

# SPECTROPHOTOMETRIC STUDIES OF ELECTROLYTIC DISSOCIATION

## PART 4.—SOME URANYL SALTS IN WATER

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The extent of ion-association between the uranyl and the chloride, bromide, thiocyanate and sulphate ions has been estimated from absorption measurements at 25° C. These extend into regions of low ionic strength in order to minimize errors in the calculated activity coefficients. A simple way of eliminating errors due to stray light is illustrated by means of uranyl perchlorate.

An essential feature in determining true thermodynamic constants in ionic systems is that the data should be amenable to extrapolation to zero ionic strength or that the constants should be obtained at low ionic strengths so that activity coefficients can be calculated with some degree of certainty. In the present studies

TABLE 1.—MOLAR EXTINCTION COEFFICIENTS OF  $\text{UO}_2(\text{ClO}_4)_2$  SOLUTIONS

	300 m $\mu$ , 1-cm cells						
$10^4a$	29.16	48.60	68.77	85.05	105.7	123.0	127.3
$10^4d$	60.8	85.1	110.3	130.7	156.5	178.0	183.5
$D$	0.181	0.298	0.420	0.515	0.640	0.741	0.769
$\epsilon'$	62.1	61.1	61.1	60.55	60.55	60.25	60.4
$10^3\Delta$	6.3	6.8	8.0	5.5	6.8	4.1	6.3
$\epsilon$	59.91	60.02	60.16	59.81	59.95	59.73	59.91

we have therefore continued with our policy<sup>1</sup> of keeping the concentrations as low as possible and also obtaining measurements over a range of ionic strengths. The systems reported here have all been examined in recent years but most of them were studied in high salt molarities. Consequently only approximate activity corrections can be made to them.

The absorption spectrum of the uranyl ion has a peak in the visible region at 400 m $\mu$  and a band in the u.-v. region which starts at 350 m $\mu$  and rapidly increases in magnitude at shorter wavelengths. The perchlorate ion has no effect upon the amount of absorption, and this is favourable evidence that ion-pairs are absent in such solutions. The Raman<sup>2</sup> and infra-red spectra<sup>3</sup> support this conclusion. One essential feature, however, is that the solutions must be sufficiently acid<sup>4</sup> since above a pH of about 2.5 the amount of absorption at any given wavelength steadily increases with the pH. This is attributed to the formation of hydrolytic products and we have accordingly based all our observations upon media where the effect of more  $\text{HClO}_4$  to the  $\text{UO}_2(\text{ClO}_4)_2$  solutions did not alter the amount of absorption.

As a preliminary step these solutions were examined to see if the Beer-Lambert law was obeyed. In table 1 the absorptions  $D$  were obtained with solutions containing  $\text{UO}_2(\text{ClO}_4)_2$  and  $\text{HClO}_4$  of molarities  $a$  and  $d$  respectively. The reference cell contained water, and before starting, the cells were compared when both were filled with water;  $D$  includes the difference of 0.001.

The molar extinction coefficient  $\epsilon'$  increases with decreasing concentration. This is not due to ion-pair formation since when this occurs, as our later results show, the effect is in the opposite direction. The most reasonable explanation is that the trend is due to some of the errors associated with spectrophotometric measurements, such as those listed and discussed by Davies and Prue.<sup>5</sup> These errors are chiefly due to spectral impurities in the light source, multiple reflections from the cell faces and non-parallel light beams, but other factors<sup>6</sup> may also need consideration.

