The Solution Properties of Bis(triphenylphosphine)iminium Salts. III. Osmotic and Activity Coefficients of [PNP]-salts in Aqueous Solution

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The osmotic coefficients of bis(triphenylphosphine)-iminium chloride, [PNP]Cl, at 45 °C, and of [PNP]Cl and [PNP]$_2$SO$_4$ at 60 °C have been measured by vapor pressure osmometry. The mean ionic activity coefficients have been calculated. The concentration dependence of the molar conductivity of [PNP]Cl and [PNP]$_2$SO$_4$ at 60 °C up to about 0.1 M is also reported.

The [PNP]-salts exhibit very low osmotic and activity coefficients. The major cause for this observation seems to be self-association of the [PNP]-cations. The association pattern, the influence of counter ion and the temperature effect are discussed and compared with main classes of associating surfactants. The data suggest that the [PNP]-cations associate to form dimers at very low concentrations. [PNP]$_2$SO$_4$ seems to exhibit a continuous association, while in the case of [PNP]Cl a critical concentration is observed.

In previous papers in this series,[1,2] we have presented studies on the thermodynamic properties of bis(triphenylphosphine)iminium chloride, abbreviated [PNP]Cl, in methanol and in water. The [PNP]-halides behave as well dissociated electrolytes in methanol. In water, on the other hand, the behaviour of [PNP]Cl can best be explained by self-association of the [PNP]-cations. In several respects this association phenomenon resembles micelle formation showing a critical concentration at 0.005 M at 25 °C. However, in other respects and from a structural point of view, stacking appears to be a more likely explanation for this process.[2]

Self-association of hydrophobic solutes in aqueous solution, primarily the micelle formation of soaps and detergents, has been studied extensively in recent years.[3] Many hydrophobic drugs, dyes, physiological surfactants such as bile salts, purines, pyrimidines and hydrophobic proteins are also known to self-associate. Mukerjee[4] has classified these associating solutes into four main classes according to their structures:

I. The flexible chain compounds containing polar head groups joined together with the nonpolar chains, e.g., soaps and detergents. This class of compounds generally forms large micelles, mainly due to the flexible chains.

II. Aromatic or heteroaromatic ring or fused ring structures which are rigid, i.e., purines, pyrimidines and a number of dyes and drugs. An important feature characterizing these compounds is that they are roughly symmetrical with respect to their hydrophobicity on both sides of their flat or nearly flat structures. These molecules are thus capable of a "stacking"-type of association in which each associating monomer can lie flat on top of the other. There are thus no geometrical restrictions to open-ended continuous self-association.

III. Alicyclic fused ring systems which may be inflexible but are not planar. Bile salts, cholesterol and similar compounds fall into this category. Like the aggregates formed by some class II-compounds,[5,6] the aggregates of class III-compounds are often termed micelles.[7] The typical size of these aggregates are 2–9 monomers.[7]

IV. This class consists of macromolecular solutes such as proteins and enzymes. This form of association can be treated as stepwise self-association partly due to hydrophobic interactions between exposed side chains.

The [PNP]-cation does not seem to fit any of these classes. The cation is inflexible but rather bulky and contains no aliphatic groups, neither chains nor rings. As an apparent intermediate, a further investigation of the self-association of the [PNP]-cations might lead to a better understanding of the various interactions responsible for association.[3,4,8-13]

In this paper we report the molal osmotic coefficients and the activity coefficients of [PNP]Cl and of [PNP]$_2$SO$_4$. The measurements have been performed at 45 °C and at 60 °C by which the solubilities are greatly enhanced.[14] Conductivity measurements have also been performed at 60 °C to aid the interpretation of the data.

EXPERIMENTAL

Materials. [PNP]Cl was prepared and purified as previously described.[1] [PNP]$_2$SO$_4$ was obtained in a manner similar to other [PNP]-salts.[15] In order to obtain the salt free from acidic impurities all the organic solvents used were distilled from magnesium or calcium hydride and the first precipitation and crystallization from water were carried out in weakly alkaline solutions. The salt was finally crystallized twice from an acetonitrile-diethyl ether mixture and dried in the same way as the chloride prior to use. Unlike most other [PNP]-salts,[15,16] [PNP]$_2$SO$_4$ was found to be hygroscopic; a weight increase of ~ 8 % was observed in moist air at room temperature. This amounts to ~ 5 mol of water. The salt was therefore carefully shielded from atmospheric moisture and the solutions were prepared in a dry box in a nitrogen atmosphere.

