Ionic Association in Low-Dielectric Media. II. The Electrical Conductance of Nitrate Salts in Tetrahydrofuran. The Conductance Equation for Quadrupole Formation

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Abstract: Electrical conductance measurements have been made on lithium nitrate and tetrabutylammonium nitrate in tetrahydrofuran at 25°. The influence of small quantities of cation solvating agents has been used to qualitatively determine the degree of contact ion pair formation in lithium nitrate. Both salts exhibit triple ion formation and also quadrupole formation. The first term of the conductance equation for quadrupole formation has been derived and it is shown that quantitative evaluation of the quadrupole formation constant cannot be made using electrical conductance alone. Furthermore, when quadrupole formation occurs, the triple ion formation constant evaluated in the usual fashion will be in error.

The aggregation of ionic species in low-dielectric media is a well-known phenomenon. The oldest method for investigation of such processes is electrical conductance measurements. Despite their age, such measurements can reveal details of the ion pairing process, triple ion formation, and quadrupole formation available from no other source. The currently available theories of electrical conductance for pair formation are in a highly developed state.[1,2] The conductance curve for triple ion formation is reasonably well described by the equation derived by Fuoss and Kraus 40 years ago.[3] No quantitative conductance equation for quadrupole formation exists. Despite the great current interest in the conductance equation for ion pair formation and the great experimental interest in ionic aggregation using a host of techniques,[4,5] the theoretical development of conductance equations in very low-dielectric media has remained nearly static due largely to the great difficulties involved. We recently began studies on the conductance of lithium nitrate and tetrabutylammonium nitrate with a number of specific objectives. Foremost was a need to determine the association constant for pair formation and the triple ion formation constant. In addition we wished to determine the nature of the ion pair. That is, we wished to determine whether the pair was heavily inner sphere (contact ion pair) or outer sphere (solvent separated). The method for making this distinction will be described in the Discussion section. Finally we needed to ascertain the presence of quadrupoles since ultrasonic results in this laboratory[6] implied such species.

Experimental Section

Conductances were measured using a Beckman Model RC 16 bridge. The cell was a dipping type which was calibrated using KCl solution. Measurements were made by addition of concentrated stock solution to pure solvent. The solution was thermostatted at 25.00 ± 0.02° using a Forma bath. Salts and solvents were purified as described previously.[6] For very low-conductance values, a 10 kΩ precision resistor was used in parallel with the cell.

Results and Discussion

The variation of the equivalent conductance with concentration for the two salts is shown graphically in Figures 1 and 2. The actual data can be obtained from the authors on request. The data treatment proposed by Fuoss and Kraus could be used.[3] According to this treatment

$$\Lambda C^{1/2} g(C) = \frac{\Lambda_0}{K_p^{1/2}} + \frac{\lambda_0 k_T}{K_p^{1/2}}\left(1 - \frac{\Lambda}{\Lambda_0}\right)C \qquad (1)$$

where C is the total concentration of electrolyte, K_p is the ion pair formation constant between M^+ and L^-, k_T is the triple ion formation constant, λ_0 is the limiting conductance for the hypothetical electrolyte $(M_2L^+)(ML_2^-)$, Λ_0 is the limiting ionic conductance of the electrolyte ML, and $g(c)$ is defined in ref 3. According to eq 1 a plot of $\Lambda C^{1/2} g(C)$ *vs.* $(1 - (\Lambda/\Lambda_0)C$ is linear. If the value of Λ_0 can be estimated and if the ratio λ_0/Λ_0 is chosen arbitrarily as is customary, then both K_p and k_T can be determined. We have chosen the values $\Lambda_0 = 175$ for $LiNO_3$ and 184 for tetrabutylammonium nitrate, obtained by application of Waldens' rule and the value of Λ_0 for these salts in acetonitrile. Following Fuoss and Kraus we have chosen $\lambda_0/\Lambda_0 = 1/3$. From the slopes and intercept we then calculate the values of K_p and k_T shown in Table I.

