

Evidence of Asymmetric Triple Ion Formation of Tetrapropylammonium Picrate in Chlorobenzene

TURE LINDBÄCK and PER BERONIUS

Department of Physical Chemistry, University of Umeå, S-901 87 Umeå, Sweden

The association of tetrapropylammonium picrate (QPi) to ion pairs and triple ions in chlorobenzene at 25 °C has been studied by conductance measurements in the concentration range from 6×10^{-6} to 1.5×10^{-3} mol dm⁻³. Application of the conductance equation for pairwise association to the experimental points indicates considerable triple ion formation for concentrations exceeding 3×10^{-5} mol dm⁻³. In this higher concentration range there is strong evidence of formation of negatively charged triple ions, QPi₂⁻, though a slight formation of positively charged triplets cannot be ruled out. Ion pair and triple ion association constants and estimated single ion conductivities for Q⁺, Pi⁻ and QPi₂⁻ are reported. Contour diagram representations have been introduced to illustrate the dependence of the goodness of fit of the free ion/ion pair/triple ion conductance equation on any pair of values for the triple ion association constant and triple ion mobility.

Calculations based on a model of the picrate ion yield 4.3 Å for its radius along the phenolic oxygen–*p*-nitro group axis.¹ According to an estimate of Gilkerson and Stamm the charge may be said to reside on this axis at a distance of about 3.3 Å from the phenolic oxygen, *i.e.* at 1 Å distance from the geometrical center.¹ Because of the asymmetry in charge distribution of the picrate ion and steric hindrance positively charged triple ions, Q⁺Pi⁻Q⁺, of quaternary ammonium picrates would be less stable than the corresponding negatively charged species (Pi⁻Q⁺Pi⁻) and a higher probability of forming QPi₂⁻ triplets as compared with Q₂Pi⁺ may be expected.

The purpose of the present paper is to discuss the results of a conductimetric investigation of the kinds of triple ions formed in solutions of tetrapropyl-

ammonium picrate in chlorobenzene at 25 °C. In this low dielectric constant solvent triple ion formation may be expected even at very low electrolyte concentrations, *cf.* Ref. 2.

EXPERIMENTAL

Chlorobenzene (*purum* grade) was passed through a 60 cm column packed with molecular sieve (Linde 4 A). It was subsequently fractionally distilled twice. The middle fractions were collected. The final product had an electrolytic conductivity of 5.5×10^{-12} S cm⁻¹ and a density of 1.10087 g cm⁻³ (lit.³ 1.10085 g cm⁻³) at 25 °C. The lit.³ values, $\eta = 0.00758$ P for the viscosity and $\epsilon = 5.612$ for the relative permittivity at this temperature, were used in the calculations.

Tetrapropylammonium picrate was prepared according to Ref. 4.

The conductivity cell used was of the Daggett-Bair-Kraus type⁵ with a capacity of 1300 ml. Bright platinum electrodes were used. The cell constant, the exact value of which was determined by repeated calibrations with aqueous potassium chloride,⁶ was of the order 0.03 cm⁻¹. The cell was thermostatted at 25.00 ± 0.02 °C in a constant temperature kerosene bath.

Portions of a stock solution of tetrapropylammonium picrate in chlorobenzene were successively added to the cell initially containing about 1250 ml of pure solvent. A calibrated precision buret (Metrohm Herisau, Dosimat E 535), kept in an air thermostat at 25.00 ± 0.02 °C was used for this purpose. For the highest concentrations investigated, portions of the pure salt were transferred to the cell. The cell solution was agitated by means of a magnetic stirrer.

For each concentration investigated, the resistance of the cell was determined at different frequencies between 2 and 5 kHz using a Leeds and

Table 1. Conductance data of tetrapropylammonium picrate in chlorobenzene at 25 °C.

