# Solutions of Electrolytes in Liquid Ammonia. Part V.[1] Ion-pair Formation by Ammonium Nitrate and Ammonium Iodide in Liquid Ammonia at −40 °C

By **J. B. Gill**, Department of Inorganic Chemistry, The University, Leeds LS2 9JT
**B. M. Lowe**,* Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

Ion-pair and triple ion formation constants ($K_A$ and $K_T$) have been obtained for $NH_4NO_3$ and $NH_4I$ in liquid ammonia at −40 °C from previously reported activity coefficient measurements. For $NH_4NO_3$, $K_A = 401 \pm 9$ dm$^3$ mol$^{-1}$ and $K_T = 11{\cdot}4 \pm 0{\cdot}7$ dm$^3$ mol$^{-1}$, and for $NH_4I$, $K_A = 476 \pm 20$ dm$^3$ mol$^{-1}$ and $K_T = 6{\cdot}5 \pm 0{\cdot}8$ dm$^3$ mol$^{-1}$, when the size parameter in the Debye–Hückel equation is set at the Bjerrum critical distance ($16{\cdot}22 \times 10^{-10}$ m). Revised activity coefficients based on this analysis are presented.

Two previous papers [1,2] in this series have dealt with the activities of ammonium nitrate and ammonium iodide in liquid ammonia solutions determined from the e.m.f.'s of concentration cells with transport. In both papers the activity coefficients were established empirically by the extrapolation of $\log_{10}(\gamma/\gamma_1)$ [where $\gamma$ and $\gamma_1$ are the mean molal stoicheiometric activity coefficients at molalities $m$ and $m_1$ ($= 0{\cdot}01$ mol kg$^{-1}$) respectively] † against a function of concentration. It was found, for both salts, that when this function was $m^{\frac{1}{4}}$ rather than $m^{\frac{1}{2}}$, or $m^{\frac{1}{2}}/(1 + m^{\frac{1}{2}})$, which would be expected from the Debye–Hückel theory, an almost linear relationship over the concentration range $10^{-3}$—$10^{-1}$ mol kg$^{-1}$ was obtained. It was noted [2] that the apparent breakdown of the Debye–Hückel equation might have arisen from ion-pair formation but no attempt was made to obtain activity coefficients from the experimental $\log_{10}(\gamma/\gamma_1)$ results on this basis. The relative permittivity of liquid ammonia [3] ($\varepsilon_r = 22{\cdot}1$) is so low that the Bjerrum critical distance ($q = z^2e^2/2\varepsilon_0\varepsilon_r kT = 16{\cdot}22 \times 10^{-10}$ m) for a 1 : 1 electrolyte [4-6] at −40 °C is much larger than the sum of the ionic crystal radii $(1{\cdot}43 + 1{\cdot}96) \times 10^{-10}$ for $NH_4NO_3$ and $(1{\cdot}43 + 2{\cdot}24) \times 10^{-10}$ m for $NH_4I$.[7] Ion-pairing and even triple ion formation in these solutions is therefore probable and consequently we have reanalysed the $\log_{10}(\gamma/\gamma_1)$ results [1,2] with the assumption that ion association occurs and that the activity coefficients, $\gamma_i$, of the free non-associated ions may be described by the Debye–Hückel equation.

The association processes may be represented by the equations,

$$M^+ \text{(solv)} + X^- \text{(solv)} = M^+X^- \text{(solv)} \quad (1)$$

$$M^+ \text{(solv)} + M^+X^- \text{(solv)} = M^+X^-M^+ \text{(solv)} \quad (2)$$

$$X^- \text{(solv)} + M^+X^- \text{(solv)} = X^-M^+X^- \text{(solv)} \quad (3)$$

where $M^+X^-$ (solv), $M^+X^-M^+$ (solv), and $X^-M^+X^-$ (solv) represent ion clusters within which the ions may or may not be solvent separated. From the experimental measurements it is impossible to distinguish between the two possible triple ions, and we shall assume $X^-M^+X^-$ occurs. (The equations which result are independent of this choice.) The concentrations may then be represented by $[M^+] = m\alpha$, $[X^-M^+X^-] = m\beta$, $[X^-] = m(\alpha - \beta)$, and $[M^+X^-] = m(1 - \alpha - \beta)$ where $m$ is the stoicheiometric molality. The ionic strength $I$ is independent of the triple ion concentration and is given by $I = m\alpha$. The ion-pair and triple ion formation constants are respectively,

$$K_A = (M^+X^-)/(M^+)(X^-) = (1 - \alpha - \beta)/\alpha(\alpha - \beta)\, m\, \gamma_i^2 \quad (4)$$

$$K_T = (X^-M^+X^-)/(X^-)(M^+X^-) = \beta/(\alpha - \beta)(1 - \alpha - \beta)\, m \quad (5)$$

