

# The Ion Pair Formation of Quaternary Ammonium Picrates in Aqueous Methylene Chloride at 25 °C Studied by Conductivity and Distribution

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Electrical conductance measurements of  $\text{Me}_4\text{N}^+\text{Pi}^-$ ,  $\text{Et}_4\text{N}^+\text{Pi}^-$ , and  $\text{Pr}_4\text{N}^+\text{Pi}^-$  in water saturated methylene chloride at 25 °C were performed for several concentrations below  $5 \times 10^{-4}$  M. The data were analyzed by means of the expanded Fuoss-Hsia and Pitts' equations for associated electrolytes. Limiting single ion conductances were estimated by means of an indirect method. The data indicate a stronger ion-solvent interaction for  $\text{Me}_4\text{N}^+$  as compared with  $\text{Et}_4\text{N}^+$  and  $\text{Pr}_4\text{N}^+$ . Ion-pair association constants,  $K_A$ , which increase in the order,  $\text{Pr}_4\text{N}^+\text{Pi}^- < \text{Et}_4\text{N}^+\text{Pi}^- \ll \text{Me}_4\text{N}^+\text{Pi}^-$ , are discussed in terms of the Bjerrum theory.

The values of  $K_A$  according to conductance measurements and distribution measurements in the two-phase system, water/methylene chloride, are in almost complete agreement.

Measurement of electrolytic conductivity is considered to be one of the most accurate methods for determining ion pair association constants, cf. Ref. 1. Unfortunately, unequivocal evaluation of the association constant is in general not possible because of the uncertainty concerning proper choice of value for the distance parameter in the conductance equation and in the Debye-Hückel equation.<sup>2-4</sup>

One possibility of attacking this problem might be to investigate the equilibrium between free and paired ions by independent methods. The present study of the association of quaternary ammonium picrates in aqueous methylene chloride by conductance and partition measurements, cf. Refs. 5-6, constitutes part of such an investigation. By contrast with the present study, previous investigations

(Table 3) of quaternary ammonium picrates refer to pure solvents.

## EXPERIMENTAL

Water saturated methylene chloride was prepared by shaking the organic solvent (Merck, *p.a.*) with distilled water for 10 min. The system was left for 1 h before separating the two phases. Analysis according to the Karl Fischer method indicated a water concentration of 0.2 % by volume in the organic liquid.

The permittivity,  $\epsilon$ , of the water saturated methylene chloride was measured by means of a Ferisol M 803 A Q-meter. The value,  $\epsilon = 8.94$ , at 25 °C was obtained. The viscosity,  $\eta = 0.00416$  P at this temperature, was established using an Ubbelohde viscometer. The viscosity of anhydrous methylene chloride is 0.00410 P. This value was calculated<sup>7,8</sup> using the expression,  $1/\eta = A \exp(-E/RT)$ . The density,  $d_4^{25} = 1.3147$  g cm<sup>-3</sup>, was determined by means of a Lipkin pycnometer. The electrolytic conductivity was,  $\kappa = 1 \times 10^{-9}$   $\Omega^{-1}$  cm<sup>-1</sup>;  $\kappa = 4.3 \times 10^{-11}$   $\Omega^{-1}$  cm<sup>-1</sup> for anhydrous methylene chloride.<sup>8</sup>

The tetraalkylammonium picrates were prepared from the corresponding bromides or hydrogen sulfates. They were repeatedly recrystallized from 99.5 % ethanol. For the density of the picrates the value 1.4 g cm<sup>-3</sup> was used in making buoyancy corrections.

Measurements of electrolytic conductivity at  $25.00 \pm 0.01$  °C were performed using a Daggett-Bair-Kraus type conductivity cell,<sup>9</sup> of 1300 cm<sup>3</sup> capacity, connected to a Leeds and Northrup conductivity bridge. The cell constant ( $\sim 0.03$  cm<sup>-1</sup>) was established by several calibrations with aqueous potassium chloride.<sup>10</sup> The cell was thermostated in a kerosene filled constant temperature bath, the temperature of

which was determined using a Leeds and Northrup platinum resistance thermometer.