$c \times 10^5$ mol dm ⁻³	Λ S cm ² mol ⁻¹	$c \times 10^5$ mol dm ⁻³	Λ S cm ² mol ⁻¹
0.59737	3.2059	6.8562	1.0248
1.1898	2.3312	7.4002	0.98869
1.7776	1.9304	7.9401	0.95619
2.3608	1.6897	8.4759	0.92747
2.9393	1.5234	9.0077	0.90173
3.5135	1.4016	11.095	0.81844
4.0832	1.3061	27.473	0.54282
4.6485	1.2288	50.277	0.41910
5.1990	1.1669	110.83	0.31251
5.7557	1.1123	153.94	0.28273
6.3081	1.0658		

Northrup 4666 conductivity bridge. Extrapolation of the resistance to infinite frequency was performed in the usual manner.

RESULTS

The measured values of the molar conductivity, Λ , corrected for the conductivity of the solvent, and the corresponding electrolyte concentrations, c , are given in Table 1.

DISCUSSION

Free ion/ion pair concentration range. According to theory,² the maximum concentration c_0 for which triple ion formation of a univalent electrolyte in a solvent of relative permittivity ϵ may be neglected is given by eqn. (1), where T is the absolute temperature.

$$c_0/\text{mol dm}^{-3} = 1.19 \times 10^{-14} (\epsilon T)^3 \quad (1)$$

For the present system studied, eqn. (1) yields $c_0 = 5.6 \times 10^{-5}$ mol dm⁻³ for the upper limit of the free ion/ion pair concentration range. According to this result the nine lowest concentration points in Table 1 would fall within the concentration range of negligible triple ion formation.

To investigate if this is so, the PFPP^{7,8} and FHFP^{9,10} conductance equations were first fitted to the four lowest concentration points (c, Λ) as outlined in Ref. 11 to obtain K_A , the association constant for pairwise association, and Λ_∞ , the limiting molar conductivity of simple ions. This curve fitting was performed for different values, $R = 10, 20, 25, 30, 40$, and 50 \AA (Bjerrum radius), of the distance parameter

in the conductance equation and in the Debye-Hückel equation for the mean activity coefficient of free ions. These calculations were then successively extended to the five, six, etc. lowest concentration points to investigate any possible dependence of K_A on the upper limit of the concentration interval studied.

Graphic representations of the dependence of K_A on the upper concentration limit are shown in Fig. 1 for the two different conductance equations concerned. Since the different R values used yielded similar curves, only the two referring to $R = 10$ and 50 \AA are included in Fig. 1. For electrolyte concentrations above 3×10^{-5} mol dm⁻³ K_A shows a definite concentration dependence, which is to be expected in the case of triple ion formation. Hence, the experimental data indicate an upper concentration limit of $c_0 = 3 \times 10^{-5}$ mol dm⁻³ for the

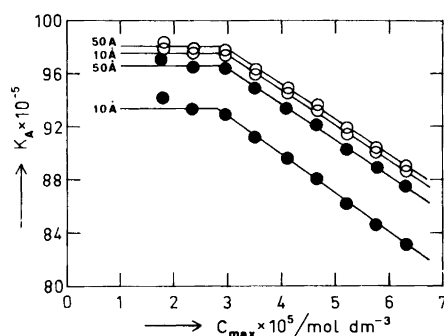


Fig. 1. Dependence of K_A on upper concentration limit of Pr_4NPi in $\text{C}_6\text{H}_5\text{Cl}$ at 25 °C. Open circles, PFPP equation; full circles, FHFP equation.

Table 2. Data for Pr₄NPi in C₆H₅Cl at 25 °C. Conc. < 3 × 10⁻⁵ mol dm⁻³. K_A on molarity scale.

Cond. equation	R Å	K _A × 10 ⁻⁶	Λ _∞ S cm ² mol ⁻¹	σ(Λ) S cm ² mol ⁻¹
PFPP	10	9.75 ± 0.13 ^a	25.40 ± 0.30	0.00065
	25	9.92 ± 0.13	25.60 ± 0.30	0.00067
	50	9.79 ± 0.13	25.45 ± 0.29	0.00065
FHFP	10	9.29 ± 0.14	24.86 ± 0.32	0.00066
	25	9.55 ± 0.13	25.17 ± 0.30	0.00064
	50	9.64 ± 0.12	25.27 ± 0.29	0.00064

^aStandard deviation.

free ion/ion pair range to be compared with $c_o = 5.6 \times 10^{-5}$ mol dm⁻³ according to eqn. (1).