Potassium and sodium chloride, both Baker *p.a.* were dried for 24 h at 200 °C at reduced pressure (0.1 mm Hg) prior to use.

Water was purified in an FI-STREEM distillation apparatus. Its conductivity was less than 1.5×10^{-6} S cm^{-1} at 60 °C.

Conductivity. The conductivity was measured with equipment previously described.[1] The temperature dependence of the cell constant, determined by calibrations at 25 °C according to semi-empirical equations of Fuoss *et al.*,[17,18] was found to be negligible. The temperature fluctuations were less than ±0.01 °C.

Vapor pressure measurements. Osmotic coefficients were measured at 45 and at 60 °C with a modified KNAUER Vapor Pressure Osmometer. The basis of this method has been outlined by Burge.[19] The measured resistance ΔR, the difference between the resistance of a thermistor holding a drop of the sample solution and that of a thermistor holding

a drop of pure solvent, is related to the molal osmotic coefficient ϕ by eqn. 1, where v is the

$$\Delta R = K \phi v m \qquad (1)$$

number of mol of ions per mol of the salt and m is the molality. The calibration constants K were determined by using osmotic coefficient data for NaCl.[20]

RESULTS

In Fig. 1 the molar conductivities of [PNP]Cl and of [PNP]$_2$SO$_4$ (Λ 1/2[PNP]$_2$SO$_4$) at 60 °C are plotted *versus* the square root of the molarity covering the concentration range from about 0.1 M to infinite dilution. The dotted lines indicate the respective Onsager slopes calculated according to Ref. 21 using literature values for the physical properties of water.[20] The Λ°-values, 165.5 and 176.4 S cm^2 mol^{-1} for the chloride and the sulfate respectively, were determined by the Shedlovsky method.[22]

The calculated osmotic coefficients have an estimated error of about 5 % for the lowest concentration decreasing to less than 2 % for concentrations greater than 0.1 molal. The upper limit for the concentration range studied was at 45 °C governed by the solubility, 9.75×10^{-2} m.[14] Difficulties during the transfer of concentrated solutions caused an upper limit of about 1.4 molal at 60 °C.

By a least squares technique the experimental osmotic coefficients were fitted to a power series of the form (2), where A, B, C, D and E are empirical

$$\phi = A + Bm^{1/2} + Cm + Dm^{3/2} + Em^2 \qquad (2)$$

constants. The data were weighted according to their errors. For [PNP]Cl at 45 °C the last term could be omitted. The experimental values are plotted *versus* $m^{1/2}$ in Fig. 2 and the fitted ϕ-values are tabulated in Table 1.

The osmotic coefficients are related to the mean ionic activity coefficient, $\gamma \pm$, through the Gibbs-Duhem equation in the form (3). For the calculation

$$d \ln \gamma \pm = d\phi + (\phi - 1) d \ln m \qquad (3)$$

of $\gamma \pm$, however, the functional relationship of ϕ or $(\phi - 1)/m$ versus m must be known toward infinite dilution. This is particularly difficult in the present case. Previous results obtained at other temperatures[1,2] and the conductivity curves shown in Fig. 1 make it unreasonable, especially for [PNP]Cl,
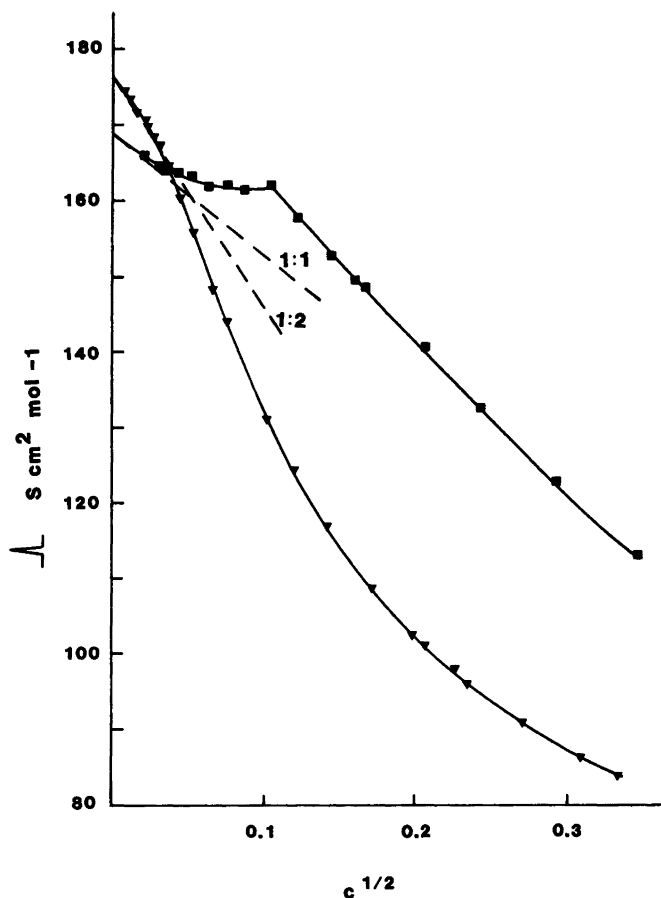
Fig. 1. The molar conductivity *versus* the square root of the molarity for [PNP]Cl (■) and for [PNP]$_2$SO$_4$ (▼) at 60 °C. The dotted lines indicate the respective Onsager-slopes.