The conductivity of a predetermined quantity of water saturated methylene chloride was measured. Several portions of the salt under investigation were then successively added by means of a Hawes-Kay salt cup dispensing device.<sup>11,12</sup> The cell content was agitated by a magnetic stirrer to reduce the time required to dissolve the salt. After each addition of a portion of the salt the cell resistance was repeatedly measured until a constant resistance was attained. The time required for this was 2–6 h for tetramethyl ammonium picrate and less than 1 h for the other two picrates. Measurements were performed at 5.0, 3.3, 2.5, and 2.0 kHz and extrapolation of the resistance to infinite frequency performed. The correction for the conductivity of the solvent was 0.1 % or less. The densities of the solutions were taken to be the same as that of the solvent.

The distribution measurements were performed as described by Gustavii.<sup>5–8</sup> The concentrations in both layers were determined photometrically by comparison with a standard curve. The molar absorbance for tetramethylammonium picrate in methylene chloride was found to be significantly lower than those of other quaternary ammonium picrates.

From the distribution values both  $K_A$  and  $E$  were calculated using the equation,

$$c_s = E c_w^2 + (E/K_A)^{1/2} c_w / \gamma_s \quad (1)$$

where  $c_s$  is the concentration in the organic layer and  $c_w$  that in the aqueous layer.  $E$  is the extraction constant and  $\gamma_s$  the mean activity coefficient of free ions in the methylene chloride layer.

The procedure starts with a calculation of  $[Q^+]_s$  and  $\gamma_s$  by iterations in the association equation and the Debye-Hückel equation,

$$\gamma_s = \exp - (30.53[Q^+]_s^{1/2} / (1 + 30.53[Q^+]_s^{1/2})) \quad (2)$$

$$K_A \gamma_s^2 [Q^+]_s^2 = c_s - [Q^+]_s \quad (3)$$

To avoid the difficulties in the least-squares treatment of eqn. (1), which arise from the fact that both  $c_s$  and  $c_w$  are subjected to errors, which are very different for different pairs of values, an error normalisation was performed in the following way. The "error",  $F$ , in the measurement is defined by,

$$F = c_s - E c_w^2 - (E/K_A)^{1/2} c_w / \gamma_s \quad (4)$$

In this we introduce,

$$c_w = A_w n_w / \epsilon_w \quad (5a)$$

$$c_s = A_s n_s / \epsilon_s \quad (5b)$$

where  $A$  is the absorbance,  $n$  the factor by which the solution is diluted before measure-

ments, and  $\epsilon$  the molar absorption coefficient in the solvent indicated. From other measurements we know that the variance in  $A_w$  and  $A_s$  are equal. We denote them by "Var  $A$ ". From elementary statistics we have,

$$\text{Var } F = (n/\epsilon_s)^2 \text{Var } A \quad (6)$$

where,

$$n^2 = n_s^2 + (n_w \epsilon_s / \epsilon_w)^2 [2E c_w + (E/K_A)^{1/2} / \gamma_s]^2 \quad (7)$$

The non-linear least-squares treatment is therefore performed on the normalized "error" function,  $F/n$ , where  $n$  is calculated for every pair of  $c_w$  and  $c_s$ . From Var  $F/n$ , we can calculate the standard deviations,  $\sigma(A)$ ,  $\sigma(E)$ , and  $\sigma(K_A)$ .

## RESULTS AND DISCUSSION

In Table 1 corrected values of the molar conductivity,  $\Lambda$ , and the corresponding concentrations,  $c$ , are listed. Two independent

Table 1. Molar conductivities of tetraalkylammonium picrates in water saturated methylene chloride at 25 °C.

Run A		Run B	
$c \times 10^4$	$\Lambda$	$c \times 10^4$	$\Lambda$
M	$\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$	M	$\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$
<b>Me<sub>4</sub>NPi</b>			
0.51124	45.175	0.56690	43.740
0.78735	38.456	0.84892	37.503
1.0723	34.111	1.1029	33.814
1.3764	30.901	1.3791	30.935
2.3802	24.752	2.1800	25.688
4.9651	18.289	4.5622	18.945
<b>Et<sub>4</sub>NPi</b>			
0.25233	94.630	0.22915	96.096
0.51329	81.950	0.48566	82.947
0.78395	73.866	0.73594	75.023
4.7355	42.610	0.99607	69.250
		1.2601	64.831
		2.2154	54.743
<b>Pr<sub>4</sub>NPi</b>			
0.21651	90.009	0.23399	88.863
0.45811	79.538	0.46706	79.167
0.68506	73.118	0.70867	72.517
0.95186	67.657	0.99158	66.958
1.1920	63.942	1.2700	62.877
2.1488	54.437	2.2113	53.965
4.7051	43.043	4.5270	43.535

