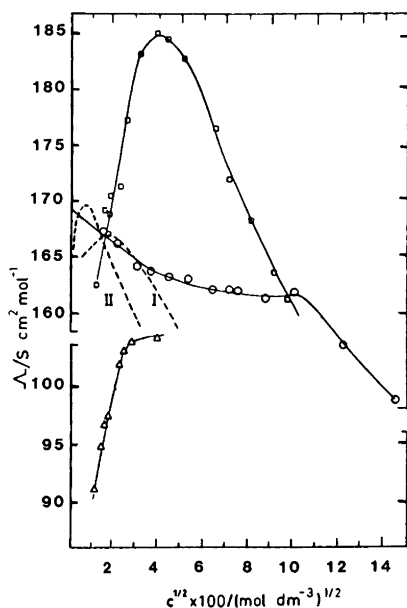


Fig. 1. The molar conductivity of  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  ( $\square$ ) and of  $[\text{PNP}]\text{Cl}$  ( $\circ$ ) at  $60^\circ\text{C}$  (upper part), and of  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  ( $\triangle$ ) (lower part) plotted vs. the square root of the molarity. The dotted lines are values calculated according to a dimerization model (see text).

for  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  (squares; this study) and for  $[\text{PNP}]\text{Cl}$  (circles; from Ref. 21). The upper concentration limits for  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  are determined by the solubility, viz.  $\sim 1.9 \times 10^{-3}$  and  $\sim 1.5 \times 10^{-2}$   $\text{mol dm}^{-3}$  at 25 and  $60^\circ\text{C}$ , respectively. The dotted curves at  $60^\circ\text{C}$  are values calculated according to a dimerization model due to Mukerjee *et al.*<sup>40</sup> and will be discussed below.

The molar conductivity of  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  was also determined in methanol at  $25.00^\circ\text{C}$ . In contrast to the conductivity plots in water (Fig. 1), this plot is linear within experimental error up to  $\sim 3.5 \times 10^{-3}$   $\text{mol dm}^{-3}$  with a slope of  $1.97 \text{ S dm}^{7/2} \text{ mol}^{-3/2}$ . The slope calculated from Onsager's limiting law is slightly larger, viz.  $2.22 \text{ S dm}^{7/2} \text{ mol}^{-3/2}$ . Linear  $\Lambda\text{-}c^{1/2}$  plots in methanol have previously been observed for  $[\text{PNP}]^+$  chloride, bromide and iodide.<sup>24</sup> From an extrapolation according to the Fuoss-Onsager equation<sup>47</sup> a  $\Lambda_0$  of  $80.4(3) \text{ S cm}^2 \text{ mol}^{-1}$  for  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  in methanol at  $25.00^\circ\text{C}$  was found. The corresponding value for  $[\text{PNP}]\text{Cl}$  is  $83.5(2) \text{ S cm}^2 \text{ mol}^{-1}$ .<sup>24</sup>

The peculiar form of the conductivity plots for  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  in water makes extrapolation to infinite dilution impossible. The conductivity of water prevented reliable measurements being made below  $1 \times 10^{-4}$   $\text{mol dm}^{-3}$ . Assuming the ratio between the limiting ionic molar conductivity of  $[\text{PNP}]^+$  and  $[(\text{tol}_3\text{P})_2\text{N}]^+$  in water and methanol to be equal, one arrives at a  $\Lambda_0$  for  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  in water at  $25.00^\circ\text{C}$  of  $90.6 \text{ S cm}^2 \text{ mol}^{-1}$ . Provided the temperature dependence of  $\lambda_0([(\text{tol}_3\text{P})_2\text{N}]^+)$  is as for  $\lambda_0([\text{PNP}]^+)$ , one may estimate  $\Lambda_0$  for  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  at  $60^\circ\text{C}$  to be approximately  $165.2 \text{ S cm}^2 \text{ mol}^{-1}$ . These two values seem to be of the right order of magnitude seen in relation to the conduc-

tivity plots shown in Fig. 1. The decrease relative to the corresponding values for  $[\text{PNP}]\text{Cl}$ , i.e.  $92.2(3)$ <sup>24</sup> and  $168.5 \text{ S cm}^2 \text{ mol}^{-1}$ ,<sup>21</sup> accords with expectations based upon the size of the two cations.

Fig. 2 shows the conductivity plots for  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  at  $45^\circ\text{C}$  determined at pressures from 1 to 1200 bar. The drawn line links the experimental points at normal pressure. The uncertainty in  $\Lambda$  is only  $\sim 0.2\%$  at the highest concentrations but increases to as much as  $\sim 5\%$  for the lowest. From the data for  $[\text{PNP}]\text{Cl}$ <sup>21</sup> and the assumptions mentioned above,  $\Lambda_0$  at  $45.00^\circ\text{C}$  can be estimated as  $133.0 \text{ S cm}^2 \text{ mol}^{-1}$  at 1 bar. This value appears reasonable seen in relation to the  $\Lambda\text{-}c^{1/2}$  plot in Fig. 2.