Providing that the solutions are not so dilute that the spectral impurities cannot be completely absorbed, it is reasonable to suppose that the errors under a given set of conditions, such as constant wavelength, slit-width and cell, can be represented by a constant factor. To test this we calculated molar extinction coefficients from the equation,

$$\epsilon'' = (D_a - D_b)/(m_a - m_b)$$

where  $D_a$  and  $D_b$  are the values of  $D$  for solutions of molarities  $m_a$  and  $m_b$  respectively. The  $\epsilon''$  values so obtained show no significant trends with concentration or with the combinations chosen, provided the concentrations were not so close together that  $(D_a - D_b)$  becomes too small. The average value is  $\epsilon'' = 59.91 \pm 0.25$ . By using this to calculate values of  $D$  for each concentration, the factor  $\Delta = D(\text{expt.}) - D(\text{calc.})$  given in the table was obtained. Within experimental error these differences are constant ( $0.0063 \pm 0.0009$ ) and they can be regarded as the amount of radiation which is totally absorbed by all the solutions. Using the average value of  $\Delta$  to correct each  $D(\text{expt.})$ , the final row in table 1 gives the true molar extinction coefficients  $\epsilon$ . The average is  $59.93 \pm 0.11$ , which verifies the Beer-Lambert law for this salt. Thus provided ion-association is absent we have a simple way of correcting the stray light error in spectrophotometry, but it will apply only when the absorption measurements are obtained with the solvent as reference. With the methods used for the results given in tables 2, 3, 4 and the first method used for  $\text{UO}_2\text{SO}_4$  (table 5), and for those of part 3 of this series,<sup>1</sup> where the reference is a solution of the absorbing ion in the absence of ion-pairs, the stray light factor cancels out. On the other hand with the second and third methods of studying  $\text{UO}_2\text{SO}_4$ , since the reference is the solvent, allowance has to be made. This is also true for our results for thiosulphates<sup>18, 19</sup> since these are based upon extrapolations to obtain the extinction coefficient of the thio-sulphate ion using absorptions of the sodium salt against the solvent. Since the stray light factor was not considered in these systems, the results are consequently in error to some extent. This applies particularly to the work where the solvent was 50 % ethanol,<sup>19</sup> and our present findings no doubt account for the difficulty in obtaining a linear extrapolation; this was commented upon at the time.

## EXPERIMENTAL

Optical measurements were made with a Hilger Uvispek and a Unicam S.P.500 spectrophotometer, using 1- and 4-cm quartz cells. The cells were maintained at 25° C by using water-jacketed cell holders through which flowed water from a constant-head thermostat. The technique of filling the cells has been described previously.<sup>7</sup>

Uranyl perchlorate was made by precipitating  $\text{UO}_3$  from solutions of the A.R. nitrate or acetate, washing this free from foreign salts and then dissolving it in A.R.  $\text{HClO}_4$ . The U content was found by gravimetric analysis via  $\text{U}_3\text{O}_8$  and the total  $\text{ClO}_4$  by passing a sample of the solution through a  $\text{H}^+$ -ion exchange resin column and titrating the liberated acid with  $\text{NaOH}$ . The excess  $\text{HClO}_4$  was calculated from these two figures. All the other chemicals used were of A.R. quality, the  $\text{NaClO}_4$  being formed from the acid and base.

### CHLORIDE

Some specimen data are given in table 2, where  $b = \text{NaCl}$ ,  $c = \text{NaClO}_4$  molarities,  $I =$  ionic strength,  $D_1 - D_2 =$  absorption difference between solutions of molarities

$a + b + c + d$  and  $a + d$  respectively, and  $K$  = dissociation constant. The figures given in the left-hand columns were used to obtain, by the constant  $I$  method <sup>1</sup> (method 1, part 3), the values of  $1/(\epsilon_2 - \epsilon_1)$ , where  $\epsilon_1$  and  $\epsilon_2$  are the molar extinction coefficients of

TABLE 2.—DATA FOR  $K(\text{UO}_2\text{Cl}^+)$   
320  $\text{m}\mu$ , 1-cm cells,  $10^3a = 13.10$ ,  $10^3d = 13.1$ ,  $1/(\epsilon_2 - \epsilon_1) = 0.0125$

	7.00	6.00	5.00	4.00	2.00	2.50	3.50	5.00	6.00
$10^2b$	8.00	—	—	—	—	—	—	—	—
$10^2c$	1.0	2.0	3.0	4.0	—	—	—	—	—
$D_1 - D_2$	0.220	0.195	0.167	0.137	0.086	0.098	0.127	0.169	0.195
$I$	0.85	0.85	0.852	0.852	0.254	0.303	0.403	0.552	0.651
$K$	0.63	0.63	0.63	0.63	0.60	0.60	0.61	0.61	0.61