In equation (4) the activity coefficient of the electrically neutral ion pair has been neglected and in equation (5) we assume the activity coefficient product $(\gamma_{XMX^-}/\gamma_{X^-}\gamma_{M^+X^-}) = 1$. When triple ions are not formed $\beta = K_T = 0$ and equation (4) becomes

$$K_A = (1 - \alpha)/\alpha^2 m\, \gamma_i^2 \quad (6)$$

The stoicheiometric activity coefficient of the salt is related to the ionic activity coefficient by the equation

$$\gamma^2 = \gamma_i^2\alpha(\alpha - \beta) \quad (7)$$

or when $\beta = 0$ by

$$\gamma = \gamma_i\alpha \quad (8)$$

Provided that the mean ionic strength $m\alpha$ is small it may be assumed that the mean molal ionic activity coefficient $\gamma_i$ is given by the Debye–Hückel equation in the form

$$\log \gamma_i = -A\, d_0^{\frac{1}{2}}(m\alpha)^{\frac{1}{2}}/[1 + B\, d(d_0 m\alpha)^{\frac{1}{2}}] \quad (9)$$

where $A = 4{\cdot}9341$ dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$, $10^{-10}$ $B = 0{\cdot}7006$ dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$ m$^{-1}$, and $d_0$ the density of liquid ammonia [8] at −40 °C = 0·6990 kg dm$^{-3}$. (The values of $A$ and $B$ were derived [9] with fundamental constants from ref. 10,

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† In Part II [2] and Part IV [1] $\gamma$ and $m$ were denoted by $\gamma_2$ and $m_2$.

[1] Part IV, J. Baldwin, J. Evans, and J. B. Gill, *J. Chem. Soc.* (*A*), 1971, 3389.

[2] J. Baldwin and J. B. Gill, *J. Chem. Soc.* (*A*), 1971, 2040.

[3] J. Baldwin and J. B. Gill, *Phys. and Chem. Liquids*, 1970, **2**, 25.

[4] N. Bjerrum, *Kgl. Danske Vid. Selsk.*, 1926, **7**, No. 9.

[5] R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' Butterworths, London, 1959, ch. 14.

[6] J. E. Prue, ' Ionic Equilibria,' Pergamon, London, 1966, ch. 10.

[7] W. L. Masterton, D. Bolocofsky, and T. P. Lee, *J. Phys. Chem.*, 1971, **75**, 2809.

[8] C. S. Cragoe and D. E. Harper, *J. Amer. Chem. Soc.*, 1920, **42**, 206.

[9] Ref. 5, ch. 9.

[10] F. D. Rossini, *Pure Appl. Chem.*, 1964, **9**, 453.

using $\varepsilon_r = 22{\cdot}1$ for the relative permittivity.[3]) For solutions in which extensive ion pair formation occurs the size parameter $d$ is best treated as the ionic separation beyond which ion pair formation can be considered to have ceased, and in this case the best estimate of $d$ is probably the Bjerrum critical distance $q$.[4-6]

### PROCEDURE

Two approaches were adopted for the calculations. For the first, triple ion formation was neglected and the values of $K_A$ and $\gamma_1$ (the value of $\gamma$ for the 0·01 molal reference solution) which provided the ' best fit ' to the experimental $\log_{10}(\gamma/\gamma_1)$ results were obtained by the use of equations (6), (8), and (9), whilst in the second, ' best fit ' values of $K_A$, $K_T$, and $\gamma_1$ were obtained by means of equations (4), (5), (7), and (9). The two computer programmes * (G1 and G2) used for these calculations were written in Fortran and used a general least squares procedure to obtain the values of the parameters which gave the ' best fit ' to the experimental results as measured by the standard deviation $\sigma$ given by equation (10) in which $n$ is the number of unknown

$$\sigma = \left\{\frac{1}{N-n}\sum_{1}^{N}\left[\log_{10}\left(\frac{\gamma}{\gamma_1}\right)_{\text{obs}} - \log_{10}\left(\frac{\gamma}{\gamma_1}\right)_{\text{calc}}\right]^2\right\}^{\frac{1}{2}} \qquad (10)$$

parameters and $N$ the number of observations. Calculations were carried out for fixed values of the $d$-parameter.