The change in the molar conductivity with increasing pressure is within only some few per cent. In the case of the most concentrated solutions, for which this change is outside the experimental error, the molar conductivity seems to increase slightly on going from 1 bar to 300 and 600 bar. For higher pressures a small decrease is observed. The observed pressure effect can presumably be attributed to hydration effects of the chloride ions.<sup>42</sup>

The conductivity plots in Figs. 1 and 2 show distinct maxima at  $\sim 1.2 \times 10^{-3}$   $\text{mol dm}^{-3}$  at  $45^\circ\text{C}$  and  $\sim 1.9 \times 10^{-3}$   $\text{mol dm}^{-3}$  at  $60^\circ\text{C}$ . In the case of  $[\text{PNP}]\text{Cl}$  in water at 25, 45 and  $60^\circ\text{C}$  the increase in  $\Lambda$  with concentration was not sufficiently large to create distinct maxima in the conductivity plots.<sup>21,25</sup> Such maxima have previously been reported for surfactants with rather low critical micelle concentrations<sup>43,47</sup> and for some associating bile salts.<sup>26,45,46</sup> No similar conductivity behaviour has been observed in the extensive studies on  $\text{Ph}_4\text{M}^+$  salts ( $\text{M} = \text{P}, \text{As}$  and  $\text{Sb}$ ) in aqueous solution.<sup>47-50</sup>

**Solubility data.** Table 1 summarizes the results obtained from the solubility study at  $25.00^\circ\text{C}$ . From the saturation concentrations,  $c_{\text{sat}}$ , the standard free energy of solution,  $\Delta G_{\text{sol}}$ , can be calculated from eqn. (1)

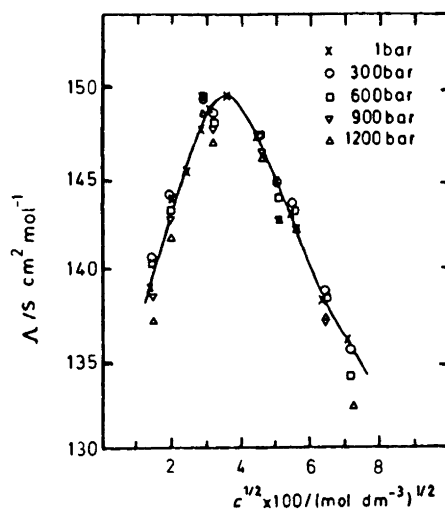


Fig. 2. The major conductivity of  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  plotted vs. the square root of the molarity at  $45^\circ\text{C}$  at various pressures.

Table 1.  $\lambda_{\max}$ , maximum solubility ( $c_{\text{sat}}$ ) in H<sub>2</sub>O and D<sub>2</sub>O at 25.00°C and the free energy of transfer,  $\Delta G_{\text{trans}}^{\circ}$ , for transfer from H<sub>2</sub>O to D<sub>2</sub>O for various salts of ions containing phenyl groups.

Salt	$\lambda_{\max} / \text{nm}$	$c_{\text{sat}} \text{ H}_2\text{O} / \text{mol dm}^{-3}$	$c_{\text{sat}} \text{ D}_2\text{O} / \text{mol dm}^{-3}$	$\Delta G_{\text{trans}}^{\circ} / \text{kJ mol}^{-1}$
[(tol <sub>3</sub> P) <sub>2</sub> N]Br	264.0	$1.8 \times 10^{-4}$	$1.7 \times 10^{-4}$	0.28
[PNP]Br	266.3	$2.9 \times 10^{-3}$	$1.7 \times 10^{-3}$	2.52
[PNP]I	266.5	$9.9 \times 10^{-5}$	$6.1 \times 10^{-5}$	2.39
Ph <sub>4</sub> AsI	263.5	$2.8 \times 10^{-3}$	$2.6 \times 10^{-3}$	0.36
Ph <sub>4</sub> AsClO <sub>4</sub>	263.7	$6.8 \times 10^{-5}$	$5.9 \times 10^{-5}$	0.70
Ph <sub>4</sub> PBr	268.2	$5.4 \times 10^{-2}$	$3.4 \times 10^{-2}$	2.10
Ph <sub>4</sub> PI	267.9	$2.6 \times 10^{-3}$	$1.5 \times 10^{-3}$	2.80
Ph <sub>4</sub> PClO <sub>4</sub>	268.1	$9.6 \times 10^{-5}$	$7.7 \times 10^{-5}$	1.08
Ph <sub>3</sub> MePI	266.3	$3.7 \times 10^{-2}$	$3.0 \times 10^{-2}$	0.92

$$\Delta G_{\text{sol}}^{\circ} = -RT \ln K_{\text{sp}} \quad (1)$$

where  $K_{\text{sp}}$  is defined as  $K_{\text{sp}} = (c_{\text{sat}} \times f_{\pm})^2$ , and  $f_{\pm}$ , the mean ionic activity coefficient, is calculated from eqn. (2).<sup>1</sup>

$$\log f_{\pm} = -A \frac{I^{1/2}}{1 + I^{1/2}} + 0.30 AI \quad (2)$$

$A$  in eqn. (2) is the Debye-Hückel constant<sup>3</sup> and  $I$  is the ionic strength.