TABLE 3.—DATA FOR  $K(\text{UO}_2\text{Br}^+)$   
338  $\text{m}\mu$ , 1-cm cells,  $10^3a = 22.6$  (45.20\*),  $10^3d = 9.1$  (18.2\*)

	25.0	20.0	15.0	10.0	15.0	25.0	40.0
$10^2b$	30.0	—	—	—	—	—	—
$10^2c$	5.0	10.0	15.0	—	—	—	—
$D_1 - D_2$	0.133	0.090	0.068	0.057	0.089	0.126	0.334*
$I$	0.367	0.367	0.367	0.168	0.217	0.317	0.532*
$K$	1.7	1.7	1.7	1.7	1.5	1.55	1.7*

the  $\text{UO}_2^{2+}$  and  $\text{UO}_2\text{Cl}^+$  species. The values of  $K$  were calculated for each solution by 1 method 2 of part 3, using  $C = 0.2$  in the activity coefficient expression (eqn. (7), part 3). The ionic strengths were calculated from  $I = 3a + b + c + d - 2x$ , where  $x = [\text{UO}_2\text{Cl}^+]$ .

TABLE 4.—DATA FOR  $K(\text{UO}_2\text{CNS}^+)$ ; 430 m $\mu$ , 1-cm cells

$10^3a$	13.01	13.01	13.01	11.30	11.30	11.30	11.30
$10^3d$	2.9	2.9	2.9	4.6	4.6	4.6	4.6
$10^3b$	68.6	29.1	19.4	14.6	24.3	24.3	24.3
$10^3c$	—	9.9	29.8	—	—	—	—
$D_1 - D_2$	0.475	0.390	0.206	0.153	0.238	0.238	0.238
$I$	0.077	0.077	0.077	0.047	0.056	0.056	0.056
$K$	0.12	0.12	0.12	0.122	0.118	0.118	0.118

TABLE 5.—DATA FOR  $K(\text{UO}_2\text{SO}_4)$ 

	300 m $\mu$ , 1-cm cells, $10^3a = 48.60$ , $10^3d = 85.1$ , $D_2 = 0.298$											
$10^3b$	50.06	45.11	40.16	35.02	30.07	25.12	10.28	19.99	35.02	56.15	—	—
$10^3c$	—	15.3	30.5	45.7	50.9	75.1	—	—	—	—	—	—
$D$	0.743	0.708 <sub>5</sub>	0.674	0.634 <sub>5</sub>	0.593 <sub>5</sub>	0.552	0.416	0.515	0.641	0.778	—	—
$10^3x$	17.22	15.89	14.55	13.02	11.44	9.83	4.57	8.40	13.27	18.57	—	—
$10^3y$	9.15	8.17	7.18	6.20	5.30	4.33	1.76	3.58	6.32	10.26	—	—
$10^3I$	29.4	30.15	31.0	31.7	31.55	33.55	24.0	25.0	27.0	30.45	—	—
$10^3K$	11.9	11.8	11.8	11.4	11.5	11.1	11.6	11.4	11.8	11.9	—	—

## BROMIDE

Similar measurements using NaBr are summarized in table 2. The value of  $1/(\epsilon_2 - \epsilon_1)$  is 0.0075, but a second series at  $I = 0.54$  gave 0.0085. The mean of these was used to calculate  $K$ , which has a consequent uncertainty of 6 %. With large dissociation constants such as this considerable variations are to be expected.

## IODIDE AND CHLORATE

No real indication of ion-association was found but owing to the slow liberation of iodine, precise data could not be obtained for the iodide.

## THIOCYANATE

Three constant  $I$  runs (using  $\text{NH}_4\text{CNS}$ ) gave  $1/(\epsilon_2 - \epsilon_1) = 0.00370 \pm 0.00009$ . Some of our results are given in table 4.

