# Conductimetric Studies in Ketonic Solvents. Part V.<sup>1</sup> Quaternary Ammonium Salts in Ethyl Methyl Ketone

By S. R. C. Hughes and D. H. Price, Department of Chemistry, Chelsea College, London S.W.3

Conductances in ethyl methyl ketone at 25° are reported for a series of quaternary alkylammonium salts including the tetra-n-alkylammonium iodides and bromides from methyl up to n-octyl. Single-ion conductances have been evaluated by use of n-butyltri-isopentylammonium tetraphenylboride as the reference electrolyte. Hydrodynamic radii give no evidence of solvation of the cations while association parameters indicate anion penetration of the cations in association.

IT was remarked<sup>1</sup> that the association constant of tetra-n-butylammonium iodide in ethyl methyl ketone is considerably greater than would be predicted from sphere-in-continuum models and the suggestion has been advanced that this is due to anion penetration of the cation in association. These measurements were made to extend observations to quaternary alkylammonium ions covering a wide range of size and structural patterns.

## EXPERIMENTAL

Ethyl methyl ketone (Hopkin and Williams Ltd.) was distilled twice from Union Carbide molecular sieve type 3A, the final distillate being collected in the conductivity cell handled in a nitrogen-filled dry box. It had D = 18.014;  $\eta_0^{25} = 0.003774$  poise; \*  $d_4^{25} = 0.79955$ ; specific conductance =  $2-8 \times 10^{-10}$  ohm<sup>-1</sup> cm.<sup>-1</sup>

Tetra-n-pentylammonium bromide and iodide, tetra-nhexylammonium bromide, tetra-n-heptylammonium bromide and iodide, and tetra-n-octylammonium bromide and iodide were prepared by heating equivalent amounts of the tertiary amine and the alkyl halide in ethyl methyl ketone at 78° for up to 3 days. The product in each case was precipitated by cooling the mixture and adding ether. All these salts were purified by at least four recrystallisations from acetone-ether.

n-Butyltri-isopentylammonium iodide and n-butyltriisopentylammonium tetraphenylboride were prepared and purified as described by Coplan and Fuoss.<sup>4</sup>

Tetra-n-butylammonium tetraphenylboride was prepared by metathesis of tetra-n-butylammonium iodide and sodium tetraphenylboride in 2% aqueous solution and recrystallised from acetone-water.

Methyltri-n-propylammonium, methyltri-n-butylammonium, and methyltri-n-heptylammonium iodides were prepared by adding methyl iodide to the tertiary amine in ethanol solution. The heptyl salt required heating but the other two salts were precipitated immediately. The full vields were obtained by cooling and adding ether. The heptyl salt crystallised with difficulty owing to its low m. p.  $(43^{\circ})$ . The salts were recrystallised from acetone-ether.

The remaining quaternary ammonium salts were East-

\* Viscosities quoted in previous Parts have been based on the value for water  $\eta_0^{25} = 0.008937.^2$  The later value of  $0.008903^3$ has been used in the present work.

<sup>1</sup> Part IV, S. R. C. Hughes and S. H. White, J. Chem. Soc., 1966, 1216.

<sup>2</sup> E. C. Bingham and R. F. Jackson, Bull. U.S. Bur. Stand., 1919, **14**, 59.

<sup>3</sup> J. F. Swindells, J. R. Coc, and T. B. Godfrey, J. Res. Nat. Bur. Stand., 1952, **48**, 1.

<sup>4</sup> M. A. Coplan and R. M. Fuoss, J. Phys. Chem., 1964, 68 1177.

man-Kodak products recrystallised from methanol-water (tetramethylammonium iodide and bromide), ethanol-water (tetraethylammonium iodide and bromide), and acetoneether (the remaining salts). The salts were finely ground and dried under vacuum in the dark. Tetraethylammonium, tetra-n-butylammonium, and tetra-n-hexylammonium bromides are hygroscopic. The conductivity bridge, cells, and procedure have been described.1,5 The cells were calibrated by use of the conductance equation of Lind, Zwolenik, and Fuoss.<sup>6</sup> All additions of salts were made in the dry box and conductance runs were repeated after successive recrystallisations of each salt until agreement between  $\Lambda_0$  values was better than 0.1%. Densities of solids were determined <sup>7</sup> for all salts for use in the buoyancy corrections.