A check on programme G2 was obtained from an analysis of the log $(\gamma/\gamma_1)$ results obtained by Pethybridge and Prue [11] for iodic acid solutions in which the triple ion $H^+(IO_3^-)_2$ is formed. The value obtained for $\log_{10}\gamma_1$ (Table 1) is in excellent agreement with that of Pethybridge and Prue.[11] The slight differences between our values and theirs for $K_A$ and $K_T$ may be readily accounted for since a small decrease in $K_A$ can be compensated for by an increase in $K_T$ with very little effect on the standard deviation.

TABLE 1

Recalculation of $\gamma_1$, $K_A$, and $K_T$ for iodic acid [a]

| $10^{10}\,d$/m | $\gamma_1$ | $-\log_{10}\gamma_1$ | $K_A$/kg mol$^{-1}$ | $K_T$/kg mol$^{-1}$ | $10^3\,\sigma$ | |
|---|---|---|---|---|---|---|
| 5 | $0{\cdot}582_8 \pm 0{\cdot}0003$ | $0{\cdot}234_5$ | 7·34 ± 0·06 | 1·75 ± 0·14 | 0·3 | Programme G2 [b] |
| 5 | $0{\cdot}583_5 \pm 0{\cdot}0003$ | $0{\cdot}234_0$ | 7·16 ± 0·05 | 2·04 ± 0·10 | 0·4 | Programme G2 [c] |
| 5 | $0{\cdot}582_3$ | $0{\cdot}234_5$ | 6·37 | 4·0 | 2·5 [d] | Ref. 11 |

[a] From values of $\log_{10}\gamma/\gamma_1$ given in ref. 11. [b] The point $\log_{10}\gamma/\gamma_1 = 0{\cdot}0$ for $m = m_1 = 0{\cdot}09362$ mol kg$^{-1}$ was omitted. [c] The point $\log_{10}\gamma/\gamma_1 = 0{\cdot}0$ for $m = m_1 = 0{\cdot}09362$ mol kg$^{-1}$ was included. [d] Calculated with programme G2 for the parameters reported in ref. 11.

TABLE 2

Parameters for ammonium nitrate solutions

| | $K_T = 0$ | | | | $K_T \neq 0$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $10^{10}\,d$/m | $K_A$/kg mol$^{-1}$ | $\gamma_1$ | $-\log_{10}\gamma_1$ | $10^3\,\sigma$ | $K_A$/kg mol$^{-1}$ | $K_T$/kg mol$^{-1}$ | $\gamma_1$ | $-\log_{10}\gamma_1$ | $10^3\,\sigma$ |
| 20·0 | 369 ± 12 | 0·362 ± 0·004 | 0·441 | 5·2 | 289 ± 6 | 7·7 ± 0·4 | 0·379 ± 0·002 | 0·421 | 4·4 |
| 16·22 | 362 ± 12 | 0·359 ± 0·004 | 0·445 | 5·4 | 277 ± 6 | 8·0 ± 0·5 | 0·378 ± 0·002 | 0·423 | 4·4 |
| 10·0 | 328 ± 12 | 0·358 ± 0·004 | 0·446 | 5·6 | 240 ± 6 | 7·6 ± 0·5 | 0·377 ± 0·002 | 0·424 | 4·4 |
| 5·0 | 215 ± 8 | 0·373 ± 0·003 | 0·429 | 4·7 | 179 ± 5 | 2·6 ± 0·6 | 0·381 ± 0·002 | 0·419 | 4·4 |
| 3·39 | 97 ± 7 | 0·399 ± 0·004 | 0·399 | 5·8 | 148 ± 5 | −3·2 ± 0·6 | 0·385 ± 0·002 | 0·414 | 4·5 |