Admittedly, the extensive association that seems to take place in aqueous solution may invalidate the use of the Debye-Hückel limiting law. The salts selected for the solubility study, however, are only slightly soluble in H<sub>2</sub>O and D<sub>2</sub>O. Since the deviations from ideality in these two solvents are probably equal and small, the free energy of transfer,  $\Delta G_{\text{trans}}^{\circ}$ , from H<sub>2</sub>O to D<sub>2</sub>O can be calculated by eqn. (3).

$$\begin{aligned} \Delta G_{\text{trans}}^{\circ} &= \Delta G_{\text{sol}}^{\circ}(\text{D}_2\text{O}) - \Delta G_{\text{sol}}^{\circ}(\text{H}_2\text{O}) \\ &= -RT \ln [K_{\text{sp}}(\text{D}_2\text{O})/K_{\text{sp}}(\text{H}_2\text{O})] \end{aligned} \quad (3)$$

The calculated values for  $\Delta G_{\text{trans}}^{\circ}$  are listed in Table 1, last column. The error in the relative differences in  $\Delta G_{\text{trans}}^{\circ}$  will probably be negligible.

For all salts examined,  $\Delta G_{\text{trans}}^{\circ}$  for transfer from H<sub>2</sub>O to D<sub>2</sub>O is positive, i.e. D<sub>2</sub>O is a less favourable solvent than H<sub>2</sub>O. For some of the salts, e.g. the bromides and iodides of [PNP]<sup>+</sup> and Ph<sub>4</sub>P<sup>+</sup>, the free energy of transfer is from 2 to 3 kJ/mol<sup>-1</sup>, which is extraordinarily large compared to values for other types of salts.<sup>51</sup> Generally, the sign and magnitude of  $\Delta G_{\text{trans}}^{\circ}$  is as for several planar non-electrolytes.<sup>52</sup>

## Discussion

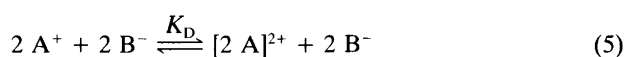
Evans *et al.*<sup>26</sup> have discussed the various factors affecting the concentration dependence of the molar conductivity in terms of (1) interionic effects, (2) cation-anion association, (3) dimerization, aggregation or micellation, and (4) viscosity effects. These authors concluded that only some form of aggregation of ions of like charge could explain an increase

in the molar conductivity with increasing concentration. The argument is based upon the reasonable assumption that a pair will be smaller than the sum of two individual ions. The effective gain in the molar ionic conductivity for the dimers, or for larger aggregates, can then be deduced from Stokes' law [eqn. (4)]

$$\lambda = 0.820 z/\eta r_s \quad (4)$$

where  $z$  is the effective charge,  $r_s$  is the effective radius of the species in Å (10<sup>-10</sup> m), and  $\eta$  is the viscosity of the medium in poise. Due to this gain in conductivity, the slope of the  $\Lambda-c^{1/2}$  plot will be smaller than calculated from Onsager's limiting law. The slope alone, however, may not be a reliable criterion for the absence or presence of dimers derived from ions of like charge; numerous cases are known of slopes significantly different from the calculated one without any evidence of pair formation.<sup>53</sup> Furthermore, sizable formation constants for associated species derived from dimers and counterions, [A<sub>2</sub><sup>2+</sup>B<sup>-</sup>] or [A<sup>+</sup>B<sub>2</sub><sup>2-</sup>], will counteract the anticipated gain in conductivity due to cation-cation or anion-anion pairing. Recently, Perie and co-workers<sup>48</sup> have shown from a study on Ph<sub>4</sub>PCl in water that a slope in reasonable agreement with the calculated one may still be observed when some pairing of the Ph<sub>4</sub>P<sup>+</sup> ions takes place, provided the ionic transference numbers are sufficiently concentration-dependent. A maximum in the conductivity plot, however, as observed by Evans *et al.*<sup>26</sup> in the case of the bile salt sodium taurodeoxycholate and [(tol<sub>3</sub>P)<sub>2</sub>N]Cl (Figs. 1 and 2), is a clear indication of the formation of dimers or larger aggregates of ions of like charge which in dilute solution do not associate significantly with the counterions.