For R values from 10 to about 100 Å (twice the Bjerrum radius) the PFPP and FHFP equations fit the experimental points below $c = 3 \times 10^{-5}$ mol dm⁻³ equally well, see Fig. 2 where $\sigma(\Lambda)$, the standard deviation between experimental and computed Λ values, is shown as a function of R . Within this range of R values $\sigma(\Lambda)$ is almost constant.

The values of K_A , Λ_∞ , and $\sigma(\Lambda)$ obtained upon application of the PFPP and FHFP equations to the five lowest concentration points in Table 1 are given in Table 2 for three different R values.

Asymmetric triple ion formation. Let us assume that only one kind of triplets, QPi₂⁻, appear at higher concentrations, *i.e.* that we are concerned with "asymmetric" triple ion formation. If this is so, the molar conductivity may be represented by the expression (2), where m is a mobility correction factor,

$$\Lambda = m[\alpha\Lambda_\infty + \alpha_T\Lambda_\infty^*] \quad (2)$$

which corrects for ion atmosphere effects,

$$\alpha = [\text{Pi}^-]/c \quad (3)$$

$$\alpha_T = [\text{QPi}_2^-]/c \quad (4)$$

where c is the analytical concentration of tetrapropylammonium picrate and Λ_∞ and Λ_∞^* are given by eqns. (5) and (6).

$$\Lambda_\infty = \lambda_\infty(\text{Q}^+) + \lambda_\infty(\text{Pi}^-) \quad (5)$$

$$\Lambda_\infty^* = \lambda_\infty(\text{Q}^+) + \lambda_\infty(\text{QPi}_2^-) \quad (6)$$

Two different forms of eqn. (2), eqns. (2a) and (2b), where m_p and m_F are mobility correction factors according to the PFPP^{7,8} and FHFP^{9,10} treatments, respectively, were investigated.

$$\Lambda = m_p[\alpha\Lambda_\infty + \alpha_T\Lambda_\infty^*] \quad (2a)$$

$$\Lambda = m_F[\alpha\Lambda_\infty + \alpha_T\Lambda_\infty^*] \quad (2b)$$

Eqns. (2a) and (2b) were fitted to the experimental points (c, Λ) in the concentration range $6.8562 \leq c \times 10^5 \leq 153.94$ mol dm⁻³ using a computer programme outlined in Ref. 12. By this means $\sigma(\Lambda)$ was obtained for preselected combinations of Λ_∞^* and K_T , the triple ion association constant, which is defined by the relation (7).

$$K_T = \alpha_T/[c\alpha(1-\alpha-2\alpha_T)] \quad (7)$$

The following procedure was adopted to obtain a clear picture of the goodness of fit on variations in the two adjustable parameters, K_T and Λ_∞^* . Using a preselected value of Λ_∞^* , for convenience expressed

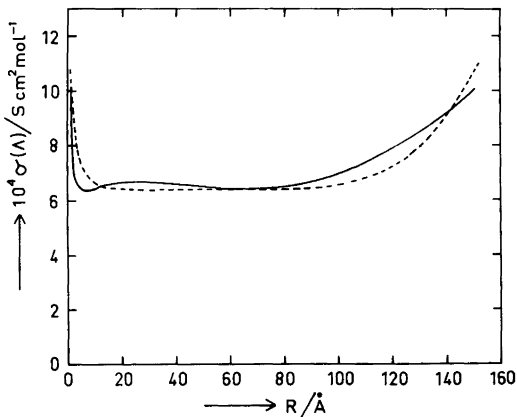


Fig. 2. Dependence of $\sigma(\Lambda)$ on distance parameter, R , for Pr₄NPi in C₆H₅Cl at 25 °C according to PFPP equation (fulldrawn curve) and FHFP equation (dashed curve). Conc. < 3 × 10⁻⁵ mol dm⁻³.