#### RESULTS

All results were analysed by the Fuoss-Kraus,8 Shedlovsky,<sup>9</sup> and Fuoss-Onsager<sup>10</sup> equations. The associated salts conformed best to the Fuoss-Onsager equation (1)

$$\Lambda = \Lambda_{0} - S_{\Lambda} \sqrt{(c\gamma)} + Ec \gamma \log c\gamma + Jc\gamma - Fc\Lambda_{0} - K_{A}c\gamma f_{\pm}^{2}\Lambda \quad (1)$$

and the two tetraphenylboride salts (unassociated) to equation (2).

$$\Lambda = \Lambda_0 - S_\Lambda \sqrt{c} + Ec \log c + Jc - Fc \Lambda_0 \qquad (2)$$

The Fuoss-Kraus equation fitted all sets of measurements better than did the semi-empirical Shedlovsky equation but both gave higher  $\Lambda_0$  and  $K_{\Lambda}$  values than the Fuoss-Onsager equation. The FOF equation,<sup>1</sup> in which  $K_{\rm A}$  is given its Fuoss value of  $(4\pi N_0 a_{\rm F}^3/3000) \exp(\epsilon^2/DkTa_{\rm F})$ , is inapposite here owing to large disparities between the  $a_J$ and  $a_{\rm F}^{\rm FO}$  parameters. Equations (1) and (2) were solved by Kay's procedure <sup>11</sup> [using the weighting factor  $(c\gamma)^{\frac{1}{2}}$ ]. The viscosity correction coefficient F was set equal to

$$2(\pi N r_{\pm}^{3})/300$$
 where  $r_{\pm} = \{(R_{+}^{3} + R_{-}^{3})/2\}^{1/3}$   
(R = Stokes radius)

The observed equivalent conductances and concentrations are in Table 1 and the parameters obtained by applying equations (1) and (2) together with the standard deviations of the individual points,  $\sigma_{\Lambda}$ , in Table 2.

- J. F. J. Dippy and S. R. C. Hughes, J. Chem. Soc., 1954, 953.
- F. E. Lind, jun. J. J. Zwolenik, and R. M. Fuoss, *J. Amer. Chem. Soc.*, 1959, 81, 1557.
  - <sup>7</sup> S. R. C. Hughes and S. H. White, unpublished work.
- <sup>6</sup> R. M. Fuoss, J. Amer. Chem. Soc., 1935, 57, 488.
  <sup>9</sup> T. Shedlovsky, J. Franklin Inst., 1938, 225, 739; R. M. Fuoss and T. Shedlovsky, J. Amer. Chem. Soc., 1949, 71, 1496.
  <sup>10</sup> R. M. Fuoss and F. Accascina, "Electrolytic Conductance,"

Interscience, New York, 1959. <sup>11</sup> R. L. Kay, J. Amer. Chem. Soc., 1960, 82, 2099.

The derived ion-size parameters and single-ion conductances are in Table 3.

Coplan and Fuoss have shown 4 that the single-ion conductances of the n-butyltri-isopentylammonium and tetraphenylboride ions are equal to within 1% in methanol. Single-ion conductances here have therefore been calculated by applying the Fowler and Kraus principle 12 to measurements for the salt n-butyltri-isopentylammonium tetraphenylboride. The average of the two results, weighted, is

$$\begin{split} [\mathrm{Pe}^{i} = (\mathrm{CH}_{3})_{2} \mathrm{CH} \cdot \mathrm{CH}_{2} \cdot \mathrm{CH}_{2} \cdot ] \\ \lambda_{0}^{+} (\mathrm{Bu}^{n} \mathrm{Pe}^{i}_{3} \mathrm{N}^{+}) = \lambda_{0}^{-} (\mathrm{Ph}_{4} \mathrm{B}^{-}) = 50 \cdot 16 \end{split}$$

The results for n-butyltri-isopentylammonium iodide yield the single-ion conductance for the iodide ion

$$\lambda_0^{-}(I^-) = 89.03$$

The average difference in  $\Lambda_0$  values for the bromide and iodide salts (excluding the methyl and ethyl salts) is 2.18 giving

$$\lambda_0^{-} (Br^{-}) = 86.85$$

The hydrodynamic radii R in Table 3 are calculated by means of Stokes law 13 from the single-ion conductances. The values of  $a_{\rm F}^{\rm FO}$  are calculated from the association constant by the Fuoss expression: 14