## SULPHATE

In table 5,  $b = \text{Li}_2\text{SO}_4$ ,  $D_2$  is the absorption of the  $\text{UO}_2(\text{ClO}_4)_2 + \text{HClO}_4$  solution against water, and  $D$  is the corresponding absorption containing  $\text{Li}_2\text{SO}_4$  (and  $\text{NaClO}_4$  in some cases).

Figures from the first six columns of table 5 were used to obtain  $1/(\epsilon_2 - \epsilon_1)$  by the constant  $I$  method, exactly<sup>1</sup> as for  $\text{CuSO}_4$  in part 3. Here  $x = [\text{UO}_2\text{SO}_4]$  and  $y = [\text{HSO}_4^-]$ . These gave the figure of 0.00387, and this was used to calculate the  $K$  values given in the table.

An alternative procedure is to find that concentration of  $\text{UO}_2(\text{ClO}_4)_2$  which has the same  $D$  value as a solution containing  $\text{UO}_2\text{SO}_4$  ion-pairs. We then have

$$x = (a_2 - a_1)\epsilon_1/(\epsilon_2 - \epsilon_1),$$

where  $a_2$  and  $a_1$  are the stoichiometric molarities of  $\text{UO}_2^{2+}$  in the solutions with and without sulphate respectively. Since it has been established from the data in table 1 that  $\epsilon_1 = 59.93$ , it is easy to calculate the values of  $a_1$  corresponding to the  $D$  values in table 5, and hence  $x$  can be calculated. However, the measured values of  $D$  need correcting for the stray light factor  $\Delta$ , and this has been taken to be identical with that found for  $\text{UO}_2(\text{ClO}_4)_2$ , i.e. 0.0063. The  $K$  values obtained in this way are almost identical with those obtained by the first method and the average of the two sets is  $K = 0.00116 \pm 0.000025$ .

An alternative procedure of plotting the constant  $I$  data has been given by Newton and Arcand.<sup>8</sup> Using the present symbols this involves plotting  $D$  against

$$(D - D_2)/(b - x - y).$$

Extrapolation (after applying the stray light correction of 0.0063) to the point where the latter function is zero gives a value of  $D$  corresponding to all the uranyl ion being present as  $\text{UO}_2\text{SO}_4$  ion-pairs. By the method of least mean squares our results give 1.557 and this corresponds to  $1/(\epsilon_2 - \epsilon_1) = 0.00386$ . This is only 0.3 % different from the figure given earlier and would result in  $K$  being 1 % higher than that cited.

All our answers for the sulphate so far depend upon one set of constant  $I$  data. To obtain some independent answers, runs at another wavelength (330  $\mu\mu$ ) and under varying conditions were made. These are summarized below.

$10^3a$	$I$	$1/(\epsilon_2 - \epsilon_1)$	$10^4K$
5.65	0.30	0.0201	11.3 ( $\pm 0.2$ )
1.13	0.01-0.09	0.0201	11.6 ( $\pm 0.4$ )
12.20	0.085	0.0204	12.5 ( $\pm 0.3$ )
12.20	0.056-0.123	0.0204	11.5 ( $\pm 0.3$ )

Another approach which proved of interest was to take a very dilute  $\text{UO}_2(\text{ClO}_4)_2$  solution and to measure the absorption differences with a very wide concentration of sulphate. The measurements obtained using low sulphate concentrations were then used to calculate values of  $K$  using various values of  $1/(\epsilon_2 - \epsilon_1)$ . The consequences of this are shown by fig. 1. On plotting  $K$  against  $I$ , they all tend to the value of  $0.00105 \pm 0.00005$ , which is about 10 % lower than the average of the other figures. This somewhat empirical approach confirms that even if our derived values of  $1/(\epsilon_2 - \epsilon_1)$  are not exact, any error does not seriously affect the final answer. One explanation for this last answer being lower than the others is that our extrapolations are not very certain. Another

point which may have some significance is that no allowance has been made anywhere for the possible  $\text{LiSO}_4$  and  $\text{NaSO}_4$  ion-pairs. It has been calculated from conductivity evidence<sup>9</sup> that these have dissociation constants of about 0.2. It may be significant that the results given in table 5 tend to become a little smaller at lower sulphate concentrations and a rough extrapolation would place the answer at zero concentration about 4 to 5 % lower than the overall average figure of 0.00116 quoted for those results. In addition if allowance is made for these species in fig. 1, the top curves tend to flatten