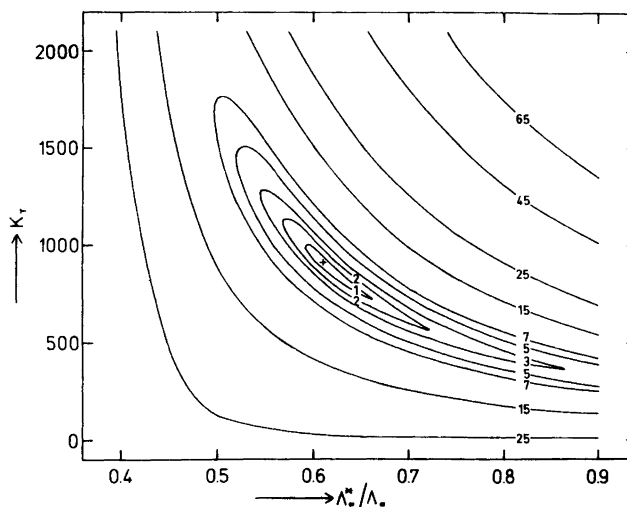


Fig. 3. Contour diagram for the standard deviations of F eqn. (2b) for asymmetric triple ion formation of Pr_4NPI in $\text{C}_6\text{H}_5\text{Cl}$ at 25°C . Concentration range, $6.8562 \leq c \times 10^5 \leq 153.94 \text{ mol dm}^{-3}$. The figures on the contours are values of $10^3 \sigma(\Lambda)/S \text{ cm}^2 \text{ mol}^{-1}$. The + sign marks the best fit point. $R = 50 \text{ \AA}$.

as a fraction of Λ_∞ , values of $\sigma(\Lambda)$ were computed for a series of triple association constants in the range, $0.1 \leq K_T \leq 2500 \text{ dm}^3 \text{ mol}^{-1}$. These calculations were repeated for a series of Λ_∞^* values. The computed sets of data were used to construct the contour diagram shown in Fig. 3, which refers to the F version of eqn. (2) with R set equal to 50 \AA . A similar picture is obtained for the P version, eqn. (2a). The figures on the contours are values of $10^3 \sigma(\Lambda)$. A sharp minimum, denoted by the + sign in Fig. 3, appears for both forms of eqn. (2). The values of K_T , $\Lambda_\infty^*/\Lambda_\infty$, and $\sigma(\Lambda)$ corresponding to this minimum, i.e. best-fit parameter values, are given in Table 3.

In Fig. 4 the conditional minimum $\sigma(\Lambda)$ is shown as

Table 3. Data for asymmetric triple ion formation according to P and F eqns. (2a) and (2b), for Pr_4NPI in $\text{C}_6\text{H}_5\text{Cl}$ at 25°C . Conc. range, $6.8562 \leq c \times 10^5 \leq 153.94 \text{ mol dm}^{-3}$.

Cond. equation	$R \text{ \AA}$	$K_T \text{ dm}^3 \text{ mol}^{-1}$	$\Lambda_\infty^*/\Lambda_\infty$	$\sigma(\Lambda) \text{ S cm}^2 \text{ mol}^{-1}$
P	10	906	0.608	0.00037
	25	910	0.601	0.00036
	50	1011	0.596	0.00034
F	10	979	0.618	0.00036
	25	895	0.617	0.00039
	50	901	0.612	0.00037

a function of $\Lambda_\infty^*/\Lambda_\infty$ for significantly different R values corresponding to the Bjerrum radius, $q = 50 \text{ \AA}$, $q/2$, and $q/5$. From this graph it is obvious that the location of the minimum, and hence the best-fit