## $K_{\rm A} = (4\pi N_{\rm o} a_{\rm F}^3/3000) \exp(\varepsilon^2/D\boldsymbol{k}T a_{\rm F})$

The  $a_J$  values are calculated from the J coefficient of equations (1) and (2) and  $r_+, r_-$  from current estimates of ionic radii based on crystallographic and structural considerations.15

#### TABLE 1

## Equivalent conductivities of quaternary ammonium salts in ethyl methyl ketone at $25^{\circ}$

104c	$\Lambda$	10 <sup>4</sup> c	Λ	$10^{4}c$	Λ		
Me₄NI		Pe	₽NI	MeP	MePr <sup>n</sup> .NI		
0.7521	148.00	1.5579	193.73	1.9549	130.80		
0.8181	146.92	3.3494	116.17	3.0654	194.90		
0.9854	144.88	4.3093	113.02	4.0193	119.74		
1.1457	142.65	6.6444	106.90	5.1548	115.24		
1.2523	141.49	8.0738	103.86	8.2078	106.08		
1.4240	139.63	9.4788	101.25	9.5746	102.88		
1.5132	138.58	11.5176	97.939	11.4152	99.171		
		13.7654	94.844	14.1526	94.555		
		16.2301	91.905	15.6176	92.422		
Et₄NI		Hx	4NI	MeBu <sup>n</sup> 3NI			
1.7674	143.06	1.8803	119.18	2.5121	121.93		
3.1274	136.16	3.1907	114.02	4.0232	114.74		
4.0982	$132 \cdot 20$	4.3543	110.39	5.5086	109.30		
7.4190	122.01	6.4025	$105 \cdot 20$	6.6602	105.78		
8.5065	119.42	7.5611	102.79	7.9365	$102 \cdot 44$		
9.7559	116.81	8.9454	100.21	10.6771	96.567		
10.9759	114.49	10.5601	97.574	11.9804	$94 \cdot 222$		
$12 \cdot 1112$	112.53	12.0845	95.346	$13 \cdot 1199$	92.372		
13.5889	110.18	$13 \cdot 5386$	$93 \cdot 445$	$14 \cdot 8241$	89·891		
15.0496	108.08	15.1321	91.565	16.3862	87.833		
Pr <sup>n</sup> <sub>4</sub> NI		Hpt	Hpt <sup>n</sup> <sub>4</sub> NI		MeHpt <sup>n</sup> 3NI		
2.0754	130.52	5.1483	106.22	$2 \cdot 1539$	115.62		
3.7377	$123 \cdot 14$	6.2976	103.52	3.5421	109.22		
4.7743	119.49	7.5261	101.01	4.5583	105.46		
7.0278	113-11	8.8669	98.557	5.6864	101.93		
8.0068	110.80	<b>9·996</b> 0	96.708	7.5255	97.179		
9.3016	108.07	11.5346	$94 \cdot 420$	8.5582	94.902		
11.0381	$104 \cdot 88$	12.9043	92.611	9.8482	92.379		
13.0885	101.60	14.5098	90.674	10.7590	90.757		
14-4839	99·63			13.5116	86.508		
				15.0614	84.470		

