

The Solution Properties of Bis(triphenylphosphine)iminium Salts. II. Partial Molal Volume and Compressibility Studies

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The partial molal volume and isentropic partial molal compressibility of bis(triphenylphosphine)iminium chloride, [PNP]Cl, in water have been measured at 25 and 45 °C. The data support the previous conclusion from conductance and surface tension measurements that the positively charged [PNP]⁺-ions aggregate in water at a critical concentration in a manner reminiscent of micelle formation. The aggregation number, however, appears to be small; ~6, and the fraction of associated counterions derived from EMF measurements is also much smaller than for ordinary micelles, in accordance with what one would expect from the presumably low surface charge density of [PNP]-aggregates. The possibility of stacking as an alternative explanation is briefly discussed.

Partial molal volumes of [PNP]Cl, [PNP]Br and [PNP]I in methanol have also been determined and the infinite dilution values are discussed and compared with the data obtained in aqueous solution.

Recently, the results from a study on the molar conductivity and the surface tension of aqueous solutions of bis(triphenylphosphine)iminium chloride, [(Ph₃P)₂N]Cl, abbreviated [PNP]Cl, were reported.¹ In this study, in which the interest was focused primarily on dilute solutions, it was found that both these quantities showed an irregularity. When plotted against concentration both the conductance and the surface pressure slopes displayed a discontinuity at approximately 5.0×10^{-3} M at 25.0 °C. The evidence pointed towards an aggregation of [PNP]-cations in aqueous solution resembling micelle formation. In methanol, on the other hand, [PNP]Cl and also other [PNP]-salts showed

no irregular behaviour and acted as well-dissociated electrolytes over a considerable concentration range.¹

The exceptional behaviour of [PNP]Cl in water seemed to merit further investigations. The partial molal volumes and compressibilities of solutes at infinite dilution have proved useful for discussing and interpreting ion-solvent interactions. Furthermore, the concentration dependence of these two quantities have led to valuable information with regard to solute–solute interactions; for leading references, Refs. 2–4. In the present paper we will therefore present the results from a study on the partial molal volumes and compressibilities of [PNP]Cl in water at 25.0 and 45.0 °C. Since most thermodynamic quantities show a discontinuity at a critical micelle concentration⁵ a comparison between the thermodynamics of the [PNP]-aggregation with other forms of aggregation, primarily micelle formation, was desirable. The partial molal volume and compressibility generally increase upon micelle formation which is largely a reflection of the liquid hydrocarbonlike core of the micelles.^{6–11} Owing to the considerable difference between the behaviour of [PNP]-salts in water and methanol,¹ partial molal volume data of several [PNP]-halides in methanol were also determined.

EMF measurements with ion exchange membranes have also indicated a discontinuity at the critical micelle concentration, c.m.c., and the results of this type of experiments have also been used for the calculation of the fraction of associated counterions in micelles.¹² A slightly modified version of this EMF method was used in the present study to estimate the fraction of associated chloride ions in any such [PNP]-aggregates.

EXPERIMENTAL

[PNP]Cl, [PNP]Br and [PNP]I were synthesized and purified as previously described.^{1,13,14}

Water was distilled once in an FI-STREAM distillation apparatus. Methanol, *p.a.*, Merck, was purified according to Hartley and Raikes.¹⁵ The density was 0.78637 g cm⁻³ at 25.0 °C.

Apparent molal volumes were determined from density measurements with a Paar density meter, models DMA O2C or DMA 601, and calculated according to eqn. (1), where d_o and d are densities

$$V_\phi = \frac{(d_o - d)}{mdd_o} + \frac{M}{d} \quad (1)$$

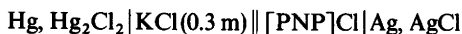
of solvent and solution, respectively, m the molality of the solution and M the molecular weight of the solute. The molal volumes were determined with an accuracy ranging from ± 1 cm³ mol⁻¹ for the lowest concentrations to ± 0.5 cm³ mol⁻¹ for the highest concentrations.