TABLE 3

Parameters for ammonium iodide solutions

| | $K_T = 0$ | | | | $K_T \neq 0$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $10^{10}\,d$/m | $K_A$/kg mol$^{-1}$ | $\gamma_1$ | $-\log_{10}\gamma_1$ | $10^3\,\sigma$ | $K_A$/kg mol$^{-1}$ | $K_T$/kg mol$^{-1}$ | $\gamma_1$ | $-\log_{10}\gamma_1$ | $10^3\,\sigma$ |
| 20·0 | 397 ± 23 | 0·363 ± 0·007 | 0·439 | 8·3 | 340 ± 14 | 4·4 ± 0·6 | 0·374 ± 0·004 | 0·427 | 7·9 |
| 16·22 | 392 ± 23 | 0·361 ± 0·007 | 0·443 | 8·5 | 328 ± 14 | 4·5 ± 0·6 | 0·373 ± 0·004 | 0·429 | 8·0 |
| 10·00 | 359 ± 23 | 0·359 ± 0·007 | 0·445 | 8·8 | 290 ± 13 | 4·4 ± 0·7 | 0·372 ± 0·004 | 0·429 | 8·0 |
| 5·0 | 243 ± 16 | 0·373 ± 0·006 | 0·428 | 7·6 | 226 ± 12 | 0·8 ± 0·7 | 0·377 ± 0·004 | 0·424 | 7·8 |
| 3·67 | 143 ± 14 | 0·393 ± 0·006 | 0·406 | 8·5 | 196 ± 11 | −2·2 ± 0·7 | 0·381 ± 0·003 | 0·420 | 7·6 |

### RESULTS AND DISCUSSION

The parameters obtained for selected values of $d$ are shown for ammonium nitrate in Table 2 and ammonium iodide in Table 3. For the ammonium nitrate calculations the six experimental results [2] for the highest molalities and that for the lowest were omitted. When the results for the high concentrations (*i.e.*, >0·1 mol kg$^{-1}$) were included systematic deviations from the best fit curve which we attribute to the breakdown of the Debye–Hückel equation occurred. The point at the lowest concentration ($0{\cdot}1026 \times 10^{-2}$ mol kg$^{-1}$) was omitted in the original analysis [2] and is believed to be unreliable as the observed e.m.f. did not lie on the smooth e.m.f. *vs.* concentration curve.[2] The elimination of these seven ammonium nitrate results meant that the analyses made for both nitrate and iodide salts covered comparable concentration ranges. For the calculation of the parameters in Tables 2 and 3 the value log $(\gamma/\gamma_1) = 0$ for $m = 0{\cdot}01$ was treated as an unweighted experimental observation; its omission had no significant effect on the values obtained for $\gamma_1$, $K_A$, and $K_T$.

The standard deviations in Tables 2 and 3 are all consistent with uncertainty in the experimental values of log $(\gamma/\gamma_1)$ [±0·008 based on ±0·2 mV in the observed e.m.f. and ±0·004 in $\log_{10}(m/m_1)$] and it follows that the

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* Copies of programmes will be supplied on request.

[11] A. D. Pethybridge and J. E. Prue, *Trans. Faraday Soc.*, 1967, **63**, 2019.

experimental results for the two salts may be accounted for by both theoretical models. Although smaller standard deviations are obtained when triple ion formation is assumed the decrease (always $<0{\cdot}0015$) is not significant but is merely the consequence of introducing a third adjustable parameter. However the assumption of triple ion formation leads to marked differences in the parameters; for most values of $d$ the differences between the estimates of $\log_{10} \gamma_1$ is larger than the uncertainty in the experimental measurements and cannot therefore be ignored. Calculations[12] based on the Fuoss treatment[13,14] indicate that some triple ions should exist in these solutions and the results obtained with $K_T \neq 0$ are therefore to be preferred although the correlation between $K_A$ and $K_T$ is so high that their values must be treated with caution. This problem could be resolved by the independent determination of $K_A$ by some other method or perhaps by very precise e.m.f. measurements at concentrations lower than those used.[1,2]

As is to be expected, the value of $\gamma_1$ is insensitive to the $d$-parameter (especially for $10 < 10^{10}\ d/\mathrm{m} < 20$) whereas that for $K_A$ increases with $d$. The corresponding change in the standard deviations is insignificantly small and cannot be used as a basis for the choice of $d$. Although the best available estimate of $d$ is the Bjerrum distance $q$ ($= 16{\cdot}22 \times 10^{-10}$ m), this choice is not critical for the extraction of activity coefficients from the experimental results,[1,2] since the change in $\gamma_1$ (Tables 2 and 3) which occurs where $10^{10}\ d$ is increased from 10 to 20 m is less than the experimental error in $\gamma/\gamma_1$. The parameters calculated for low values of $d$ ($\leqslant 5 \times 10^{-10}$ m) which we include for completeness in Tables 2 and 3 are not physically significant as the Debye–Huckel equation is unlikely to apply to ions at these distances in liquid ammonia. The negative values of $K_T$ could perhaps be interpreted as an indication that if the only ion pairs present are those which occur at short distance, triple ions are unlikely.

