

Short Communications

On the Study of Triple Ion Formation. Electrolytes Forming Only One Kind of Triplet

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In a previous investigation¹ of triple ion formation of lithium bromide in 1-octanol at 25 °C electrical conductance data were analyzed using a new method of computation assuming equal probabilities of forming the two different kinds of triplets, Li_2Br^+ and LiBr_2^- . The triple ion association constant and the limiting molar conductivity of the triplets were derived from an equation involving these quantities as adjustable parameters. The present study was undertaken to investigate the possibility of applying a similar method to electrolytes assumed to form only one kind of triplets, A_2B^+ or AB_2^- .

The method of computation was tested by application to electrical conductance data for tetrabutylammonium picrate in chlorobenzene as solvent at 25 °C reported by McIntosh, Mead, and Fuoss.²

Table 1. Conductance data for tetrabutylammonium picrate in chlorobenzene at 25 °C according to Ref. 2.

Conc. range of negligible triple ion formation		Conc. range of non-negligible triple ion formation	
$c \times 10^4$ M	Λ $\text{S cm}^2 \text{ mol}^{-1}$	$c \times 10^4$ M	Λ $\text{S cm}^2 \text{ mol}^{-1}$
0.091	2.72	1.310	0.770
0.172	2.02	2.827	0.542
0.407	1.340	6.50	0.380
0.610	1.103	6.94	0.370
		11.87	0.305
		14.24	0.284
		19.62	0.266

Their data are reproduced in Table 1, the left hand part of which refers to the dilute concentration range of negligible triple ion formation,³ cf. Refs. 1 and 4.

Because of steric hindrance the formation of positively charged triplets, Q_2Pi^+ , appears less probable than the formation of the corresponding negatively charged species, QPi_2^- . Hence, let us first assume that association occurs according to the following equilibria,



i.e. that any triple ion formation according to the equilibrium,



may be neglected.

Denoting the concentrations of unassociated picrate ions and negatively charged triplets,

$$[\text{Pi}^-] = c\alpha \quad (4)$$

$$[\text{QPi}_2^-] = c\alpha_T \quad (5)$$

where c is the analytical concentration of the salt, it can be shown that,

$$[\text{Q}^+] = c(\alpha + \alpha_T) \quad (6)$$

$$[\text{Q}^+\text{Pi}^-] = c(1 - \alpha - 2\alpha_T) \quad (7)$$

Using eqns. (4–7) the following expressions for the ion pair and triple ion association constants, K_A and K_T , cf. (1) and (2), are obtained:

$$K_A = (1 - \alpha - 2\alpha_T) / [c\gamma^2\alpha(\alpha + \alpha_T)] \quad (8)$$

$$K_T = \alpha_T / [c\alpha(1 - \alpha - 2\alpha_T)] \quad (9)$$

In eqn. (8) γ is the mean molar activity coefficient of free ions which was calculated using the Debye-Hückel equation, cf. Ref. 4, with the distance parameter set equal to the Bjerrum radius, $q = 49.93 \text{ \AA}$.

The molar conductivity, Λ , may be expressed,

$$\Lambda = m[\alpha\Lambda_x + \alpha_T\Lambda_x^*] \quad (10)$$

where,

$$\Lambda_x = \lambda_x(Q^+) + \lambda_x(\text{Pi}^-) \quad (11)$$

$$\Lambda_x^* = \lambda_x(Q^+) + \lambda_x(\text{QPi}_2^-) \quad (12)$$

and m is a correction factor, which corrects the mobilities of the ions for ion atmosphere effects, cf. Ref. 1.

Two different forms of eqn. (10) based on mobility corrections, m , according to the FHFP⁵⁻⁷ and PFPP^{8,9} equations were investigated. Below these two versions of eqn. (10) will be labelled "F" and "P", respectively.

On the basis of the conductance data referring to the lower concentration range of negligible triple ion formation in Table 1 values of K_A and Λ_x , according to the FHFP and PFPP equations for pairwise associated electrolytes, were iteratively calculated using the computer programme outlined in Ref. 10 and references therein. The values, $\epsilon = 5.612$ and $\eta = 0.00758 P$, for the relative permittivity and viscosity of the solvent were used.¹¹ The distance parameter, R , in the conductance equation was set equal to q .