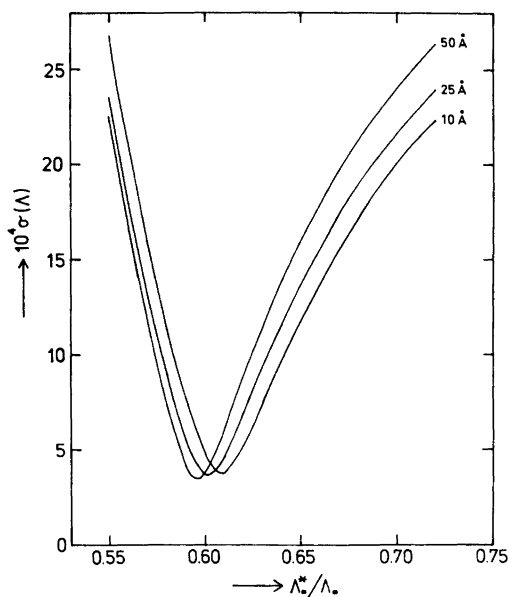


Fig. 4. Dependence of conditional minimum $\sigma(\Lambda)$ on $\Lambda_\infty^*/\Lambda_\infty$ according to P eqn. (2a) for asymmetric triple ion formation of the same system as in Fig. 3.

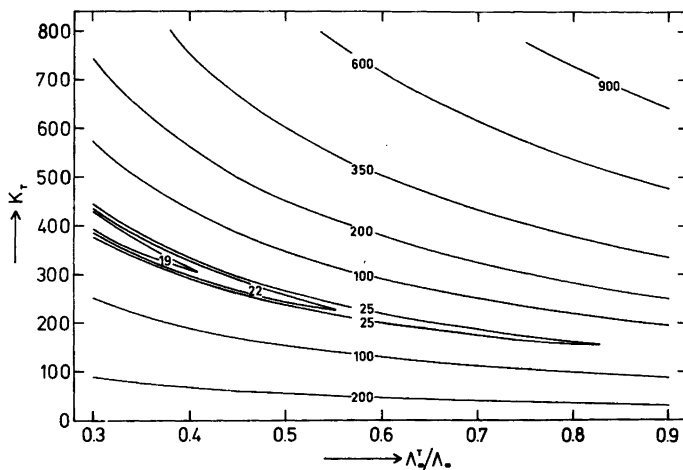


Fig. 5. Contour diagram for the standard deviations of F eqn. (8b) for symmetric triple ion formation of the same system as in Fig. 3. The figures on the contours are values of $10^4\sigma(\Lambda)/S \text{ cm}^2 \text{ mol}^{-1}$. $R = 50 \text{ \AA}$.

values of K_T and Λ_∞^* , depend only slightly on the distance parameter value used.

Symmetric triple ion formation. Using the PFPP and FHFP functions to correct mobilities for ion atmosphere effects, the molar conductivity may in the case of equal probabilities¹³ of forming the two different kinds of triplets, $Q_2\text{Pi}^+$ and $Q\text{Pi}_2^-$, be represented by eqns. (8a) and (8b), respectively, where α , α_T and Λ_∞^T are given by eqns. (9)–(11).

$$\Lambda = m_P[\alpha\Lambda_\infty + \alpha_T\Lambda_\infty^T] \quad (8a)$$

$$\Lambda = m_F[\alpha\Lambda_\infty + \alpha_T\Lambda_\infty^T] \quad (8b)$$

$$\alpha = [Q^+]/c = [Pi^-]/c \quad (9)$$

$$\alpha_T = [Q_2\text{Pi}^+]/c = [Q\text{Pi}_2^-]/c \quad (10)$$

$$\Lambda_\infty^T = \lambda_\infty(Q_2\text{Pi}^+) + \lambda_\infty(Q\text{Pi}_2^-) \quad (11)$$

Using a procedure of computation similar to that outlined above, cf. Ref. 13, the goodness of fit of eqns. (8a) and (8b) to the experimental points was established for different combinations of K_T and Λ_∞^T . The contour diagram in Fig. 5, which refers to the F eqn. (8b), illustrates the dependence of $\sigma(\Lambda)$ on the two adjustable parameters, K_T and Λ_∞^T expressed as a fraction of Λ_∞ . The P equation (8a) yields a similar contour diagram. Within the range of triple ion conductivities in Fig. 5, $0.3 \leq \Lambda_\infty^T/\Lambda_\infty \leq 0.9$, there is no minimum similar to that denoted by the + sign in Fig. 3 for asymmetric triple ion formation.