The fit between the observed and calculated values of $\log_{10} \gamma/\gamma_1$ is illustrated in Tables 4 and 5 for the case $K_T \neq 0$, $10^{10}\ d = 16{\cdot}22$ m. These Tables also include values for $\alpha$, $\beta$, and the difference $\Delta = [\log_{10} (\gamma/\gamma_1)_{\mathrm{cal}} - \log_{10} (\gamma/\gamma_1)_{\mathrm{obs}}]$. None of the parameter sets in Tables 2 and 3 lead to systematic trends in $\Delta$ and the distribution of $\Delta$ values in Tables 4 and 5 may be taken as representative.

The Bjerrum treatment[4-6] for ion association gives the equation

$$K_A = 4\pi N \int_{r=a}^{r=d} \exp\,(2q/r) r^2 \mathrm{d}r \qquad (11)$$

in which $a$ is the closest distance of approach of the ions in the ion pair, and the equation

$$\Delta K_A = 4\pi N \int_{r=d_1}^{r=d_2} \exp\,(2q/r) r^2 \mathrm{d}r \qquad (12)$$

for the change in $K_A$ which results from a change in the closest distance of approach of the free ions.[15,16] Values of $\Delta K_A$ (Table 6) calculated with equation (12) and $10^{10}\ d_2 = 16{\cdot}22$ m, $10^{10}\ d_1 = 10{\cdot}0$ m are somewhat larger than the experimental ones. A very similar discrepancy

TABLE 4

Comparison of observed and calculated values of $\log_{10} \gamma/\gamma_1$ for ammonium nitrate ($10^{10}\ d = 16{\cdot}22$ m, $-\log_{10} \gamma_1 = 0{\cdot}4228$, $K_A = 276{\cdot}5\ \mathrm{kg\ mol^{-1}}$, $K_T = 7{\cdot}99\ \mathrm{kg\ mol^{-1}}$)

| $10^2\ m/$ mol kg$^{-1}$ | $\log_{10} (\gamma/\gamma_1)$ (obs.) | $\log_{10} (\gamma/\gamma_1)$ (calc.) | $\Delta$ | $\alpha$ | $10^2\ \beta$ |
|---|---|---|---|---|---|
| 0·1427 | 0·240 | 0·236 | 0·004 | 0·832 | 0·15 |
| 0·1892 | 0·210 | 0·209 | 0·001 | 0·802 | 0·24 |
| 0·1915 | 0·203 | 0·208 | −0·005 | 0·800 | 0·24 |
| 0·2348 | 0·188 | 0·188 | 0·000 | 0·777 | 0·32 |
| 0·2871 | 0·170 | 0·166 | 0·004 | 0·753 | 0·42 |
| 0·3559 | 0·141 | 0·141 | 0·000 | 0·726 | 0·55 |
| 0·4357 | 0·117 | 0·116 | 0·001 | 0·699 | 0·71 |
| 0·4441 | 0·114 | 0·114 | 0·000 | 0·697 | 0·73 |
| 0·5712 | 0·077 | 0·081 | −0·005 | 0·662 | 0·98 |
| 0·6310 | 0·070 | 0·068 | 0·003 | 0·649 | 1·10 |
| 0·7197 | 0·042 | 0·049 | −0·007 | 0·631 | 1·27 |
| 0·8601 | 0·026 | 0·024 | 0·002 | 0·606 | 1·54 |
| 1·0000 | 0·000 | 0·001 | −0·001 | 0·585 | 1·80 |
| 1·2846 | −0·034 | −0·038 | 0·004 | 0·551 | 2·32 |
| 1·5118 | −0·064 | −0·064 | 0·000 | 0·529 | 2·70 |
| 1·7449 | −0·091 | −0·088 | −0·003 | 0·510 | 3·08 |
| 1·8376 | −0·104 | −0·097 | −0·007 | 0·503 | 3·22 |
| 1·9639 | −0·112 | −0·108 | −0·004 | 0·494 | 3·42 |
| 2·0018 | −0·107 | −0·111 | 0·004 | 0·492 | 3·47 |
| 2·1834 | −0·129 | −0·126 | −0·003 | 0·481 | 3·74 |
| 2·2346 | −0·132 | −0·130 | −0·001 | 0·478 | 3·81 |
| 2·4529 | −0·141 | −0·147 | 0·006 | 0·466 | 4·12 |
| 2·6663 | −0·155 | −0·162 | 0·006 | 0·456 | 4·40 |
| 2·7059 | −0·166 | −0·164 | −0·002 | 0·454 | 4·45 |
| 2·8880 | −0·168 | −0·175 | 0·007 | 0·447 | 4·68 |
| 3·0960 | −0·184 | −0·189 | 0·005 | 0·438 | 4·94 |
| 3·7423 | −0·218 | −0·224 | 0·006 | 0·417 | 5·68 |
| 3·9523 | −0·237 | −0·234 | −0·003 | 0·411 | 5·91 |
| 4·3905 | −0·263 | −0·254 | −0·009 | 0·400 | 6·35 |
| 5·8637 | −0·311 | −0·311 | 0·000 | 0·371 | 7·65 |