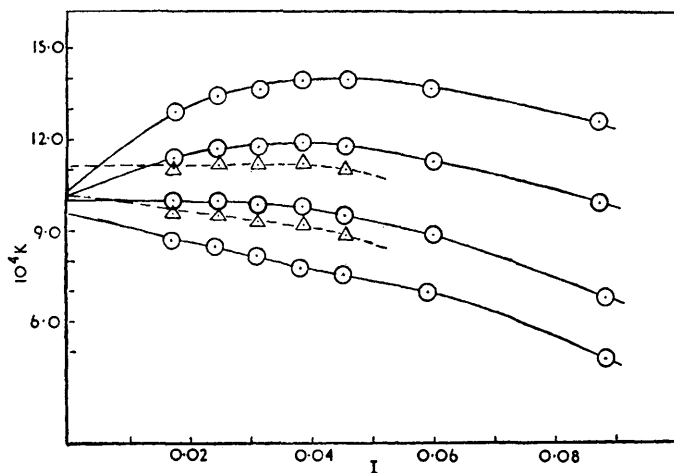


FIG. 1.—Plot of  $K(\text{UO}_2\text{SO}_4)$  against  $I$ ; broken lines, allowing for  $\text{LiSO}_4^-$ .

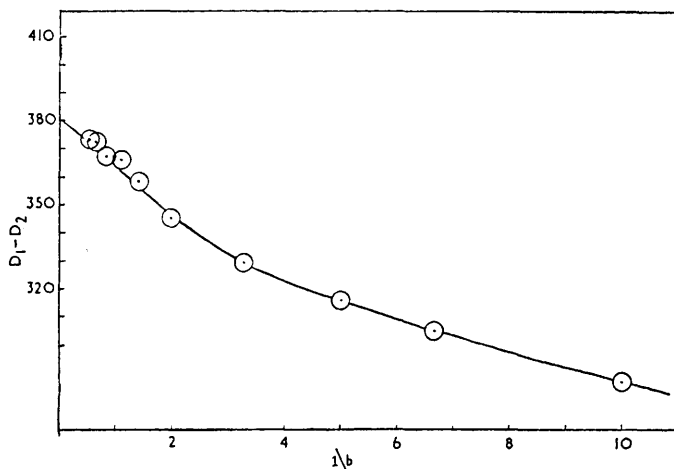


FIG. 2.—Plot of  $D_1 - D_2$  against  $1/[\text{sulphate}]$ .

out and the lower ones tend to be a little steeper. This is shown by the dotted lines, which are based on such an allowance. The top one is remarkable constant over the last four points ( $K = 0.00111$ ) and in closer agreement with our other results. However, without further evidence to support that from conductivity, one cannot fully justify this extra correction. In general, the overall average of  $K = 0.0011 \pm 5\%$  is probably a fair estimate.

In the presence of high concentrations of sulphate it was found that the absorptions were higher than expected. As fig. 2 shows, the limiting value of  $D_1 - D_2$  is about 0.380 while the calculated value for complete  $\text{UO}_2\text{SO}_4$  formation is around 0.290. Due allowance was made for the absorptions of the concentrated  $\text{Li}_2\text{SO}_4$  solutions used. This

high limiting value of  $D_1 - D_2$  can be attributed to a second stage of association resulting in the formation of  $\text{UO}_2(\text{SO}_4)_2^{2-}$ . An estimate of the second dissociation constant, i.e.,

$$K_2 = [\text{UO}_2\text{SO}_4][\text{SO}_4^{2-}]/[\text{UO}_2(\text{SO}_4)_2^{2-}]$$