Mukerjee *et al.*<sup>40</sup> have similarly proposed a dimerization model to explain the positive deviation from the Onsager slope in conductivity plots of some amphiphilic salts. These authors assumed that the solution contains a mixture of the dissociated salt and a dimer, with concentrations determined by an equilibrium constant,  $K_D$ , for the dimerization process [eqn. (5)].



The conductivity contributions from the monomers and the dimers were taken to be additive, and the mixture effect was neglected. Based upon these assumptions, they proposed an equation for the molar conductivity of the solution.<sup>40</sup>

In this study a similar equation has been tested in an attempt to account for the conductivity behaviour of  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$ . When the total concentration of the monomer is  $c$  and the concentration of the dimer is  $\alpha c$ ,  $\alpha$  being less than 0.5, the dimerization constant for the equilibrium in eqn. (5) is

$$K_D = \frac{\alpha}{(1-2\alpha)^2 c} \quad (6)$$

The molar conductivity of the mixture is then given by eqn. (7)

$$\Lambda = \Lambda'(1-2\alpha) + \Lambda''\alpha \quad (7)$$

where  $\Lambda'$  and  $\Lambda''$ , the molar conductivities of the 1:1 and the 2:1 electrolyte, respectively, can be expressed by the Onsager equations<sup>1</sup> [eqns. (8) and (9)].

$$\Lambda' = \Lambda_0 - \left[ \frac{8.204 \times 10^6}{(\epsilon T)^{3/2}} \Lambda_0 + \frac{82.50}{\eta(\epsilon T)^{1/2}} \right] [c(1+\alpha)]^{1/2} \quad (8)$$

$$\Lambda'' = (\gamma\lambda_0^+ + \lambda_0^-) - \left[ \frac{5.602 \times 10^6}{(\epsilon T)^{3/2}} \frac{q^*}{(1 + \sqrt{q^*})} (\gamma\lambda_0^+ + \lambda_0^-) + \frac{123.75}{\eta(\epsilon T)^{1/2}} \right] \times [c(1+\alpha)]^{1/2} \quad (9)$$

$q^*$  in eqn. (9) is given by

$$q^* = \frac{2(\gamma\lambda_0^+ + \lambda_0^-)}{3(\gamma\lambda_0^+ + 2\lambda_0^-)} \quad (10)$$

while  $\gamma$  is an effective size parameter for the mobility of the dimer.  $\gamma\lambda_0^+$  will then represent the molar conductivity of the dimer at infinite dilution. The ionic strength of the solution is given by  $c(1+\alpha)$ . Eqn. (7) can be rearranged to give

$$\Lambda = \Lambda_0 + B\alpha + C[\alpha(1+c)]^{1/2} + D\alpha[\alpha(1+c)]^{1/2} \quad (11)$$

in which  $B$ ,  $C$  and  $D$  are functions of  $\Lambda_0$  and  $\gamma$  only. When  $\Lambda_0$  is known, eqn. (11) may in principle be solved for  $\alpha$  and  $\gamma$ .

To test whether this equation could account for the maximum in the conductivity plot at 60 °C,  $d\Lambda/dc$  was calculated and attempts were made to find values for  $\alpha$  and  $\gamma$  that could lead to  $d\Lambda/dc = 0$  at  $c_{\text{max}}$  equal to  $1.9 \times 10^{-3} \text{ mol dm}^{-3}$ . This was not found to be possible for physically reasonable values of  $\gamma$  and  $\alpha$ . The dotted curves in Fig. 1 represent calculated conductivity plots for  $K_D = 10^3$  and  $\gamma = 1.8$  (I) and for  $K_D = 10^5$  and  $\gamma = 1.4$  (II). Apparently, the dimerization hypothesis may in some cases lead to an absolute

maximum in  $\Lambda$ - $c^{1/2}$  plots. Examination of eqn. (11) shows that this will require  $K_D$  to be fairly high, presumably larger than  $10^3$ . The magnitude of  $(\Lambda_{\text{max}} - \Lambda_0)$  will obviously depend on the  $\gamma$  value. For  $K_D = 3 \times 10^3$ , an absolute maximum will appear even when  $\gamma = 1.3$ .