TABLE 5

Comparison of observed and calculated values of $\log_{10} \gamma/\gamma_1$ for ammonium iodide ($10^{10}\ d = 16{\cdot}22$ m, $-\log_{10} \gamma_1 = 0{\cdot}4286$, $K_A = 328{\cdot}1\ \mathrm{kg\ mol^{-1}}$, $K_T = 4{\cdot}53\ \mathrm{kg\ mol^{-1}}$)

| $10^2\ m/$ mol kg$^{-1}$ | $\log_{10} (\gamma/\gamma_1)$ (obs.) | $\log_{10}(\gamma/\gamma_1)$ (calc.) | $\Delta$ | $\alpha$ | $10^2\ \beta$ |
|---|---|---|---|---|---|
| 0·1131 | 0·242 | 0·252 | −0·010 | 0·835 | 0·07 |
| 0·1509 | 0·223 | 0·226 | −0·003 | 0·804 | 0·11 |
| 0·1886 | 0·211 | 0·204 | 0·007 | 0·779 | 0·15 |
| 0·2543 | 0·176 | 0·172 | 0·004 | 0·742 | 0·22 |
| 0·3435 | 0·138 | 0·137 | 0·001 | 0·703 | 0·32 |
| 0·4403 | 0·108 | 0·106 | 0·003 | 0·669 | 0·44 |
| 0·5760 | 0·070 | 0·070 | 0·000 | 0·632 | 0·59 |
| 0·7266 | 0·037 | 0·037 | 0·000 | 0·600 | 0·77 |
| 1·0000 | 0·000 | −0·011 | −0·011 | 0·555 | 1·08 |
| 2·2401 | −0·158 | −0·143 | −0·016 | 0·448 | 2·29 |
| 2·8604 | −0·194 | −0·186 | −0·008 | 0·418 | 2·81 |
| 3·5466 | −0·217 | −0·225 | 0·008 | 0·393 | 3·33 |
| 4·5332 | −0·266 | −0·271 | 0·005 | 0·366 | 4·00 |
| 5·6951 | −0·322 | −0·314 | −0·008 | 0·343 | 4·69 |
| 7·7580 | −0·370 | −0·375 | 0·005 | 0·315 | 5·72 |

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[12] B. M. Lowe, unpublished results.

[13] R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 2387; 1935, **57**, 1.

[14] H. S. Harned and B. B. Owen, ' The Physical Chemistry of Electrolytic Solutions,' Reinhold, New York, 1958 (3rd edn.), pp. 74, 297.

[15] E. A. Guggenheim, *Trans. Faraday Soc.*, 1966, **62**, 2750.

[16] E. A. Guggenheim and R. H. Stokes, ' Equilibrium properties of aqueous solutions of single strong electrolytes,' Pergamon, London, 1969, ch. 4.

is observed[17] for the association constants obtained from the activity coefficient of dithionates of divalent cations in water at 0 °C ($10^{10}\,q = 13{\cdot}9$ m) and it appears that equation (12) tends to overestimate the change in $K_A$. The values of $a$ calculated with equation (11) and $10^{10}\,d = 16{\cdot}22$ and 10·0 m (Table 6) are in good agreement. Those found from the $K_A$ results for $K_T \neq 0$ and $10^{10}\,d = 16{\cdot}22$ m are larger than the sum $(r_+ + r_-)$ of the crystal radii[7] of $NH_4NO_3$ ($3{\cdot}4 \times 10^{-10}$ m) and $NH_4I$ ($3{\cdot}7 \times 10^{-10}$ m) by $1{\cdot}1 \times 10^{-10}$ m and $0{\cdot}5 \times 10^{-10}$ m respectively. Although both these separations are consistent with solvent separated ion-pairs some of the other values of $10^{10}\,[a - (r_+ + r_-)]$/m in Table 6 indicate that the existence of contact ion-pairs cannot be ruled out. The most important conclusion to be drawn from this analysis is that the association constants of both salts are certainly not larger than expected from electrostatic and statistical considerations.