was attempted as follows. If  $x_2$  is the concentration of the second complex, at the higher concentrations of  $\text{Li}_2\text{SO}_4$ ,  $[\text{UO}_2^{2+}]$  is negligible and  $[\text{UO}_2\text{SO}_4] = a - x_2$ . We thus have

$$D_1 - D_2 = a(\epsilon_2 - \epsilon_1) + x_2(\epsilon_3 - \epsilon_2),$$

where  $\epsilon_3$  refers to the second complex. From fig. 1 a possible value of  $1/(\epsilon_2 - \epsilon_1) = 0.0182$ , giving  $\epsilon_2 - \epsilon_1 = 55.0$ . From  $(D_1 - D_2)_{\text{max.}} = 0.380$  in 4-cm cells,  $\epsilon_3 - \epsilon_1 = 72.0$ , whence  $\epsilon_3 - \epsilon_1 = 17.0$ . Our resultant calculations are shown in table 6.

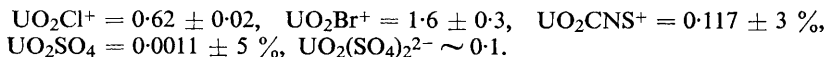
TABLE 6.—DATA FOR  $K(\text{UO}_2)(\text{SO}_4)_2^{2-}$ . 326  $\mu$ , 4-CM CELLS,  $10^4 a = 13.20$

$b$	$d$	$(D_1 - D_2)(\text{obs.})$	$(D_1 - D_2)(\text{corr.})$	$K_2$
0.20	0.0044	0.330	0.316	0.52
0.30	0.0053	0.350	0.329	0.40
0.50	0.0065	0.380	0.345	0.32
0.70	0.0076	0.405	0.358	0.28
0.90	0.0085	0.426	0.366	0.17
1.20	0.0098	0.398	0.367	—
1.50	0.0107	0.410	0.372	—
1.80	0.0120	0.418	0.373	—

The  $K_2$  figures extrapolate to about 0.1, but this is only a rough value. Owing to the large and somewhat uncertain corrections for the  $\text{Li}_2\text{SO}_4$  absorption, the corrected measurements are not very precise and any errors have a large effect upon  $K_2$  and upon the limiting value of  $D_1 - D_2$ .

## DISCUSSION

The average dissociation constants obtained in the present work are:



Ahrland<sup>10</sup> has reviewed the evidence obtained up to 1951 for the dissociation of  $\text{UO}_2\text{Cl}^+$ . From this earlier work  $K = 0.42$ . Ahrland himself used potentiometric and absorption methods and obtained 1.25 and  $2.0 \pm 0.3$  at  $I = 1.0$ . Making an allowance for activity coefficients<sup>1</sup> (eqn. (7), part 3) lowers these to 0.3 and 0.5. These roughly correspond to our own figure but owing to the high value of  $I = 1.0$  the corrections are very uncertain. His figure for the bromide,<sup>10</sup> obtained by potentiometry is 2.0, i.e. 0.5 when corrected. This is somewhat lower than our estimate but Ahrland states that owing to systematic errors his method probably gives low results (in terms of dissociation constants).

The only previous study of the thiocyanate system appears to be that of Ahrland,<sup>11</sup> who from absorption measurements postulated that  $\text{UO}_2\text{CNS}^+$ ,  $\text{UO}_2(\text{CNS})_2$  and  $\text{UO}_2(\text{CNS})_3^-$  ion-pairs can form. In terms of dissociation constants and applying the rough correction for  $I = 1.0$  mentioned above, his result for the first species is 0.045, i.e. about half our value. We did not obtain any evidence to suggest that the other species can form.