The results shown in Fig. 2 suggest that an increase in pressure does not introduce significant changes in the association pattern. This must imply that the volume change in the association process is small. A similar conclusion was arrived at from volumetric studies of  $[\text{PNP}]\text{Cl}$  in water.<sup>25</sup> Since the volume change in the dimerization process appears to be negligible, one may conclude from Stokes' law that a reasonable value for  $\gamma$  in eqn. (6) will be approximately 1.4 provided the monomer and the dimer can be assumed to be ideal spheres. This latter assumption, however, is indeed a crude one when considering the structure of the  $[(\text{tol}_3\text{P})_2\text{N}]^+$  cation.<sup>30</sup>

The present results show that a distinct maximum in the  $\Lambda$ - $c^{1/2}$  plot may be explained by dimerization. The calculations illustrate, however, that such a maximum will only occur at rather low concentrations, less than  $\sim 5 \times 10^{-4} \text{ M}$ . The data for  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  cannot therefore be quantitatively accounted for by the Mukerjee model.<sup>40</sup> An alternative model for the association process in dilute solutions may rather involve a multi-step equilibrium cation association in which the general step is described by eqn. (12).<sup>54</sup>



The equilibrium constant for the formation of the  $n$ -mer may be denoted by  $K_n$ . The steep increase in  $\Lambda$  for  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  in water (Fig. 1) must then imply that for some value of  $n$  larger than 2,  $K_n$  will be much larger than  $K_{n-1}$ . The formation of large aggregates, like micelles, has to be associated with counterion binding, causing a net decrease in the molar conductivity. Aggregates or oligomers with  $n$  in the range 3–5 therefore seem necessary in order to be able to explain the present observations. It may also be mentioned that for concentrations higher than  $c_{\text{max}}$ , the slope of the  $\Lambda$ - $c^{1/2}$  plots is about twice the theoretical Onsager slope for the hypothetical 2:1 electrolyte. This observation strengthens the suggestion that higher aggregates than the dimers are present in this concentration range.

Regardless of the size of the aggregates in the dilute aqueous solutions of  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$ , some types of attractive forces between the cations have to be sufficiently strong to overcome the Coulombic repulsion. According to Hemmes,<sup>12</sup>  $K_D$  [eqn. (5)] will increase with the third power of the interionic distance. A cation of radius 0.575 nm would be sufficiently large to dimerize in water with a resultant decrease in free energy, i.e.  $K_D > 1$ . The ionic radius of the  $[\text{PNP}]^+$  cation is of this order of magnitude.<sup>31–33</sup> The radius of the  $[(\text{tol}_3\text{P})_2\text{N}]^+$  cation is some 18 % greater,<sup>30</sup> which will cause an increase in  $K_D$  by a factor of 1.6.<sup>12</sup> It is apparent that other attractive forces have to be involved to explain the extent of association of  $[\text{PNP}]\text{Cl}$

and  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  in dilute aqueous solution. There are numerous reports in the literature that show that water cannot be treated as a continuum dielectric at all interionic distances.<sup>55-57</sup>

Dimers and other types of aggregates seem only to be formed in aqueous solutions from ions with sterically screened charges.<sup>48</sup> This is as expected from Coulombic considerations. It is notable, however, that only ions with several phenyl groups form aggregates in dilute solutions;<sup>8,9,16,17,21,48</sup> large  $\text{R}_4\text{N}^+$  cations form aggregates only in very concentrated solutions.<sup>14,15,18</sup> Apparently, when aggregation of ions of like charge is considered, an effective screening of the ionic charge by large alkyl groups is not sufficient. Desnoyers *et al.*<sup>59</sup> have argued convincingly that this difference is due to the ability of the phenyl groups to act as hydrophilic groups rather than hydrophobic.<sup>47</sup> Due to interaction between the hydrophilic ions and the surrounding water molecules, the water molecules close to two adjacent ions of similar charge will be oriented in such a way that they will interact and thus promote pairing.<sup>50,59</sup> The hydrophobic  $\text{R}_4\text{N}^+$  ions will also stabilize the bulk structure of water.<sup>54,80</sup> The ion-water interaction, however, will not be sufficient to create the necessary cosphere overlap in dilute solutions. The hydrophilic character assumed for phenyl groups, and thus for ions with several phenyl groups,<sup>58</sup> would be caused by the rather large polarizability due to the  $\pi$  electrons and delocalized charges on them induced by the large electronegativity of the adjacent heteroatoms (P and As) bearing the positive charge.<sup>61</sup>

The cosphere model seems to provide a feasible explanation for the ability of  $\text{Ph}_4\text{P}^+$  ( $\text{Ph}_4\text{As}^+$ ) to form dimers in dilute aqueous solutions.<sup>48</sup> This ability seems to increase tremendously from  $\text{Ph}_4\text{P}^+$  to  $[\text{PNP}]^+$ ,<sup>24</sup> an increase which can hardly be due to the two extra phenyl groups. Presumably, the weaker positive charge on the P atoms in the  $[\text{PNP}]^+$  ion<sup>62</sup> will increase the polarizability of the phenyl groups and thus make the  $\pi$  electrons more disperse. Dispersive forces are often considered as a possible driving force for the aggregation of highly polarizable species. Additionally, a bent structure of the  $[\text{PNP}]^+$  ion combined with the  $\text{P}^{\delta+} - \text{N}^{\delta-} - \text{P}^{\delta+}$  charge distribution will create some amphiphilic character which will enhance the ability of this ion to aggregate.