Isentropic apparent molal compressibilities were determined from speed of sound data as previously described¹⁶ and were calculated by eqn. (2), where

$$K_{\phi,s} = \frac{(\beta_s - \beta_{s,o})}{md_o} + \beta_s V_\phi \quad (2)$$

$\beta_{s,o}$ and β_s are the isentropic compressibilities of solvent and solution, respectively, as calculated from the speed of sound, $\beta_s = 1/u^2d$. Owing to the limited solubility of [PNP]Cl in water, 1.3×10^{-2} M,¹ $K_{\phi,s}$ could only be determined with an accuracy ranging from $\pm 3 \times 10^{-4}$ cm³ mol⁻¹ bar⁻¹ at the highest concentrations to $\pm 10 \times 10^{-4}$ cm³ mol⁻¹ bar⁻¹ at the lowest.

The following cell was used for the EMF measurements:



Usually the calomel electrode utilizes a saturated KCl solution as the reference electrolyte. However, the low solubility of [PNP]Cl in water prevented the use of such a saturated KCl solution since crystals of [PNP]Cl were rapidly formed at the tip of the calomel electrode. The calomel electrode was therefore filled with a 0.3 M KCl solution and the electrode was soaked in the same solution for several weeks before stable readings of the EMF could be obtained. The uncertainty in each EMF value was estimated to ± 0.3 mV.

RESULTS AND DISCUSSION

In Fig. 1 the apparent molal volume of [PNP]Cl in water has been plotted *versus* $c^{1/2}$. At 25.0 °C the slope of this plot is zero over the entire concentration range. At 45.0 °C the slope is still zero at low concentration. However, a distinct break in the slope is apparent at 0.0075 M.

It has become customary to extrapolate apparent molal volumes to infinite dilution by the Redlich equation,¹⁷ eqn. (3). S_v is the theoretical slope

$$V_\phi = V_\phi^\circ + S_v c^{1/2} + b_v c \quad (3)$$

calculated from the Debye-Hückel limiting law and b_v is a measure of the deviation from the limiting law.^{17,18} Eqn. (3) may be rearranged to eqn. (4) by

$$V_\phi - S_v c^{1/2} = V_\phi^\circ + b_v c \quad (4)$$

which b_v can be determined from a plot of $V_\phi - S_v c^{1/2}$ *versus* c . From a least squares analysis of the data b_v was calculated to (0 ± 10) cm³ mol⁻¹. The large error in b_v is simply a result of the very narrow concentration range that was available for apparent molal volume determinations in combination with the experimental error in each single measurement. The solubility of [PNP]Cl sets an upper limit. As the concentration decreases the difference $(d_o - d)$ in eqn. (1) becomes less and less accurate, in effect setting a lower limit. A discussion of solute-solute interactions based on b_v is thus of no value in this case.

The relation between partial and apparent molal volume is given by eqn. (5). Desnoyers and co-

$$V_2 = V_\phi + \frac{1}{2} m^{1/2} \left(\frac{\partial V_\phi}{\partial m^{1/2}} \right) \quad (5)$$

workers^{9,19} have shown that if the experimental points are sufficiently close, the partial molal volume can also be calculated as $\Delta(mV_\phi)/\Delta m$. At 25.0 °C the partial and apparent molal volumes are equal. At 45.0 °C they are equal at low concentrations. Above 0.0075 M the partial molal volume has been calculated from eqn. (5) and the result is plotted in Fig. 1.