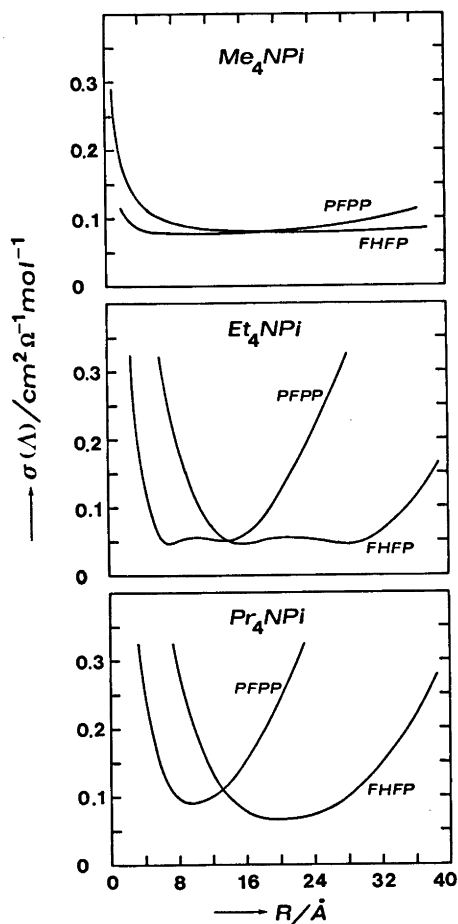


Fig. 1. Conditional minimum  $\sigma(A)$  vs. association distance according to FHFP and PFPP equations for quaternary ammonium picrates in water saturated methylene chloride at 25 °C.

series of measurements were made for each picrate.

The conductance data were analyzed by means of the Fuoss-Hsia equation in the form of Fernández-Prini,<sup>13</sup> and the Pitts' equation as developed by Fernández-Prini and Prue.<sup>14</sup> Below these two conductance equations will be denote "FHFP" and "PFPP", respectively. The method of computing the values of  $\Lambda_\infty$  and  $K_A$  which minimize  $\sigma(A)$  for some selected value of the distance parameter,  $R$ , in the conductance equation, and in the Debye-Hückel equation<sup>15</sup> for the mean activity coefficient of free ions, has been described.<sup>3</sup> ( $\Lambda_\infty$  = limiting molar con-

ductivity;  $K_A$  = ion-pair association constant;  $\sigma(A)$  = standard deviation between experimental and computed  $\Lambda$  values;  $R$  = maximum distance between centres of charge in the ion-pair.)

The FHFP and PFPP equations fit the experimental data with almost the same precision as is evident from Fig. 1, where  $\sigma(A)$  has been plotted vs.  $R$ . Especially for  $\text{Me}_4\text{N}^+$ , but also for  $\text{Et}_4\text{N}^+$ , the  $\sigma(A)$  -  $R$  curves are quite shallow. The minimum values of  $\sigma(A)$  for the two equations appear at significantly different values of  $R$ . It follows that the condition,  $\sigma(A)$  = minimum, is not useful as criterion of "best set" conductance parameters. This is in accord with previous experience.<sup>3,4</sup> In the following calculations  $R$  will be set equal to the Bjerrum radius,<sup>16</sup>  $q$ .

The conductance parameters derived are within experimental errors independent of the upper limit of the concentration interval studied (Table 2). This independence may be taken as evidence of the absence of significant amounts of higher aggregates than ion-pairs.