to extrapolate according to eqn. 2 from the higher concentrations to infinite dilution. Since the A-values in eqn. 2 are 1.294 and 1.236 for [PNP]Cl at 45 and at 60 °C, respectively, and thus significantly different from unity, the extrapolation to infinite dilution will not be valid.

However, by splitting up the integration of eqn. 3, $\gamma \pm$ may be expressed by eqn. (4). In this equation

$$\ln \gamma \pm = \phi(0.01) - 1 +$$
$$\int_0^{0.01} \frac{\phi - 1}{m} \, dm + \int_{0.01}^m d\ln \gamma \pm \qquad (4)$$

the first integral can be solved graphically while the last one can be determined by direct integration using eqn. 2. The $\gamma \pm$-values calculated by this

method, *cf.* Table 1, may be subject to a small constant correction in $\ln \gamma \pm$ if precise data on highly dilute solutions can be aquired. However, this error in $\ln \gamma \pm$ is estimated to be less than ± 0.07.

DISCUSSION

As shown in Fig. 2, the osmotic coefficients, ϕ, of aqueous solutions of the [PNP]-salts are low even for highly dilute solutions and decrease rapidly as the concentration increases. For [PNP]$_2$SO$_4$ a minimum is observed at about 0.2 m, followed by a marked increase at higher concentrations. The $\gamma \pm$-values will show the same general trend, *cf.* Table 1, but the minimum will necessarily appear
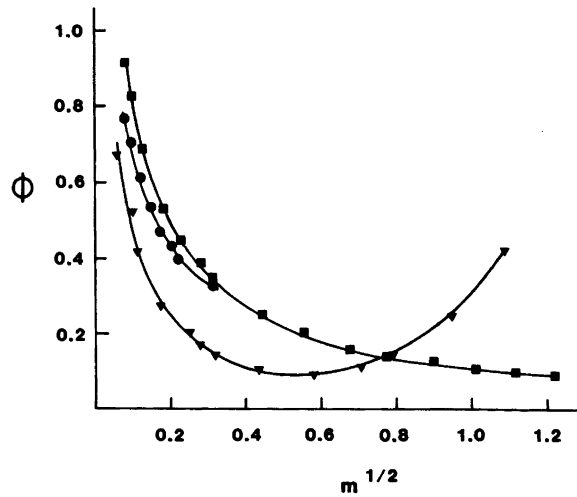
Fig. 2. Experimental osmotic coefficients ϕ plotted *versus* the square root of the molality: ■, [PNP]Cl at 60 °C; ●, [PNP]Cl at 45 °C; ▼, [PNP]$_2$SO$_4$ at 60 °C.