		TABLE 1	(Continue	d)			
Bun <sub>4</sub> NI		Oct <sup>n</sup> <sub>4</sub> NI		Bu <sup>n</sup> P	Bu <sup>n</sup> Pe <sup>i</sup> <sub>3</sub> NI		
2.1978	124.53	2.3413	112.90	2.7304	119.96		
3.1907	120.37	4.1458	107.01	3.9527	115.46		
4.3713	116.28	5.0384	104.65	5.1196	111.90		
5.2538	113.62	6.1202	102.12	6.2942	$108 \cdot 81$		
6.3779	110.67	7.2362	99.823	7.3841	106.31		
7.8083	107.43	8.5219	97.478	8.5050	104.01		
9.4348	104.24	10.0193	95.049	9.5506	102.07		
10.3924	102.03	11.0304	92.726	10.5928	100.29		
19.0595	08.606	19.4194	90.919	11.2627	98.407		
12 0020	50 000			12.0051 14.2266	95.059		
Mal	ND.	Don	ND.	Dn N			
		re-4		Du <sup>4</sup> 4D	Pn <sub>4</sub> D		
0.1791	148.68	4.4672	102.424	2.5510	94·094		
0.2534	144.49	5.4682	99.008	3.1585	93.162		
0.2989	142.09	0.3845	90.282	3.7958	92.279		
0.2522	141.81	7.4804	93.392	4.0800	91.342		
0.3003	137.02	0.7950	90.903 88.409	6.2024	90.410		
0 0002	101 52	10.6213	86.820	7.1414	88.780		
		11.5541	85.196	8.1417	87.986		
		12.5944	83.545	9.2073	87.171		
		14.1107	81.374				
Ft.N	<b>J</b> Br	Hva	NBr	BunPei 1	NPh B (i)		
1 0100	199 77	1 5001	114.00	0.0170			
1.9128	132.11	1.9281	114.89	2.3170 9.9719	92.066		
5.7795	112.91	4.9999	06.330	3.2713 4.1056	90.000		
6.7867	108.72	8.1830	90.806	4.7894	88.865		
7.6130	106.22	9.4409	88.233	5.4608	88.181		
8.8519	102.87	10.8563	85.668	6.1488	87.528		
10.2537	99.57	12.1817	$83 \cdot 544$	6.9615	86.829		
		$13 \cdot 8665$	81.106	7.7370	86.239		
		15.1480	79.431	8.4692	85.692		
				9.1741	85.199		
Pr <sup>a</sup> 4	NBr	$Hpt^n$	₄NBr	Bu <sup>n</sup> Pe <sup>i</sup> sl	NPh <sub>4</sub> B (ii)		
1.8160	$123 \cdot 18$	1.6890	111.50	2.7342	91.621		
3.1449	114.51	2.7994	105.63	3.5508	90.497		
4.8005	106.73	3.7183	101.74	4.5591	89.325		
7.8743	96.658	$5 \cdot 4903$	95.797	5.3452	88.523		
9.3974	92.937	6.4398	93.174	6.3358	87.593		
10.9750	89.618	7.4213	90.782	7.1051	86.936		
12.7175	86.462	8.2876	88.873	7.9929	86.242		
14.4301	83.751	10.6559	84.429	8.9267	85.578		
10.1949	81.300	12.1828	82·004 79·743	9.9700	84.899		
		10 1000					
Bu <sup>n</sup> 4	NBr	Oct <sup>n</sup> ,	<sub>I</sub> NBr				
3.0503	111.85	2.0976	107.31				
5·0441	103.47	2.9696	103.11				
0.2948	99.403	3.9314	99.255				
8-6429	03.33K 29.993	0-1238 7.5785	99°314 88.079				
10.8130	88.915	8.7784	86.461				
11.8554	87.080	10.1504	83.949				
13.2416	84.849	11.8358	81.236				
14.7378	82.718	13.3792	79.036				
$Pe^n =$	$n-C_5H_{11};$	$Pe^i = (CH_3)$	),CH·CH,·	CH,; Hx =	$n-C_6H_{12}$ ;		

 $Hpt^{n} = n - C_{7}H_{15}$ ;  $Oct^{n} = n - C_{8}H_{17}$ . Other abbreviations have their usual significance.

Radii  $r_{\pm}(V_{o})$  calculated by extrapolation of partial molar volumes of aqueous solutions 16 are given for comparison in column 6 of Table 3.

The self-consistency of the cation conductances show the

12 D. L. Fowler and C. A. Kraus, J. Amer. Chem. Soc., 1940,

62, 2237. <sup>13</sup> R. A. Robinson and R. H. Stokes, "Electrolyte Solutions,"

<sup>14</sup> R. M. Fuoss, J. Amer. Chem. Soc., 1958, 80, 5059.

<sup>15</sup> Ref. 13, p. 124.
<sup>16</sup> B. E. Conway, R. E. Verrall, and J. E. Desnoyers, *Trans. Faraday Soc.*, 1966, **62**, 2738.

accuracy of the results to be well within the 0.1% thought to be satisfactory for non-aqueous solvents,<sup>17</sup> except for the tetramethylammonium and tetraethylammonium salts. This is due to their low solubilities in ethyl methyl ketone at 25°