The apparent molal volumes of [PNP]Cl, [PNP]Br and [PNP]I in methanol have been plotted *versus* $c^{1/2}$ and also according to eqn. (3) in Fig. 2. The plots are linear over the entire concentration range which is ~ 50 times as large as in

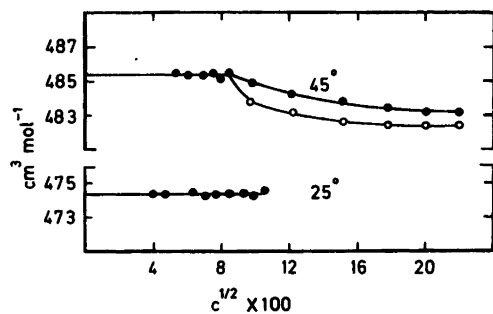


Fig. 1. Apparent molal volumes (●) and partial molal volumes (○) of [PNP]Cl in water versus $c^{1/2}$ (mol dm^{-3})^{1/2}.

water due to the increased solubility of the [PNP]-halides in methanol. The deviation constants are -1.5 ± 1 , -6.8 ± 1 and $-0.4 \pm 1 \text{ cm}^3 \text{ mol}^{-2}$, respectively.

The partial molal volumes at infinite dilution in water and methanol are presented in Table 1. The results can be separated into contributions for the cation and anion by data from ultrasonic vibration potentials.^{20,21} The partial molal volume of the [PNP]-cation in methanol can thus be determined from each of the three halides. The results agree excellently.

The partial molal volume of an ion at infinite dilution can be attributed to the components^{22,23} in eqn. (6), where $V^\circ(\text{int})$ is the intrinsic volume,

$$V^\circ(\text{ion}) = V^\circ(\text{int}) + V^\circ(\text{elect}) + V^\circ(\text{void}) + V^\circ(\text{caged}) \quad (6)$$

$V^\circ(\text{elect})$ the electrostriction partial molal volume, $V^\circ(\text{void})$ is the contribution due to void space effects, and $V^\circ(\text{caged})$ is the contribution to the partial molal volume due to formation of structured water (hydrophobic hydration).

With regard to the structure of the [PNP]-cation in solution it is presently not known whether the

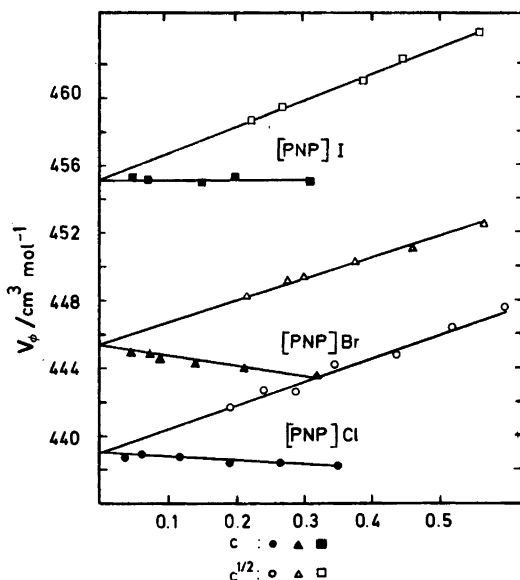


Fig. 2. Apparent molal volumes of [PNP]-halides in methanol. Closed symbols represent plots of $V_{\phi} - S_v c^{1/2}$ versus c (mol dm^{-3}), eqn. (4). Open symbols represent plots of V_{ϕ} versus $c^{1/2}$ (mol dm^{-3})^{1/2}.

bent or the linear form is the favoured one. Both forms are known to exist in the solid state.²⁴ From various crystallographic data²⁴⁻²⁶ one may calculate $V^\circ(\text{int})$ to be $\sim 1200 \text{ cm}^3 \text{ mol}^{-1}$ regardless whether a cylindrical or a spherical model is employed. Since this number is about 2.5 times the measured partial molal volume, at least one of the other terms in eqn. (6) must be large and negative. However, by defining the intrinsic volume in this way we have included at least part of the void volume. If water molecules can enter the empty space between all the phenyl groups or between the two sets of phenyl groups, $V^\circ(\text{void})$ will become negative. Tominaga²⁷ has studied the Ph_4P^+ -cation in water and observed similar effects. It was

Table 1. Partial molal volumes ($\text{cm}^3 \text{ mol}^{-1}$) and isentropic partial molal compressibilities ($\text{cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$) at infinite dilution in water and methanol.