Betts and Michels<sup>12</sup> were the first to attempt a quantitative assessment of the extent of dissociation of uranyl sulphate. Their result, obtained by spectrophotometry, when converted to a concentration dissociation constant, is about 20. Since this was obtained at  $I = 2.65$  no attempt can be made to derive the true figure. Ahrland,<sup>11</sup> working at  $I = 1.0$  concluded that up to  $\text{UO}_2(\text{SO}_4)_3^{4-}$  formation could occur. His values for the association constant of  $\text{UO}_2\text{SO}_4$  are  $50 \pm 10$  (potentiometric) and  $56 \pm 6$  (extinctionmetric). Making a rough activity coefficient correction as before, the dissociation constant is about 0.0012, in good agreement with our figure.

Another investigation is that of Brown<sup>13</sup> *et al.*, who measured the conductivity of uranyl sulphate solutions. Very large corrections were needed to allow for the acidity resulting from hydrolysis, but their average dissociation constant at 25° C from  $5 \times 10^{-5}$  to 0.05 M is  $0.00082 \pm 22\%$ , which considering the uncertainties involved, is in reasonable agreement with Åhrland's figure after correction and with our own.

From infra-red data,<sup>3</sup> the U—O distance is 1.90 Å, while the application<sup>14</sup> of Stokes's law to the conductivity value at zero concentration ( $\lambda^\circ = 132$ ) gives the cation and anion radii as 3.5 and 2.3 Å. However, there is much evidence to indicate that Stokes's law, in the form used, gives ionic radii which are too small. If the tentative correction factors of Robinson and Stokes<sup>15</sup> are applied to these two ions, the hydrated radii are 4.2 and 3.7 Å, averaging 4.0 Å. Using Bjerrum's functions<sup>16</sup> and  $K = 0.0011$ , the mean radius of the ion-pair is 2.8 Å. The difference of  $4.0 - 2.8 = 1.2$  is about the same as the radius of the water molecule<sup>17</sup> (1.7 Å). One possible explanation is that the ion-pair is formed by association of the anion with the unhydrated cation.

We wish to express thanks to the Royal Society for providing a calculating machine, and to Imperial Chemical Industries Limited for providing the Uvispeck spectrophotometer.

<sup>1</sup> Bale, Davies and Monk, *Trans. Faraday Soc.*, 1956, **52**, 816.

<sup>2</sup> Crandall, *J. Chem. Physics*, 1949, **17**, 602.

<sup>3</sup> Jones and Penneman, *J. Chem. Physics*, 1953, **21**, 542.

<sup>4</sup> Åhrland, *Acta Chem. Scand.*, 1949, **3**, 374.

<sup>5</sup> Davies and Prue, *Trans. Faraday Soc.*, 1955, **51**, 1045.

<sup>6</sup> Goldring, Hawes, Hare, Beckman and Stickney, *Anal. Chem.*, 1953, **25**, 869.

<sup>7</sup> Thomas and Monk, *Trans. Faraday Soc.*, 1956, **52**, 685.

<sup>8</sup> Newton and Arcand, *J. Amer. Chem. Soc.*, 1953, **75**, 2449.

<sup>9</sup> Righellato and Davies, *Trans. Faraday Soc.*, 1930, **26**, 592.

<sup>10</sup> Åhrland, *Acta. Chem. Scand.*, 1951, **5**, 1271.

<sup>11</sup> Åhrland, *Acta. Chem. Scand.*, 1949, **3**, 1067.

<sup>12</sup> Betts and Michels, *J. Chem. Soc.*, 1949, S286.

<sup>13</sup> Brown, Bunger, Marshall and Secoy, 1952, United States Atomic Energy Commission, AECD-3488 (rev.).

<sup>14</sup> Jenkins and Monk, *J. Chem. Soc.*, 1951, 68.

<sup>15</sup> Robinson and Stokes, *Electrolyte Solutions* (Butterworths, London, 1955), p. 119.

<sup>16</sup> Bjerrum, *Kgl. Danske Vidensk. Selskab. Mat-fys Medd.*, 1926, **7**, no. 9.

<sup>17</sup> ref. (15), p. 3.

<sup>18</sup> Gimblett and Monk, *Trans. Faraday Soc.*, 1955, **51**, 793.

<sup>19</sup> Thomas and Monk, *Trans. Faraday Soc.*, 1956, **52**, 685.