Conductance parameters in ethyl methyl ketone at 25°

Salt	$\Lambda_0$	$K_{\mathbf{A}}$	J	σΛ
Me <sub>4</sub> NI	163.63	969	901	0.123
Et <sub>4</sub> NI	160.34	434	16,776	0.042
Pr <sup>n</sup> <sub>4</sub> NI	148.66	442	14,800	0.012
Bu <sup>n</sup> <sub>A</sub> NI	141.66	382	13,655	0.022
Pen <sub>4</sub> NI *	136.93	351	12,726	0.008
Hx <sup>n</sup> <sub>4</sub> NI	133.28	326	12,491	0.012
Hpt <sup>n</sup> ₄NI	130.50	309	12,006	0.011
Octn <sub>4</sub> NI	128.22	308	11,988	0.013
Bu <sup>n</sup> Pe <sup>i</sup> <sub>3</sub> NI	139.19	386	13,519	0.011
MePr <sup>n</sup> <sub>3</sub> NI	152.29	678	14,948	0.050
MeBu <sup>n</sup> <sub>3</sub> NI	145.69	664	14,652	0.013
MeHpt <sup>n</sup> <sub>3</sub> NI	134.93	588	13,238	0.012
Me <sub>4</sub> NBr	161.83	4544	7307	0.345
Et <sub>4</sub> NBr	158.32	958	18,556	0.023
Pr <sup>n</sup> <sub>4</sub> NBr	146.42	940	14,360	0.014
Bu <sup>n</sup> <sub>4</sub> NBr	139.50	787	13,907	0.015
Pen <sub>4</sub> NBr	134.77	761	13,754	0.012
Hx <sup>a</sup> <sub>4</sub> NBr	131.07	662	12,298	0.019
Hpt <sup>n</sup> <sub>4</sub> NBr	128.29	655	12,329	0.012
Oct <sup>n</sup> <sub>4</sub> NBr	126.08	648	12,215	0.012
Bu <sup>n</sup> <sub>4</sub> NBPh <sub>4</sub>	$102 \cdot 83$		10,817	0.009
Bu <sup>n</sup> Pe <sup>i</sup> <sub>3</sub> NBPh <sub>4</sub> (i)	100.21		10,981	0.021
Bu <sup>n</sup> Pe <sup>i</sup> <sub>3</sub> NBPh <sub>4</sub> (ii)	100.46		10,980	0.030

\* See footnote to Table 1.

### TABLE 3

## Ion conductances, ionic radii (Å), and association distances (Å)

		Ion parameters				Sa	Salt parameters			
a	Iod- ides	Brom- ides	_		r_±	Iod	lides	Bro	mides	
Cation	ծ <sub>0</sub> +	$\lambda_0^+$	$R_+$	r <sub>+</sub>	$(V_0)$	$a_{\rm J}$	$a_{\mathbf{F}}^{\mathbf{FO}}$	$a_{J}$	$a_{\mathbf{F}}^{\mathbf{FO}}$	
Me₄N+	74.60	74.98	2.91	3.47	2.85	0.6	3.38	1.7	2.73	
Et <sub>4</sub> N+	71.31	71.47	3.04	4.00	3.48	6.0	3.90	7.4	3.39	
Pr <sup>a</sup> <sub>•</sub> N <sup>+</sup>	59.63	59.57	3.64	4.52	3.98	5.5	3.89	5.4	3.40	
Bu <sup>n</sup> <sub>4</sub> N <sup>+</sup>	52.63	52.65	4.13	4.94	4.37	5.3	4.01	5.6	3.50	
Pen₄N+*	47.90	47.92	4.54	5.29	4.71	<b>4</b> ·9	4.08	5.8	3.52	
Hx <sup>n</sup> <sub>A</sub> N <sup>+</sup>	44.25	44.22	4.91	5.61	5.01	$5 \cdot 0$	<b>4</b> ·15	$5 \cdot 0$	3.60	
Hptn₄N+	41.47	41.44	5.24	5.89	5.28	<b>4</b> ·9	4.20	$5 \cdot 2$	3.61	
Oct <sup>n</sup> /N <sup>+</sup>	39.19	39.23	5.54	6.15	5.53	5.0	4.20	$5 \cdot 3$	3.62	
MePr <sup>n</sup> N <sup>+</sup>	$63 \cdot 26$		3.44	4.29		5.4	3.59		_	
MeBu <sup>n</sup> <sub>2</sub> N <sup>+</sup>	56.66		3.84	<b>4</b> ·64		5.6	3.60			
MeHpt <sup>a</sup> <sub>N</sub> <sup>+</sup>	45.90		4.73	5.46		$5 \cdot 4$	3.68			
Bu <sup>n</sup> Pe <sub>3</sub> <sup>i</sup> N <sup>+</sup>	50.16		4.33	5.21		$5 \cdot 3$	$4 \cdot 00$			
Anion	λ <sub>0</sub> -		$R_{-}$	r_						
BPh	50.16		4.33							
I- *	89.03		2.44	2.16						
Br-	86.85		2.50	1.95						
		* S	ee foo	tnote	to Ta	ble 1.				