	$t/^\circ\text{C}$	Water V_2°	$V_2^\circ[\text{PNP}]^+$	K_2°	Methanol V_2°	$V_2^\circ[\text{PNP}]^+$
[PNP]Cl	25.0	474.4	450.5	-42×10^{-4}	438.9	425.9
[PNP]Cl	45.0	485.4		65×10^{-4}		
[PNP]Br					445.3	427.0
[PNP]I					455.1	426.9

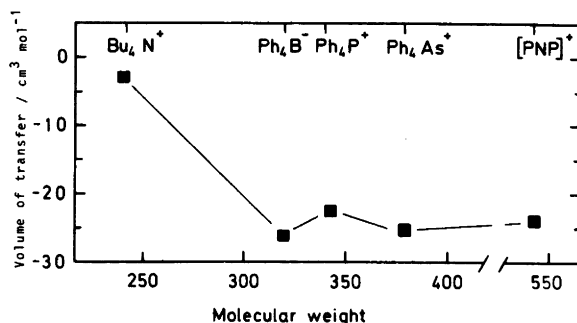


Fig. 3. Volume of transfer from water to methanol versus molecular weight of [PNP]⁺ and other large organo ions (Ref. 30).

concluded that if water could enter the empty space between the phenyl groups, it entered as monomeric water molecules.

The remaining two terms of eqn. (6) are small as seen from the following argument: The contribution of the electrostriction term can be estimated from the Drude-Nernst equation.^{28,29} It shows that the electrostriction volume amounts to about $-1 \text{ cm}^3 \text{ mol}^{-1}$ in water and about $-3.5 \text{ cm}^3 \text{ mol}^{-1}$ in methanol. It is more difficult to make a quantitative estimate of the caged term. However, on the basis of partial molal volumes of the Ph₄P⁺- and Ph₄As⁺-ions it was concluded that the phenyl groups of these cations do not stabilize the water structure as do various solutes containing alkyl chains.^{27,30,31} The similarity between these two cations and [PNP]⁺ suggests that $V^\circ(\text{caged})$ is small for the [PNP]-cation as well.

For a number of ordinary inorganic ions it has been shown that the partial molal volume of transfer from water to methanol is $-11 \pm 3 \text{ cm}^3 \text{ mol}^{-1}$ at 25 °C.²² In Fig. 3 we have extended the plot of Jolicœur *et al.*³⁰ to include the [PNP]⁺-cation. The volume of transfer from water to methanol is significantly higher than $-11 \text{ cm}^3 \text{ mol}^{-1}$ for *n*-Bu₄N⁺ while it is consistently lower for salts of phenyl substituted ions. Since the electrostriction volume of transfer appears to be small, it seems that the large negative volume of transfer for the [PNP]-cation and the other ions containing phenyl groups must again be due to the $V^\circ(\text{void})$ term. It appears reasonable to expect that the methanol molecules can penetrate the void between the phenyl groups more efficiently than water making $V^\circ(\text{void})$ even more negative in methanol than in water.

The apparent molal compressibilities, K_ϕ , were calculated according to eqn. (8). This equation,

$$K_\phi = K_\phi^\circ + S_K c^{1/2} + b_K c \quad (8)$$

however, cannot be applied as readily as the corresponding Redlich equation for apparent molal