A graphic representation of the dependence of the conditional minimum $\sigma(\Lambda)$ on the limiting molar conductivity of the triple ions is shown in Fig. 6 for the P and F equations. In this graph the computed data have been extended to lower values of Λ_∞^T as compared with the corresponding interval shown in the contour diagram, Fig. 5. For each equation a minimum appears for a value of Λ_∞^T , which

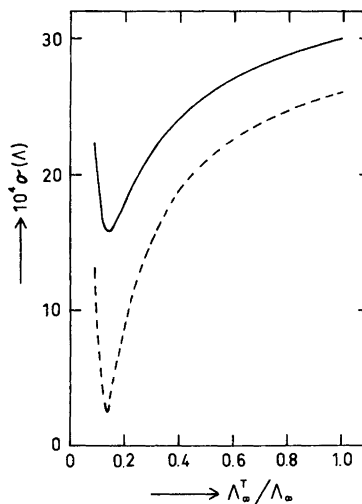


Fig. 6. Dependence of conditional minimum $\sigma(\Lambda)$ on $\Lambda_\infty^T/\Lambda_\infty$ according to P eqn. (8a), full-drawn curve, and F eqn. (8b), dashed curve, for symmetric triple ion formation of the same system as in Fig. 3. $R = 50 \text{ \AA}$.

Table 4. Data for symmetric triple ion formation according to P and F eqns. (8a) and (8b), for the same system as in Table 3 at $R = 50 \text{ \AA}$.

Cond. equation	K_T $\text{dm}^3 \text{ mol}^{-1}$	$\Lambda_\infty^T/\Lambda_\infty$	$\sigma(\Lambda)$ $\text{S cm}^2 \text{ mol}^{-1}$
P	930	0.139	0.00159
F	874	0.135	0.00028

is only about 14% of that of Λ_∞ . Hence, the assumption of equal probabilities of forming the two different kinds of triplets results in very low triple ion mobilities.

Best-fit parameters are given in Table 4 for the distance parameter set equal to q .

Transference numbers. Directly determined transference numbers for chlorobenzene as solvent do not appear to be available in the literature. An estimate of the anion transference number, $t_-(\text{Pr}_4\text{N}^+)$, was derived as follows.

Let us assume, as did D'Aprano, James, and Fuoss,¹⁴⁻¹⁶ that the transference number of the large cation in tetrabutylammonium tetraphenylboride is independent of the solvent and equal to eqn. (12).

$$\lambda_\infty(\text{Bu}_4\text{N}^+) = 0.519\Lambda_\infty(\text{Bu}_4\text{NBPh}_4) \quad (12)$$

This assumption and values of Λ_∞ for Bu_4NBPh_4 , Bu_4N^+ , and Pr_4NBPh_4 in isobutyronitrile and binary mixtures of this solvent with benzene, carbon tetrachloride, dioxane, and tetrahydrofuran according to Ref. 15 were used in calculating values of λ_∞ for Pr_4N^+ and Pi^- and, hence, the transport

Table 5. Anion transport numbers for Pr_4N^+ at 25 °C.

Solvent	ϵ	t_-
Isobutyronitrile	23.81	0.529
Isobutyronitrile-benzene	$19.04 \geq \epsilon \geq 10.38$	0.531 – 0.539
Isobutyronitrile-carbon tetrachloride	$19.49 \geq \epsilon \geq 10.36$	0.515 – 0.529
Isobutyronitrile-dioxane	$18.98 \geq \epsilon \geq 10.31$	0.531 – 0.542
Isobutyronitrile-tetrahydrofuran	$19.4 \geq \epsilon \geq 10.67$	0.533 – 0.550
Acetone	20.7	0.536
		Av: 0.5333

Table 6. Best-fit of F eqn. (2b) to conductance data of Pr_4N^+ in $\text{C}_6\text{H}_5\text{Cl}$ at 25 °C. $K_A = 9.64 \times 10^6$; $\Lambda_\infty = 25.27 \text{ S cm}^2 \text{ mol}^{-1}$; $K_T = 901 \text{ dm}^3 \text{ mol}^{-1}$; $\Lambda_\infty^*/\Lambda_\infty = 0.612$; $R = 50 \text{ \AA}$.