Table 1. Fitted osmotic coefficients ϕ and mean ionic activity coefficients $\gamma\pm$ for the [PNP]-salts.

| | [PNP]Cl | | | | [PNP]$_2$SO$_4$ | |
| | 45 °C | | 60 °C | | 60 °C | |
m	ϕ	$\gamma\pm$	ϕ	$\gamma\pm$	ϕ	$\gamma\pm$
0.01	0.692	0.572	0.801	0.671	0.491	0.257
0.02	0.551	0.382	0.668	0.489	0.375	0.155
0.03	0.474	0.290	0.582	0.386	0.304	0.110
0.04	0.427	0.236	0.519	0.318	0.255	0.0852
0.05	0.397	0.201	0.470	0.271	0.218	0.0693
0.06	0.376	0.176	0.431	0.236	0.191	0.0583
0.07	0.361	0.157	0.399	0.209	0.169	0.0503
0.08	0.350	0.143	0.372	0.187	0.152	0.0442
0.09	0.340	0.131	0.349	0.170	0.139	0.0394
0.10			0.330	0.155	0.128	0.0356
0.20			0.229	0.0848	0.091	0.0184
0.30			0.195	0.0595	0.097	0.0128
0.40			0.178	0.0463	0.109	0.0100
0.50			0.166	0.0380	0.123	0.0084
0.60			0.154	0.0323	0.139	0.0072
0.70			0.141	0.0279	0.160	0.0065
0.80			0.127	0.0245	0.189	0.0060
0.90			0.113	0.0218	0.230	0.0057
1.00			0.100	0.0196	0.286	0.0056
1.10			0.090	0.0178	0.360	0.0056
1.20			0.084	0.0163	0.455	0.0059
1.30			0.083	0.0152		

at a higher concentration due to the functional relationship between ϕ and $\gamma\pm$. This increase in free energy can probably be explained by the effect of hydration of the sulfate ion.[23,24]

Robinson and Stokes[20] have summarized the various causes for low activity coefficients: (i) Bjerrum ion-pair formation giving moderately low activity coefficients and (ii) complex ion formation giving very low activity coefficients. Compared with available data,[20] the activity coefficients of [PNP]Cl are seen to be extremely low. The $\gamma\pm$-value of a 1.3 m solution of the 1:1 electrolyte [PNP]Cl is 0.0152. This value is even lower than the corresponding activity coefficient of CdI_2; CdI_2 is referred to as an extreme example of complex ion formation.[20] For the 1:2 electrolyte $[PNP]_2SO_4$, a minimum value of 0.0056 is observed (Table 1).

However, the osmotic and the activity coefficients are a measure of association only to a first approximation. For large organo-ions, deviations from the Debye-Hückel theory in dilute solutions can be attributed to solvent effects as well as association. The positive deviations observed for tetraalkyl-ammonium salts have been explained in terms of their structure making ability.[25] For phenyl-substituted ions negative deviations have been reported.[23,26-28] Bonner et al. have found $\gamma\pm$ values in the order of 0.75 at 0.1 m in their studies on aromatic sulfonates.[26] This observation was later, supported by spectroscopic measurements, interpreted as a "structure breaking" effect of these salts.[27] Kalfoglou and Bowen[23] have taken this in support of their interpretation of the osmotic and activity coefficients of the group V tetraphenyl salts in aqueous solution attributing their low values to a structure breaking effect. However, the $\gamma\pm$-values reported for 0.1 m Ph_4AsCl and $(Ph_4As)_2SO_4$, 0.353 and 0.217, are much lower than for the aromatic sulfonates.[26] The possibility of ion association in these systems may be disregarded since the conductivity curves are linear up to 0.02 N. The possible explanation of the low limiting conductivity slope in terms of cation-cation dimerization has apparently not been considered.

The [PNP]-cation is also suggested to be a structure-breaker in aqueous solution due to its size and structure.[1] The pertinent question to ask is thus whether the low osmotic and activity coefficients of these salts can be partly explained in this way. The results reviewed above have all been determined at 25 °C. At higher temperatures these effects should be smaller due to the destructuring of water itself.

In Fig. 2, where the dependence of ϕ for [PNP]Cl at 45 and 60 °C is shown, we observe that the deviation for dilute solutions is most pronounced at 45 °C. This may in part be due to the lower critical concentration at 45 °C (0.0075 m) resulting in more extensive association at lower concentrations. However, as the activity at the critical concentration is clearly lower at 45 °C than at 60 °C, there are probably significant contributions from solvent effects.