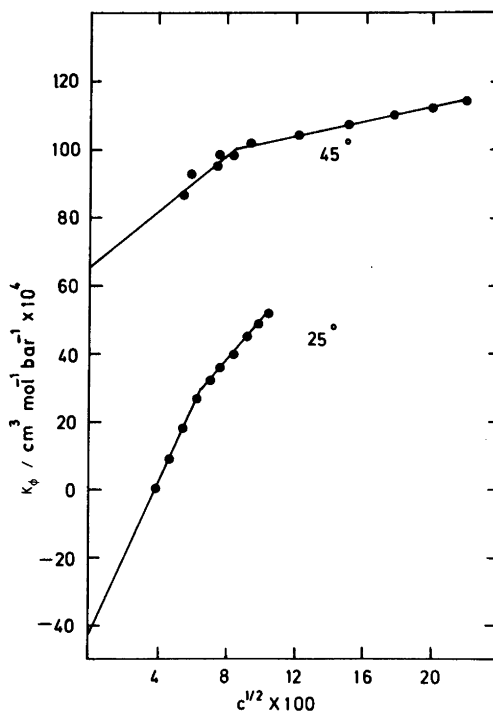


Fig. 4. Isentropic apparent molal compressibilities of [PNP]Cl in water versus $c^{1/2}$ (mol dm^{-3})^{1/2}.

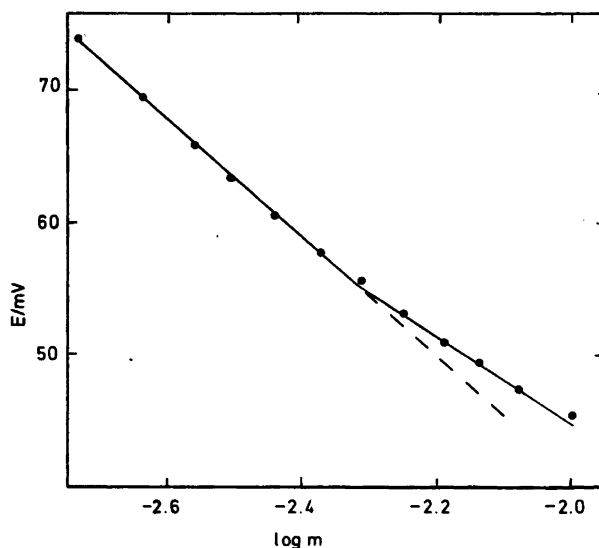


Fig. 5. Typical plot of E versus the logarithm of the molality for [PNP]Cl in water measured by the Ag/AgCl-calomel electrode system.

volumes, eqn. (3), due to the lack of data for S_K . As shown in Fig. 4 the slopes of K_ϕ versus $c^{1/2}$ are steep and much steeper than for ordinary surfactants.¹⁰ The conclusion from this observation must be that pronounced solute-solute interactions occur, even below the critical concentration.

For the determination of the isentropic apparent molal compressibilities of [PNP]Cl in water at infinite dilution only data below the critical concentration could be used. The extrapolated values are presented in Table 1 together with the partial molal data. The calculation of $K_{\phi,s}$ values according to eqn. (2) requires, however, an accurate value of the difference $\beta_s - \beta_{s,0}$. In dilute solutions this difference becomes too small for a sufficiently accurate determination with our equipment which further limits the concentration range available for extrapolating $K_{\phi,s}$ of [PNP]Cl to infinite dilution. The limited concentration range coupled with the steep slopes, *cf.* Fig. 4, makes the infinite dilution values exceptionally inaccurate. The error is probably of the order of $10 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$. The results thus merit no discussion.

In Fig. 5 is shown a typical plot of the dependence of the experimentally determined EMF and the logarithm of the concentration of [PNP]Cl in water at 25.0 °C. Once more a distinct discontinuity at $\sim 0.005 \text{ M}$ is observed which is reminiscent of the formation of aggregates of the micellar type.³²

The fraction of counter ions associated to micelles can be calculated from EMF measurements by using the formalism of the phase separation model.³² This model works well for micellar systems but may be doubtful for the [PNP]-aggregates. However, if we use this model, the EMF measurements give the fraction of chloride ions, β , associated to the positive [PNP]-aggregates as 0.24 ± 0.02 . This is a very low value compared to ordinary micellar systems in which β -values in the range 0.6–0.9 have been observed.^{12,33}

Conclusive remarks. All experiments carried out so far on the [PNP]-system in aqueous solution

Table 2. Critical concentrations for aggregation of [PNP]Cl in water.