(0.04 g./l. for tetramethylammonium iodide and 0.013 for tetramethylammonium bromide). Only one addition per run could be made for these tetramethylammonium salts, while only small (*ca.*10 mg.) additions could be made for the tetraethylammonium salts, each taking long periods to dissolve. All the other salts were sufficiently soluble to make at least 20 mg. additions.

## DISCUSSION

As explained, the absolute values of the parameters obtained for the tetramethyl and tetraethylammonium salts are less reliable than those for higher homologues although their trends with respect to the series appear to be significant (Table 3). It might be expected that the association constants for the two tetraethylammonium salts would be much higher than those found. However, considerable repetition of observations indicated the possible error in association constants for these salts to be less than 5%. In six runs with tetraethylammonium iodide, no association constant determined was higher than that obtained for tetra-n-propylammonium iodide.

As expected, the Stokes radii increase with increasing cationic weight, but less so for the larger cations owing to the larger number of conformations of the alkyl chains available to reduce overall bulk.

All the hydrodynamic radii are smaller than expected from structural estimates.<sup>15</sup> With the exception of the tetramethylammonium ion the radii of the lower-weight cations are measurably smaller than those derived from partial molar volumes in water,<sup>16</sup> but agreement becomes much closer as the series is ascended and is complete at n-octyl. Solvation of these cations, therefore, seems unlikely.

The hydrodynamic radius of the bromide ion is larger than that of the iodide ion and both are larger than the crystallographic radii suggesting that they may be solvated, bromide more so than iodide.<sup>18,1</sup> However, the association parameters of the bromides are smaller than those of the iodides. It appears that in association the anions are desolvated.

The association parameters of the quaternary ammonium salts are much smaller than the sums of the estimated overall radii, contrasting with the behaviour found for alkali halides.<sup>1</sup> This may be explained by penetration of the anion inside the external radius of the cations. This is borne out by the fact that although the comparative iodide-bromide distances remain distinct, the association parameters tend to reach constant values as the cation size increases, suggesting that the halide ion has penetrated sufficiently far inside the outer limits of the cation structure for added  $CH_2$  units to the cation to have little or no effect on the association parameter.

The three unsymmetrical methyltrialkylammonium iodides have Stokes radii in proportion to their molecular weights, but their association parameters are much smaller than those of the comparable tetra-alkylammonium iodides. Also the difference between the association parameters of methyltri-n-propylammonium and methyltri-n-heptylammonium iodides (0.09 Å) is much smaller than the difference between tetra-n-propylammonium and tetra-n-heptylammonium iodides (0.31 Å). This is again explicable on the assumption that a majority of the ion pairs are formed at optimum approach configurations unaffected by lengthening the longer alkyl chains.

The near equality of the  $a_{\rm F}^{\rm FO}$  parameters of tetra-n-

D. F. Evans, C. Zawoyski, and R. L. Kay, J. Phys. Chem., 1965, 69, 3878.
 <sup>18</sup> Ref. 13, p. 70.

butylammonium iodide and n-butyl tri-isopentylammonium iodide supports this view.

The  $a_J$  parameters show no trend with molecular weight and are almost constant  $(a_J = 5 \cdot 3 \pm 0 \cdot 3)$ .

<sup>19</sup> R. L. Kay, S. C. Blum, and H. I. Schiff, *J. Phys. Chem.*, 1963, 67, 1223; R. L. Kay, C. Zawoyski, and D. F. Evans, *ibid.*, 1965, 69, 4208. Various constant values have been found for these solutes in other solvents,<sup>17, 19</sup> making it appear that the  $a_J$ parameter depends more on the solvent than the solute.

One of us (D. H. P.) thanks the S.R.C. for a research studentship.

[6/1613 Received, December 19th, 1966]