The following values were obtained. FHFP equation: $K_A = (12.5 \pm 1.5) \times 10^6 \text{ (M}^{-1}\text{)}$; $\Lambda_x = 29.4 \pm 3.3 \text{ S cm}^2 \text{ mol}^{-1}$. PFPP equation: $K_A = (12.8 \pm 1.6) \times 10^6$; $\Lambda_x = 29.8 \pm 3.4$. The errors given are standard deviations.

Eqn. (10) was fitted to the seven points (c, Λ) referring to the higher concentration range in Table 1 using a procedure similar to that outlined in Ref. 1. The computer programme developed for this curve fitting permits $\sigma(\Lambda)$, i.e. the standard deviation between experimental and computed Λ -values, to be obtained for preselected combinations of K_T and Λ_x^* .

The values of K_T , which for given values of Λ_x^* result in the best fit of eqn. (10) to the experimental points in the higher concentration range, are given graphically in Fig. 1. According to this graph the F and P versions of eqn. (10) yield insignificantly different results; hence the following discussion will be restricted to the F version. In Fig. 1 Λ_x^* is for convenience expressed as a fraction of the limiting molar conductivity of the simple ions (Λ_x).

The fulldrawn curve in Fig. 2 demonstrates how the conditional minimum $\sigma(\Lambda)$ depends on the quotient Λ_x^*/Λ_x . A well-defined minimum appears for $K_T = 1.12 \times 10^3 \text{ M}^{-1}$ and $\Lambda_x^*/\Lambda_x = 0.53$. This quotient may be employed as follows to estimate the mobility of the triplet, QPi_2^- .

Using $\Lambda_x = 29.4$ for $\lambda_x(Q^+) + \lambda_x(\text{Pi}^-)$ derived

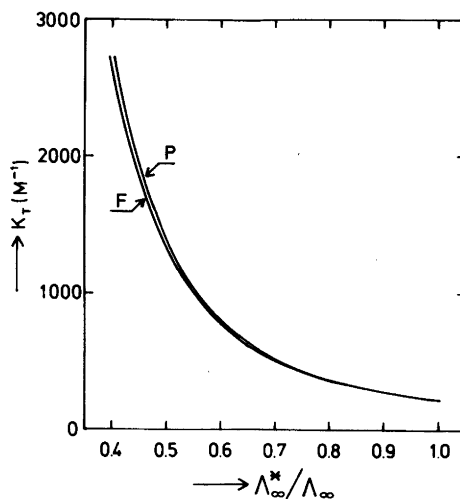


Fig. 1. Dependence of K_T on Λ_x^*/Λ_x , according to the F and P versions of eqn. (10) for tetrabutylammonium picrate in chlorobenzene at 25 °C.

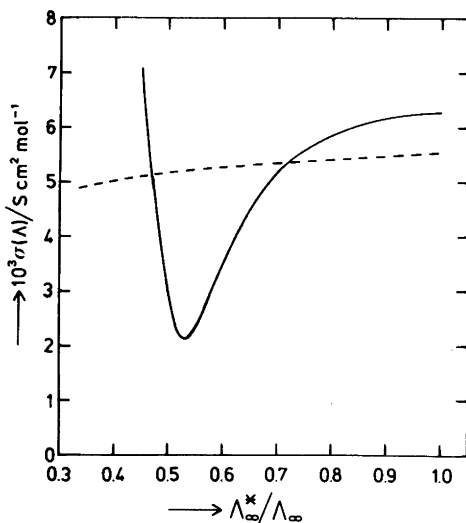


Fig. 2. Dependence of $\sigma(\Lambda)$ on Λ_x^*/Λ_x for tetrabutylammonium picrate in chlorobenzene at 25 °C. Fulldrawn curve obtained assuming only one kind of triple ions (QPi_2^-) to be formed. Dashed curve obtained assuming equal probabilities of forming the two different kinds of triplets, Q_2Pi^+ and QPi_2^- . Calculations based on the F version of eqn. (10).

above by means of the FHFP equation we obtain $\Lambda_x^* = 15.6$ for $\lambda_x(Q^+) + \lambda_x(\text{QPi}_2^-)$. No transference numbers for evaluation of the limiting molar conductivity of the tetrabutylammonium ion in chlorobenzene could be found in the literature.