$t/^\circ\text{C}$	Method of measurement	Critical conc. mol dm^{-3}
25.0	Conductance ^a	0.0052(2)
25.0	Compressibility ^b	0.0052(2)
25.0	Surface tension ^a	0.0049(4)
25.0	Density ^b	No indication
25.0	EMF ^b	0.0050(3)
45.0	Conductance ^a	0.0073(2)
45.0	Compressibility ^b	0.0074(4)
45.0	Density ^a	0.0073(3)

^aRef. 1. ^bThis study.

have shown that when a measured quantity is plotted *versus* concentration, a discontinuity is observed at a critical concentration. The change in slope occurs at the same concentration irrespective of the method used. The only exception appears to be the density at 25.0 °C, *cf.* the partial molal data shown in Fig. 1 (lower curve). The critical concentrations at 25.0 and 45.0 °C determined by the various methods are summarized in Table 2. The phenomenon resembles micelle formation of the following reasons: (a) a critical concentration is observed, (b) the conductance decreases markedly above the critical concentration,¹ (c) the surface tension decreases below the critical concentration and is practically constant above.¹ These features are distinctly different from the usual observations when ordinary (+ -) ion pairs are formed. The most reasonable conclusion thus seems to be that [PNP]-cations aggregate in a micelle-like fashion.

However, ordinary micelle formation is generally accompanied by an increase in both partial molal volume and compressibility.⁶⁻¹¹ In the case of [PNP]-aggregation the volume change is apparently zero at 25 °C and $-3.0 \text{ cm}^3 \text{ mol}^{-1}$ at 45 °C. As can be seen from Fig. 4 the isentropic partial molal compressibility also decreases after aggregation. The positive ΔV of ordinary micelle formation is largely due to the interior of the micelle where the hydrocarbon tails are in a state very similar to pure liquid hydrocarbons. Any parallel, for example a core of phenyl groups of the [PNP]-cation in a liquid benzene-like state, seems improbable.

In any case the small ΔV values of [PNP]-aggregation indicate small aggregates. In the case of micelles the aggregation number can be estimated by an equation derived by Evans,³⁴ based on the phase separation model. It requires knowledge of β and the slopes of the conductance *versus* concentration above and below the critical concentration. This equation can be used for [PNP]Cl based on the β -value reported above and conductance data previously reported.¹ The result is an aggregation number of 6. This is at best a very crude estimate, but all the data seem to point in the same direction: [PNP]⁺ ions aggregate at a critical concentration in small aggregates with a low surface charge density and low chloride ion association.

The pertinent question to be asked is what type of aggregate is formed from [PNP]Cl in aqueous solution for concentrations exceeding the apparent critical concentration. Although, as we have shown, some thermodynamic properties of the aggregation

process change as for micelle formation, the structure of the [PNP]⁺-ion is hardly comparable with that of an amphiphile of the type that is normally associated with micelle formation. The negative volume change and the low β -value also point against typical micelles. However, one must still conclude that interactions between phenyl groups are the most likely cause for aggregation. Coupled with a negative ΔV this suggests some sort of stacking which appears to be a characteristic feature of this type of interaction.^{35,36} No detailed studies in methanol and other organic solvents have so far been performed, but there appears to be no evidence for any exceptional behaviour of [PNP]-salts in nonaqueous solvents. Stacking seems to exist uniquely in water.³⁷ The diffuse charge on the [PNP]-cation and thus its relatively high polarizability combined with a dipole structure arising from the positive and negative charge on the two phosphorus atoms and the nitrogen atom, respectively, may be the cause for the distinct difference in the solution chemistry of [PNP]-salts compared to Ph_4P^+ - and Ph_4As^+ -salts.

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