Nevertheless, in the case of the [PNP]-salts, the major effect on the activity must be attributed to association. The steep fall in the osmotic coefficient and the following leveling-off show that added salt participates in the aggregation. The general feature is thus similar to well-known associating systems as typical stacking systems,[29,31] bile salts[10] or typical micellar systems.[32,33] In magnitude, however, only long chain surfactant systems with c.m.c.-values in the 10^{-3} m range exhibit $\gamma\pm$ values equally low.[33]

The association pattern in dilute solutions cannot be satisfactorily judged from the osmotic coefficient measurements as the method is restricted to concentrations above ~ 0.01 molal. For [PNP]Cl, however, they seem to support the conclusion drawn from other methods[1,2] that there is an abrupt change in solution properties at some concentration below 0.01 m. This change is most distinct in the conductivity curve for the chloride, Fig. 1. The positive deviation for concentrations below 0.01 M resulting in a weak local maximum at about 0.01 M may be interpreted as a preassociation, most probably a dimerization.[34] This effect may be understood by considering Stoke's law, eqn. 5, where λ is the molar

$$\lambda = 0.802 \, z/\eta r_s \tag{5}$$

ionic conductivity, η is the viscosity of the solution and z is the charge of the species. As the effective radius r_s of a dimer will be considerably less than twice that of a monomer, the molar conductivity will increase. Thus, higher order self-association with a very low degree of counter ion association could cause absolute maxima to appear in the conductivity curves.[35,36] The generally observed drop in conductivity with micelle formation thus reflects the magnitude of the counter ion binding, cf. Ref. 37. In the present case, the conclusion that pre-aggregation takes place is also supported by the results from the compressibility study.[2]

When altering the counter ion from a univalent to a divalent one, the c.m.c. is reduced for typical micellar systems.[38] The effect of the charge of the

counter ion on the c.m.c. has been found to be mainly of electrostatic origin; specific binding is of secondary importance.[39] For [PNP]$_2$SO$_4$, however, the conductivity curve can hardly be interpreted as showing a critical concentration at all. The negative deviation in the conductivity curve even for concentrations of about 3×10^{-4} M, cf. Fig. 1, and the steep lowering of the osmotic coefficients, cf. Fig. 2, suggest a continuous association. This might indicate that the association pattern of [PNP]-salts is not governed by charge effects but by specific interactions. Unfortunately, the low solubility of other [PNP]-salts[1] and the difficulty in obtaining [PNP]F in a pure state make this suggestion hard to verify.

It still seems difficult to classify the [PNP]-association phenomenon. Proper micelle formation, using this term in a restricted sense, is characterized by a marked cooperativity which has the consequence that a reasonably well-defined c.m.c. is displayed.[3,40] [PNP]Cl does show a method independent critical concentration. However, according to Mukerjee,[4] "if the degree of association close to the c.m.c. is low, less then 20 monomers, and if there is evidence for association well below the apparent c.m.c., care should be taken". The association of [PNP]Cl is certainly such a case.

Osmotic coefficient data have been used in the case of stacking systems to test out continuous and non-continuous stepwise association models.[29] These one- or few-parameter models cannot easily take into account the extent of counter ion binding in the aggregates which is necessary in the case of the [PNP]-salts. It is thus most difficult to obtain a reliable estimate of the aggregation number from the present data. We have previously, with reservation, used the micellar hypothesis to calculate an aggregation number of 6 for [PNP]Cl from conductivity and electromotive force data.[2] This estimate, however, may be seriously wrong if the applied model does not fit.[4]

While the very low activity coefficients suggest an extreme degree of association, the drop in conductivity is not very pronounced. The molar conductivity of the [PNP]-salt solution is certainly lower than corresponding values for simple salts,[41] but far greater than for typical micellar systems.[39,42] It seems probable that the high conductivity is reflecting moderate counter ion association and thus a relatively high concentration of the free counter ions.

As mentioned above, the measurements in this study have been performed at elevated temperatures to get available a larger concentration range while anticipating that the nature of the association phenomena remains unchanged. However, the temperature increase will generally reduce the magnitude of the association. This phenomenon has been observed for the stacking of purines,[8,43] for the association of bile salts[10,37,44] and for ionic surfactant micelles.[45,46] The increase in the apparent critical concentration with increasing temperature as observed for [PNP]Cl also indicates a destabilization of the aggregates. However, the drop in conductivity for this system is much more pronounced at 60 °C than at 25 and 45 °C. This observation may be explained by an increase in counter ion association due to dehydration of the Cl$^-$-ions.[43] An increase in temperature will reduce the dielectric constant of water[20] and will thus favour attraction between oppositely charged species. In the case of association of bile salts and of ionic surfactant micelles, this effect can be opposed by the increased repulsion of dehydrated headgroups. However, the diffuse charge on the large [PNP]-cation may cause this repulsion to be small at any temperature.

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