From a comparison with previously reported results for  $[\text{PNP}]\text{Cl}$  (Fig. 1) it is evident that the six methyl groups in  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  cause a considerable increase in the association. As viewed by the difference in solubility of these two salts in water (Table 1), the methyl groups will retain their hydrophobicity when linked to the phenyl groups. Furthermore, the methyl groups will increase the size of the cation and thus the screening of the cationic charge. The weak donor properties of the methyl groups may also lead to a slight increase in the electron density of the phenyl groups. The structural data<sup>30</sup> and the <sup>31</sup>P NMR shifts for the two cations, however, do not indicate that the P-N-P part of the cation is seriously influenced by the methyl groups. The exceptional ability of the  $[(\text{tol}_3\text{P})_2\text{N}]^+$  ion to aggregate in

aqueous solution can presumably be explained by the hydrophilicity of the aryl groups, which causes the appropriate ordering of the solvent molecules,<sup>58</sup> and the hydrophobicity of the methyl groups, which strengthens the solvent cosphere in the vicinity of the aggregates. Detailed studies of aqueous solutions of  $(4\text{-MePh})_4\text{P}^+$  salts, particularly of the type described by Perie *et al.*,<sup>48</sup> may confirm this conclusion. The entropy change related to the release of structured water from around the isolated chains has usually been considered as the unique driving force for the self-assembly of amphiphiles in aqueous solutions. In this respect, a destructuring effect of the phenyl groups may be in contradiction to a hydrophobic association phenomenon. However, as recently illustrated by Evans and Ninham,<sup>63</sup> the major driving force in the aggregation of amphiphiles is the energetics of transfer of the non-polar groups from the polar solvent.

The results of the solubility study (Table 1) indicate that the hydrophobicity of the solutes is among the factors which may explain the association of these ions.  $\Delta G_{\text{trans}}^\circ$  for transfer from  $\text{H}_2\text{O}$  to  $\text{D}_2\text{O}$  illustrates a destabilization of this class of salts when the structure of the solvent is enhanced. It is notable, however, that no correlation can be found between the solute-solvent interactions, as measured by  $\Delta G_{\text{trans}}^\circ$ , and the tendency of the various salts to associate. It seems reasonable to relate the positive  $\Delta G_{\text{trans}}^\circ$  to a structure-breaking effect of the phenyl groups. In contrast to the alkanes, the size and rigidity of the phenyl groups do not allow for a stabilizing clathrate formation.<sup>64</sup> The rigid structure of the cations will limit their ability to separate the non-polar parts of the ions from the solvent. An opposite effect of the methyl groups may therefore be the cause of the small  $\Delta G_{\text{trans}}^\circ$  for  $[(\text{tol}_3\text{P})_2\text{N}]\text{Br}$  and  $\text{Ph}_3\text{MePI}$  as compared to salts of cations containing only phenyl groups. The irregular differences between salts of the same cation seem to imply that other effects have to be taken into account.

Irrespective of effects due to the anions as shown in Table 1,  $\Delta G_{\text{trans}}^\circ$  appears to be smaller for  $\text{Ph}_4\text{As}^+$  salts than for  $\text{Ph}_4\text{P}^+$  salts. The trend in the data seems to indicate that  $\text{Ph}_4\text{As}^+$  salts discriminate less between  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  than  $\text{Ph}_4\text{P}^+$  salts. This may partly be due to the slightly larger size of the  $\text{Ph}_4\text{As}^+$  ion<sup>65</sup> and the lower electronegativity of  $\text{As}^+$ .<sup>66</sup> It is tempting to conclude that the known discrepancies arising from the use of extrathermodynamic assumptions based upon  $\text{Ph}_4\text{AsBPh}_4$  and  $\text{Ph}_4\text{PBPh}_4$ <sup>65,67,68</sup> may have their origin in the weaker  $\text{Ph}_4\text{As}^+$ -water interactions. Furthermore,  $\text{Ph}_4\text{As}^+$  ions may prove to dimerize less readily than  $\text{Ph}_4\text{P}^+$  ions.

The importance of the structure of the solvent when aggregation of ions of like charge is considered is further substantiated by the results of the conductivity studies in methanol. Although a linear  $\Lambda-c^{1/2}$  plot may not be an absolute criterion for the complete absence of this type of aggregation,<sup>48</sup> there is no evidence of any kind that  $[(\text{tol}_3\text{P})_2\text{N}]^+$  ions form aggregates in this solvent. This observation seems to confirm the conclusion by Abraham *et al.*<sup>69</sup> that "solvophobic solvation" in methanol is much

smaller than the corresponding hydrophobic hydration in water.