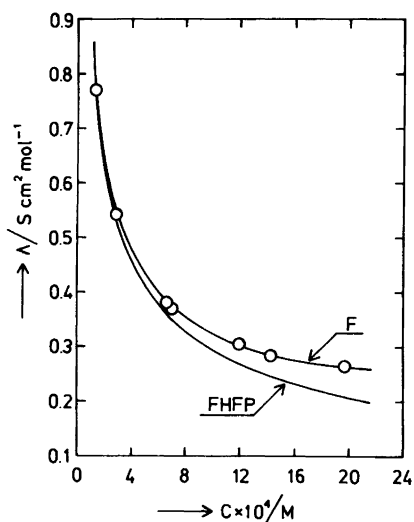


Fig. 3. Dependence of Λ on analytical concentration, c , of tetrabutylammonium picrate in chlorobenzene at 25 °C. Open circles: experimental points according to Ref. 2. Bottom curve: extrapolation of the FHFP equation from the lower concentration range. F curve: best fit of eqn. (10) to the experimental points.

The same value of $\lambda_x(Q^+)/\lambda_x(\text{Pi}^-)=0.64$ as in water¹² at 25 °C was therefore tentatively used to estimate limiting ionic conductivities in chlorobenzene. The resulting values, viz. $\lambda_\infty(Q^+)=11.5$, $\lambda_x(\text{Pi}^-)=17.9$, and $\lambda_x(\text{QPi}_2^-)=4.1 \text{ S cm}^2 \text{ mol}^{-1}$, suggest that the mobility of the negatively charged triplet is about 1/3 of that of the tetrabutylammonium ion and about 1/4 of that of the picrate ion.

In Fig. 3 the experimental points in the higher concentration range are shown by open circles. The bottom curve is an extrapolation of the FHFP equation (for pairwise association) from the lower to the higher concentration range. This extrapolated curve is equivalent to eqn. (10) with α_T set equal to zero. The curve labelled "F" was calculated from eqn. (10) with K_T and Λ_∞^* set equal to the values corresponding to the minimum $\sigma(\Lambda)$ in Fig. 2. The F curve in Fig. 3 clearly demonstrates the excellent fit of eqn. (10) to the experimental data in the higher concentration range.

So far the present interpretation of the conductance data in Table 1 is based on the assumption that only negatively charged triple ions are being formed. Let us for comparison treat the same conductance data assuming equal probabilities of forming the two different kinds of triplets, QPi_2^- and Q_2Pi^+ , which implies that the equilibrium (3) has to be considered in the calculations in addition to the equilibria (1) and (2). In this case the conductance equation may be expressed,

$$\Lambda = m(\alpha\Lambda_\infty + \alpha_T\Lambda_\infty^T) \quad (13)$$

where α , α_T , and Λ_∞^T are defined by the expressions,

$$[\text{Q}^+] = [\text{Pi}^-] = c\alpha \quad (14)$$

$$[\text{Q}_2\text{Pi}^+] = [\text{QPi}_2^-] = c\alpha_T \quad (15)$$

$$\Lambda_\infty^T = \lambda_\infty(\text{Q}_2\text{Pi}^+) + \lambda_\infty(\text{QPi}_2^-) \quad (16)$$

and m and Λ_∞ have the same significance as before.

The computer programme used to fit eqn. (13) to the experimental points in the higher concentration range is outlined in Ref. 1.

The dashed curve in Fig. 2, where Λ_∞^* now stands for Λ_∞^T as defined by eqn. (16), shows the dependence of the conditional minimum $\sigma(\Lambda)$ on $\Lambda_\infty^T/\Lambda_\infty$. As can be seen $\sigma(\Lambda)$ is in this case quite insensitive to the choice of value for the triple ion mobility. Furthermore, the assumption of equal probabilities of forming the two different kinds of triplets, Q_2Pi^+ and QPi_2^- , results in a not insignificantly worse fit of the conductance equation (13) to the experimental points as compared with eqn. (10). These findings might be taken as support of the *a priori* assumption that the formation of negatively charged triple ions is favoured over positively charged triplets.

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