TABLE 6

Results of calculations based on the Bjerrum treatment

| | $NH_4NO_3(K_T \neq 0)$ | | $NH_4NO_3(K_T = 0)$ | | $NH_4I(K_T \neq 0)$ | | $NH_4I(K_T = 0)$ | |
|---|---|---|---|---|---|---|---|---|
| $10^{10}\,d$/m | 16·2 | 10·0 | 16·2 | 10·0 | 16·2 | 10·0 | 16·2 | 10·0 |
| $K_A$(expt)/kg mol$^{-1}$ | 277 ± 6 | 240 ± 6 | 362 ± 12 | 328 ± 12 | 328 ± 14 | 290 ± 13 | 392 ± 23 | 359 ± 23 |
| $K_A$(expt)/dm$^3$ mol$^{-1}$ | 401 ± 9 | 348 ± 9 | 525 ± 17 | 476 ± 17 | 476 ± 20 | 420 ± 19 | 568 ± 33 | 520 ± 33 |
| $\Delta K_A$(expt)/dm$^3$ mol$^{-1}$ | 53 ± 18 | | 49 ± 34 | | 56 ± 39 | | 48 ± 66 | |
| $\Delta K_A$(eqn. 12)/dm$^3$ mol$^{-1}$ | 99 | | 99 | | 99 | | 99 | |
| $10^{10}\,a$/m | 4·5 | 4·3 | 4·0 | 3·9 | 4·2 | 4·0 | 3·9 | 3·8 |
| $10^{10}\,(r_+ + r_-)$/m | 3·4 | 3·4 | 3·4 | 3·4 | 3·7 | 3·7 | 3·7 | 3·7 |
| $10^{10}\,[a - (r_+ + r_-)]$/m | 1·1 | 0·9 | 0·6 | 0·5 | 0·5 | 0·3 | 0·2 | 0·1 |

TABLE 7

Parameters from conductance data for ammonium nitrate

| | $1{\cdot}016 > 10^3c$/mol dm$^{-3}$ $> 0{\cdot}00594$ | | | | | |
|---|---|---|---|---|---|---|
| | Pitts eqn. | | | Fuoss–Hsia eqn. | | |
| $10^{10}\,d$/m | $\Lambda^\circ$/$\Omega^{-1}$ cm$^2$ mol$^{-1}$ | $K_A$/dm$^3$ mol$^{-1}$ | $\sigma\Lambda$/$\Omega^{-1}$ cm$^2$ mol$^{-1}$ | $\Lambda^\circ$/$\Omega^{-1}$ cm$^2$ mol$^{-1}$ | $K_A$/dm$^3$ mol$^{-1}$ | $\sigma\Lambda$/$\Omega^{-1}$ cm$^2$ mol$^{-1}$ |
| 3·39 | 304·9 ± 0·9 | 111 ± 19 | 2·9 | 304·6 ± 0·8 | 45 ± 16 | 2·7 |
| 5·0 | 305·0 ± 0·9 | 146 ± 19 | 3·0 | 304·9 ± 0·9 | 93 ± 18 | 2·9 |
| 10·0 | 305·1 ± 0·9 | 199 ± 19 | 3·0 | 305·3 ± 1·0 | 182 ± 20 | 3·2 |
| 16·22 | 304·7 ± 0·8 | 216 ± 16 | 2·7 | 305·3 ± 1·0 | 241 ± 19 | 3·2 |

| | $1{\cdot}016 > 10^3c$/mol dm$^{-3}$ $> 0{\cdot}03659$ | | | | | |
|---|---|---|---|---|---|---|
| | Pitts eqn. | | | Fuoss–Hsia eqn. | | |
| $10^{10}\,d$/m | $\Lambda^\circ$/$\Omega^{-1}$ cm$^2$ mol$^{-1}$ | $K_A$/dm$^3$ mol$^{-1}$ | $\sigma\Lambda$/$\Omega^{-1}$ cm$^2$ mol$^{-1}$ | $\Lambda^\circ$/$\Omega^{-1}$ cm$^2$ mol$^{-1}$ | $K_A$/dm$^3$ mol$^{-1}$ | $\sigma\Lambda$/$\Omega^{-1}$ cm$^2$ mol$^{-1}$ |
| 3·39 | 308·4 ± 0·6 | 159 ± 10 | 1·3 | 307·8 ± 0·5 | 88 ± 8 | 1·0 |
| 5·0 | 308·7 ± 0·7 | 196 ± 11 | 1·4 | 308·3 ± 0·6 | 139 ± 10 | 1·3 |
| 10·0 | 308·7 ± 0·6 | 248 ± 10 | 1·4 | 309·1 ± 0·7 | 233 ± 12 | 1·7 |
| 16·22 | 307·9 ± 0·4 | 258 ± 7 | 1·0 | 309·1 ± 0·7 | 291 ± 12 | 1·6 |