$c \times 10^5$ mol dm^{-3}	$[\Lambda(\text{exp}) - \Lambda(\text{calc})] \times 10^5$ $\text{S cm}^2 \text{ mol}^{-1}$	$\Delta\Lambda$ %
6.8562	+8.4	+0.008
7.4002	-0.9	-0.001
7.9401	-45.2	-0.047
8.4759	-40.8	-0.044
9.0077	-15.4	-0.017
11.095	-6.8	-0.008
27.473	+81.0	+0.149
50.277	+6.9	+0.017
110.83	-8.3	-0.027
153.94	-15.0	-0.053

number of the picrate ion. The results are given in Table 5. The value of t_- for acetone as solvent was derived from $\lambda_\infty(\text{Pr}_4\text{N}^+) = 75.09$ and $\Lambda_\infty(\text{Pr}_4\text{N}^+) = 161.85$ according to Refs. 17 and 18.

Most of the transference numbers derived deviate by less than 1% from the average, $t_- = 0.533$, which was adopted for Pr_4N^+ in chlorobenzene.

Conclusions. On the assumption that only one kind of triple ion (QPi_2^-) appears in the system investigated, a well-defined minimum is found in the contour diagram, cf. Fig. 3, for $\Lambda_\infty^*/\Lambda_\infty \approx 0.6$. The triple ion association constant, K_T , the triple ion mobility parameter, $\Lambda_\infty^*/\Lambda_\infty$, and the standard deviation, $\sigma(\Lambda)$, referring to the minimum in the contour diagram differ only insignificantly for the P and F equations. Furthermore, within the range of distance parameter values investigated ($q/5 \leq R \leq q$) the values of K_T , $\Lambda_\infty^*/\Lambda_\infty$, and $\sigma(\Lambda)$ are practically independent of R (Table 3).

Both forms of eqn. (2) fit the experimental points (c, Λ) very well. This statement is illustrated by the compilation in Table 6, where absolute and relative deviations between experimental and computed Λ values referring to the F eqn. (2b) with R set equal to 50 \AA are given for the different concentrations investigated. The relative standard deviation between experimental and computed Λ values amounts to only 0.06%.

Let us in estimating single ion conductivities use $\Lambda_\infty = 25.27 \text{ S cm}^2 \text{ mol}^{-1}$ according to the FHFP equation for $R = 50 \text{ \AA}$ (Table 2), the corresponding value of $\Lambda_\infty^*/\Lambda_\infty = 0.612$ (Table 3), and the transference number $t_-(\text{Pr}_4\text{N}^+) = 0.533$ derived

above. Application of eqns. (5) and (6) yields, $\lambda_{\infty}(\text{Q}^+) = 11.80$, $\lambda_{\infty}(\text{Pi}^-) = 13.47$, and $\lambda_{\infty}(\text{QPi}_2^-) = 3.67 \text{ S cm}^2 \text{ mol}^{-1}$. These data indicate a triple ion mobility of about one third of that of the tetrapropylammonium ion and about one fourth of that of the picrate ion.

It may be noted that the F conductance eqn. (8b) for symmetric triple ion formation in fact results in a slightly better fit than the corresponding eqn. (2b) for asymmetric triple ion formation, compare $\sigma(\Lambda) = 0.00028 \text{ S cm}^2 \text{ mol}^{-1}$ according to eqn. (8b) with $\sigma(\Lambda) = 0.00037$ according to eqn. (2b) for $R = 50 \text{ \AA}$ in Tables 4 and 3, respectively. However, the value of $\Lambda_{\infty}^{\text{T}}/\Lambda_{\infty} = 0.135$ in the symmetric case (Table 4) indicates that the triple ion mobility would be less than that of the simple ions by a factor of 7–8. Such a low mobility appears most improbable. It may be concluded that we are here concerned with asymmetric triple ion formation though a slight contribution from symmetric triple ion formation cannot be ruled out.

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