### Conclusion

$[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  has been shown to associate extensively in dilute aqueous solution. The general association pattern and the forces involved are comparable for  $[(\text{tol}_3\text{P})_2\text{N}]\text{Cl}$  and  $[\text{PNP}]\text{Cl}$ . The effect of the methyl groups is essentially one of increasing the screening of the ionic charges and the hydrophobicity of the cation. This study seems to confirm that significant positive deviation from the Onsager slope in conductivity plots for dilute solutions is due to formation of dimers and small cation aggregates. The small or negligible counterion association allows the aggregates to be detected by conductivity measurements.

An examination of the reported data leads to the conclusion that larger aggregates must also exist. A multi-step equilibrium process, with some degree of cooperativity in an early stage of the growth, seems to be the best model for the observed association. In qualitative terms, the association pattern seems reminiscent of current descriptions of the self-association of bile salts.<sup>70,71</sup>

**Acknowledgement.** One of the authors (T.P.) is indebted to the Norwegian Research Council for Science and the Humanities, NAVF, for financial support. The authors are grateful to Dr. H. Høiland and Drs. M. and J. Perié for valuable comments.

### References

- Davies, C. W. *Ion Association*, Butterworths, London 1962.
- Bjerrum, N. K. *Danske Vidensk. Selsk. Mat. Fys. Medd.* 7 (1926) No. 9.
- Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Butterworths, London 1959, Chap. 14.
- Gestblom, B. and Songstad, J. *Acta Chem. Scand., Ser. B.* 41 (1987) 396.
- Sigvartsen, T., Gestblom, B., Noreland, E. and Songstad, J. *Acta Chem. Scand.* 43 (1989) 103.
- Fuoss, R. M. and Accascina, F. *Electrolytic Conductance*, Interscience Publishers, New York 1959, Chap. 18.
- Cavell, E. A. S. and Knight, P. C. *Z. Phys. Chem. (Neue Folge)* 57 (1968) 331.
- Lange, J. and Herre, E. *Z. Phys. Chem. A* 181 (1938) 329.
- Moseley, P. G. N. and Spiro, M. *J. Solution Chem.* 1(1972) 39.
- Pettitt, B. M. and Rosky, P. J. *J. Chem. Phys.* 84 (1986) 5836.
- Hirata, F. and Levy, R. M. *J. Phys. Chem.* 91 (1987) 4788.
- Hemmes, P. *J. Am. Chem. Soc.* 94 (1972) 75.
- Wennerstrøm, H. and Lindman, B. *Phys. Rep.* 52 (1979) 1.
- Wen, W.-Y. and Saito, S. *J. Phys. Chem.* 68 (1964) 2639.
- Wen, W.-Y. *J. Solution Chem.* 2 (1973) 253.
- Wakabayashi, T. and Takaizumi, K. *Bull. Chem. Soc. Jpn.* 56 (1983) 1749.
- Takaizumi, K. and Wakabayashi, T. *Bull. Chem. Soc. Jpn.* 56 (1983) 1896.
- Wirth, H. E. *J. Phys. Chem.* 71 (1967) 2922.
- Broadwater, T. L. and Evans, D. F. *J. Phys. Chem.* 73 (1969) 164 and 3985.
- Svorstøl, T., Sigvartsen, T. and Songstad, J. *Acta Chem. Scand., Ser. B* 42 (1988) 133.
- Pallesen, T., Høiland, H. and Songstad, J. *Acta Chem. Scand., Ser. A* 35 (1981) 803.
- Mittal, K. L. and Lindman, B. *Surfactants in Solution*, Plenum, New York 1984, Vols. 1 and 2.
- Wyn-Jones, E. and Gormally, J. *Aggregation Processes in Solution*, Elsevier, Amsterdam 1983.
- Pallesen, T., Høiland, H. and Songstad, J. *Acta Chem. Scand., Ser. A* 34 (1980) 739.
- Pallesen, T., Høiland, H. and Songstad, J. *Acta Chem. Scand., Ser. A* 35 (1981) 599.
- Evans, D. F., DePalma, R., Nadas, J. and Thomas, J. *J. Solution Chem.* 1 (1972) 377.
- Philip, P. R. and Desnoyers, J. E. *J. Solution Chem.* 1 (1972) 353.
- Cox, B. G. and Waghorne, W. E. *Chem. Rev. Chem. Soc.* 9 (1980) 381.
- Ruff, J. K. and Schlients, W. *J. Inorg. Synth.* 15 (1974) 84.
- Maartmann-Moe, K. *To be published.*
- Maartmann-Moe, K. and Songstad, J. *Acta Chem. Scand., Ser. A* 36 (1982) 829.
- Hardy, L. B., Ruff, J. K. and Dahl, I. F. *J. Am. Chem. Soc.* 92 (1970) 7327.
- Küppers, H., Kaltz, W. and Holmberg, H. *Acta Crystallogr., Sect. C* 41 (1985) 1420.
- Martinsen, A. and Songstad, J. *Acta Chem. Scand., Ser. A* 31 (1977) 645.
- Austad, T., Songstad, J. and Åse, K. *Acta Chem. Scand.* 25 (1971) 331.
- Ives, D. J. G. and Janz, G. J. *Reference Electrodes*, Academic Press, New York 1961, p. 108.
- Høiland, H. *J. Chem. Soc., Faraday Trans 1*, 70 (1974) 1180.
- Chen, C. T., Fine, R. A. and Millero, F. J. *J. Chem. Phys.* 66 (1977) 2142.
- Harned, H. and Owen, B. B. *The Physical Chemistry of Electrolyte Solutions*, Reinhold, New York 1964.
- Mukerjee, P., Mysels, K. J. and Dulin, C. I. *J. Phys. Chem.* 62 (1958) 1390.
- Fuoss, R. M. and Onsager, L. *J. Phys. Chem.* 61 (1957) 668.
- Isaacs, N. *Liquid Phase High Pressure Chemistry*, Wiley, New York 1981, Chaps. 2 and 4.
- McDowell, M. C. and Kraus, C. A. *J. Am. Chem. Soc.* 73 (1951) 2173.
- Evans, H. C. *J. Chem. Soc.* (1956) 579.
- Norman, A. *Acta Chem. Scand.* 14 (1960) 1300.
- Sesta, B., La Mesa, C., Bonincontro, A., Carnetti, C. and Di Biaso, A. *Ber. Bunsenges. Phys. Chem.* 85 (1981) 798.
- Kalfoglou, G. and Bowen, L. H. *J. Phys. Chem.* 73 (1969) 2728.
- Perié, M., Perié, J. and Chemla, M. *J. Solution Chem.* 17 (1988) 203.
- Popov, A. I. and Humphrey, R. E. *J. Am. Chem. Soc.* 81 (1959) 2043.
- Schiaco, S. and Marrosu, G. *Z. Phys. Chem. (Neue Folge)* 105 (1977) 157.
- Marcus, Y. *Pure Appl. Chem.* 55 (1983) 977.
- Kreshech, G. C., Schneider, H. and Scheraga, H. A. *J. Phys. Chem.* 69 (1965) 3132.
- Tsjentovskij, V. M., Barabanov, V. P., Tsjentovskaja, V. S. and Katstjirskaja, L. I. *Zh. Obschch. Khim.* 46 (1975) 1507.
- Danielsson, I. and Stenius, P. *J. Colloid Interface Sci.* 37 (1971) 264.
- Lindenbaum, S. and Boyd, G. E. *J. Phys. Chem.* 68 (1964) 911.
- Friedman, H. and Krishnan, C. V. *Thermodynamics of Ion Hydration*. In: Franks, F., Ed., *Water: A Comprehensive Treatise*, Plenum, New York 1973, Vol. 3, Chap. 1.
- Wolynes, P. G. *J. Chem. Phys.* 68 (1978) 473.
- Desnoyers, J. E., Arel, M., Perron, G. and Jolicoeur, C. *J. Phys. Chem.* 73 (1969) 3346.