The only experimental results with which an independent estimate of $K_A$ may be made are those obtained from the early conductance work of Franklin and Kraus[18] on ammonium nitrate solutions. We have analysed these results using both the Pitts[19,20] and the Fuoss–Hsia[21-23] equations in the form

$$\Lambda = \alpha[\Lambda^\circ - (B_1\Lambda^\circ + B_2)(c\alpha)^{\frac{1}{2}} + E\,c\alpha \log_{10} c\alpha + J_1\,c\alpha - J_2\,(c\alpha)^{\frac{3}{2}}] \quad (13)$$

(for an explanation of the symbols see the original papers and ref. 24) and the values obtained for the association constant $K_A$, the molar conductance at infinite dilution $\Lambda^\circ$, and the standard deviation $\sigma_\Lambda$ (based on the observed and calculated values of the molar conductance $\Lambda$) are given in Table 7. Franklin and Kraus[18] made measurements at −33 °C on concentrations between $5{\cdot}94 \times 10^{-6}$ and $9{\cdot}515 \times 10^{-3}$ mol dm$^{-3}$. Our analysis with all the reported results below $1{\cdot}016 \times 10^{-3}$ mol dm$^{-3}$ (19 observations) gave very high standard deviations (Table 7) which arose predominantly from the results for the lower concentrations. Franklin and Kraus[18] used a dilution technique which must necessarily have introduced larger errors in the low concentration region. When the six points at lowest concentrations are eliminated the results for the concentration range $0{\cdot}00003659 < c < 0{\cdot}001076$ mol dm$^{-3}$ give a much lower standard deviation (Table 7) although the difference between the

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observed and calculated Λ still show a slight systematic trend. For $10^{10}\,d = 16{\cdot}22$ m, the values of $K_A$ (258 ± 7 $dm^3\,mol^{-1}$ Pitts equation [19,20] and 233 ± 12 $dm^3\,mol^{-1}$ Fuoss–Hsia equation [21-23]) are in poor agreement with that obtained with $K_T = 0$ (525 ± 17 $dm^3\,mol^{-1}$, Table 5) but in somewhat better agreement with that found with $K_T \neq 0$ (401 ± 9 $dm^3\,mol^{-1}$). This suggests that the association constants obtained with the assumption of triple ion formation are to be preferred.

TABLE 8

Smoothed and rounded values of the mean molal stoicheiometric activity coefficients $\gamma_\pm$ in liquid ammonia at −40 °C

| $m$/mol $kg^{-1}$ | $\gamma_\pm$ ($NH_4NO_3$) [a] | $\gamma_\pm$ ($NH_4I$) [b] |
|---|---|---|
| 0·001 | 0·696 | 0·682 |
| 0·002 | 0·604 | 0·588 |
| 0·005 | 0·474 | 0·457 |
| 0·008 | 0·409 | 0·393 |
| 0·010 | 0·379 | 0·364 |
| 0·020 | 0·293 | 0·281 |
| 0·050 | 0·199 | 0·191 |

[a] Values calculated with $10^{10}\,d = 16{\cdot}22$ m, $-\log_{10}\gamma_1 = 0{\cdot}4228$, $K_A = 276{\cdot}5$ kg $mol^{-1}$, $K_T = 7{\cdot}99$ kg $mol^{-1}$. [b] Values calculated with $10^{10}\,d = 16{\cdot}22$ m, $-\log_{10}\gamma_1 = 0{\cdot}4286$, $K_A = 328{\cdot}1$ kg $mol^{-1}$, $K_T = 4{\cdot}53$ kg $mol^{-1}$.

Values of the mean molal stoicheiometric activity coefficients at rounded concentrations are given in Table 8. Those for ammonium nitrate are now closer to the values of Monoszan and Pleskov [25] than those originally reported,[2] although still significantly different. It is clear from these values (Table 8) and the parameters in Tables 2 and 3 that ammonium nitrate and iodide behave similarly in liquid ammonia and that the concentration dependence of the activity coefficient may be interpreted in terms of ion association.

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