In the absence of transference data the limiting molar conductivity of the picrate ion was obtained from the Walden product estimates,  $\lambda_\infty(\text{Pi}^-)\eta$  in Table 3, derived from conductance data of  $\text{Bu}_4\text{N}^+\text{FBPh}_3^-$  and  $\text{Bu}_4\text{N}^+\text{Pi}^-$  in several solvents.<sup>17-22</sup> For each series of conductance measurements  $\Lambda_\infty$  was computed by application of the FHFP equation to the four lowest concentration points. The limiting conductivity of  $\text{Bu}_4\text{N}^+$  was obtained by assuming<sup>20</sup> equal mobilities of  $\text{Bu}_4\text{N}^+$  and  $\text{FBPh}_3^-$ . Combination of  $\lambda_\infty(\text{Bu}_4\text{N}^+)$  with  $\Lambda_\infty(\text{Bu}_4\text{N}^+\text{Pi}^-)$  yielded  $\lambda_\infty(\text{Pi}^-)$ . The average value,  $0.275 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1} \text{ P}$ , of the Walden products in the last column of Table 3 yields  $66 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$  for the limiting molar conductivity of the picrate ion in water saturated methylene chloride. Adopting  $\Lambda_\infty = 121, 125, \text{ and } 111 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$  for  $\text{Me}_4\text{N}^+$ ,  $\text{Et}_4\text{N}^+$ , and  $\text{Pr}_4\text{N}^+$ , respectively, (Table 2) we arrive at the following ionic conductivities:  $\lambda_\infty(\text{Me}_4\text{N}^+) = 55$ ;  $\lambda_\infty(\text{Et}_4\text{N}^+) = 59$ ;  $\lambda_\infty(\text{Pr}_4\text{N}^+) = 45 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ .

For a homologous series of tetraalkylammonium ions one might expect that the mobility should decrease with increasing number of carbon atoms in the substituent groups. For the solvent concerned the mobility decreases in the order,  $\text{Et}_4\text{N}^+ > \text{Me}_4\text{N}^+ > \text{Pr}_4\text{N}^+$ , *i.e.* the mobility of the tetramethyl ammonium ion is

Table 2. Dependence of conductance parameters on concentration interval. The parameters, derived from the data in Table 1, refer to the FHFP equation with  $R$  set to  $q = 31.34 \text{ \AA}$ .  $N$  = number of points ( $c, \lambda$ ). Errors listed for  $\lambda_\infty$  and  $K_A$  are standard deviations.

$c_{\max} \times 10^4$ M	$N$	$\lambda_\infty$ $\text{cm}^2 \Omega^{-1} \text{ mol}^{-1}$	$K_A \times 10^{-4}$ $\text{M}^{-1}$	$\sigma(\lambda)$ $\text{cm}^2 \Omega^{-1} \text{ mol}^{-1}$
<b>Me<sub>4</sub>NPi</b>				
4.97	12	121.00 ± 1.38	10.04 ± 0.17	0.08
2.38	10	122.11	10.27	0.08
1.38	8	122.28	10.31	0.10
1.10	6	121.90	10.23	0.13
<b>Et<sub>4</sub>NPi</b>				
4.74	10	125.26 ± 0.14	1.763 ± 0.005	0.06
2.22	9	125.34	1.769	0.05
1.26	8	125.42	1.774	0.05
0.78	6	125.34	1.768	0.06
<b>Pr<sub>4</sub>NPi</b>				
4.71	14	110.60 ± 0.29	1.270 ± 0.009	0.14
2.21	12	110.93	1.290	0.06
1.27	10	111.02	1.295	0.06
0.99	8	110.99	1.293	0.07
0.71	6	110.88	1.285	0.08

Table 3. Single ion conductivities and Walden products at 25 °C. The data have been calculated from literature data<sup>17-22</sup> by means of the FHFP equation with  $R$  set equal to the Bjerrum radius,  $q$ .