59. Diamond, R. M. *J. Phys. Chem.* 67 (1963) 2513.
60. Ben Naim, A. In: *Hydrophobic Interactions*, Plenum, New York 1980, Chaps. 5-7.
61. Gim, S. O. and McFarlane, W. *Can. J. Chem.* 46 (1968) 2071.
62. Swartz, W. E., Ruff, J. K. and Hercules, D. M. *J. Am. Chem. Soc.* 94 (1972) 5227.
63. Evans, D. F. and Ninham, B. W. *J. Phys. Chem.* 90 (1986) 226.
64. Lindman, B., Forsén, S. and Forslind, E. *J. Phys. Chem.* 72 (1968) 2805.
65. Marcus, Y. *J. Chem. Soc., Faraday Trans. 1*, 83 (1987) 2985.
66. Coetzee, J. F. and Sharpe, W. R. *J. Phys. Chem.* 75 (1971) 3141.
67. French, R. N. and Criss, C. M. *J. Solution Chem.* 11 (1982) 625.
68. Abraham, M. H. and Marcus, Y. *J. Chem. Soc., Faraday Trans. 1*, 82 (1986) 3255.
69. Abraham, M. H., Marcus, Y. and Lawrence, K. G. *J. Chem. Soc., Faraday Trans. 1*, 84 (1988) 175.
70. Mazer, N. A., Carey, M. C., Kwasnick, R. F. and Benedek, G. B. *Biochemistry* 18 (1979) 3064.
71. Mukerjee, P., Moroi, Y., Murata, M. and Yang, A. Y. S. *Hepatology* 4 (1984) 618.

Received December 23, 1988.