Solvent	$\lambda_\infty(\text{Bu}_4\text{N}^+)$ $\text{cm}^2 \Omega^{-1} \text{ mol}^{-1}$	$\lambda_\infty(\text{Pi}^-)$ $\text{cm}^2 \Omega^{-1} \text{ mol}^{-1}$	$\lambda_\infty(\text{Pi}^-)\eta$ $\text{cm}^2 \Omega^{-1} \text{ mol}^{-1} \text{ P}$
Nitrobenzene <sup>17</sup>	11.73	16.15	0.292
Pyridine <sup>18,19</sup>	24.07	33.97	0.300
Ethylene dichloride <sup>20,21</sup>	26.22	31.52	0.247
Acetone <sup>22</sup>	67.17	85.20	0.259

Table 4. Distribution of tetrapropylammonium picrate between buffer (pH = 6.5,  $\mu = 0.1$ ) and methylene chloride at 25 °C.<sup>a</sup>

$c_w \times 10^4$ M	$\gamma_s$	$n$	$c_s \times 10^4$ M	$c_s(\text{calc}) \times 10^4$ M
0.6380	0.7877	7.614	1.962	1.970
0.6260	0.7887	7.561	1.924	1.915
0.5260	0.8018	7.119	1.492	1.477
0.4300	0.8174	5.131	1.096	1.102
0.3180	0.8388	3.920	0.709	0.722
0.3110	0.8392	3.881	0.702	0.701
0.3050	0.8393	3.848	0.701	0.683
0.3160	0.8395	3.908	0.698	0.715
0.3040	0.8408	3.839	0.680	0.679
0.2770	0.8461	3.679	0.608	0.600
0.2420	0.8555	3.466	0.496	0.501
0.1720	0.8745	3.047	0.324	0.323
0.1420	0.8847	2.865	0.254	0.255
0.0920	0.9040	2.563	0.155	0.152
0.0390	0.9337	2.236	0.062	0.058

<sup>a</sup>  $E = (2.24 \pm 0.06) \times 10^4$ ;  $K_A = (1.31 \pm 0.07) \times 10^4$ ;  $\sigma(\lambda) = 0.004$ .

much too low on the basis of its size. This indicates a much stronger interaction between this ion and solvent molecules as compared with the higher homologues. Similar ion-solvent effects, though not as pronounced as for the present solvent, have been observed for Me<sub>4</sub>N<sup>+</sup> in nitrobenzene<sup>17</sup> and ethylene dichloride.<sup>23</sup>

The ion-pair association constants in Table 2 indicate that association increases in the order Pr<sub>4</sub>NPi < Et<sub>4</sub>NPi < Me<sub>4</sub>NPi, i.e. with decreasing radius of the tetraalkylammonium ion (estimated<sup>24</sup> to 3.47, 4.00, and 4.52 Å for Me<sub>4</sub>N<sup>+</sup>, Et<sub>4</sub>N<sup>+</sup>, and Pr<sub>4</sub>N<sup>+</sup>, respectively). This is in accord with ion association theory. Using the Bjerrum equation<sup>16</sup> for  $K_A$  the minimum distance between the centres of charge of the ions in the ion-pair are found to be 4.4 Å for Me<sub>4</sub>NPi, 5.5 Å for Et<sub>4</sub>NPi, and 5.8 Å for Pr<sub>4</sub>NPi. These contact distances, which exceed the radii of Me<sub>4</sub>N<sup>+</sup>, Et<sub>4</sub>N<sup>+</sup>, and Pr<sub>4</sub>N<sup>+</sup> by 0.9,

Table 5. Extraction and association constants for R<sub>4</sub>N<sup>+</sup>Pi with standard deviations.

R	E <sub>QX</sub>	K <sub>A</sub> × 10 <sup>-4</sup> Distr.	K <sub>A</sub> × 10 <sup>-4</sup> Conduct.	σ(A)	σ(Δ)
CH <sub>3</sub>	1.40 ± 0.04	10.5 ± 0.8	10.27	0.003	0.08
C <sub>2</sub> H <sub>5</sub>	164.5 ± 2.2	1.89 ± 0.05	1.769	0.004	0.05
C <sub>3</sub> H <sub>7</sub>	(2.24 ± 0.06) × 10 <sup>4</sup>	1.31 ± 0.07	1.29	0.004	0.06

1.5, and 1.3 Å, respectively, seem quite reasonable taking into consideration the location of the negative charge in the picrate ion.

The results of the distribution measurements are given in Tables 4–5. From these it can be seen that the K<sub>A</sub> values obtained for tetramethyl- and tetrapropylammonium picrate are, within experimental errors, identical with the values obtained from conductivity measurements. For tetraethylammonium picrate the two sets of values seem not to be significantly different.

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