Table I. Ion Pair Formation Constant, K_p, and Triple Ion Formation Constants, k_T, for Salts in THF at 25°

System	$K_p \times 10^{-8}$	k_T
$LiNO_3$	59	182
$LiNO_3$ + DMSO	120	518
$LiNO_3$ + DME	340	742
$(M\text{-}C_4H_9)_4N^+NO_3^-$	0.070	155

One of the objectives of the work was to find the type of ion pair formed between lithium ion and nitrate ion. It is expected that there are two possibilities, a solvent-

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[1] R. M. Fuoss and K.-L. Hsia, *Proc. Nat. Acad. Sci. U. S.*, **57**, 1550 (1967).

[2] E. Pitts, B. F. Tabor, and J. Daly, *Trans. Faraday Soc.*, **65**, 849 (1969).

[3] R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, **55**, 2387 (1933).

[4] L. L. Chan and J. Smid, *ibid.*, **89**, 4547 (1967).

[5] F. C. Adams and S. J. Weissman, *ibid.*, **80**, 1580 (1958).

[6] H. Wang and P. Hemmes, *ibid.*, **95**, 5115 (1973).

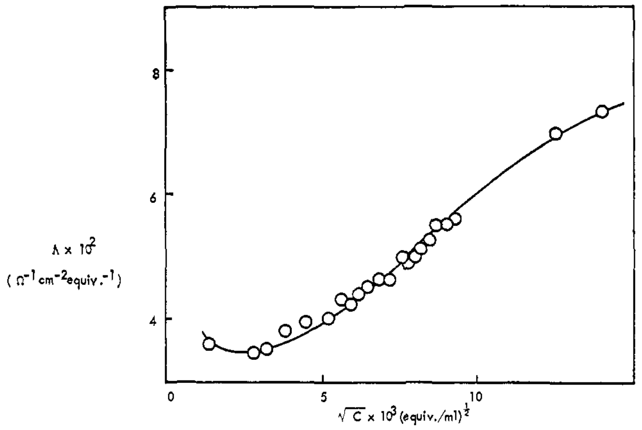

Figure 1. A plot of equivalent conductance *vs.* square root of concentration for lithium nitrate in THF at 25°.

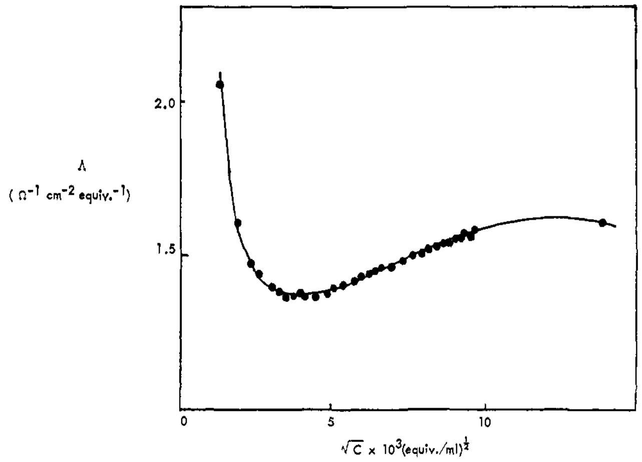

Figure 2. A plot of equivalent conductance *vs.* square root of concentration for $(n-C_4H_9)_4N^+ NO_3^-$ in THF at 25°.

separated pair and a contact pair. The experimental ion pair association constant is given by

$$K_p = K_0(1 + K_1) \qquad (2)$$

where K_0 is the formation constant of the solvent-separated pair and K_1 is the ratio of contact to solvent-separated pairs. Electrical conductance has previously been used to estimate K_1 *via* the following route. If K_p is measured experimentally, K_0 can be estimated *via* the Fuoss[7] or Bjerrum[8] association constants. In low-dielectric media, however, such an approach is fruitless since the estimated K_0 values are far too sensitive to the choice of the ion size parameter a. This is easily explained by the following considerations. The Fuoss[9] equation goes through a minimum at $a = (2/3)q$, where q is the critical distance of Bjerrum, while the Bjerrum equation goes to zero at $a = q$, but the slope of the K_{Bj} *vs.* a plot is not large near $a = q$. For high-dielectric media q is not too much larger than the ionic dimensions. Hence almost any reasonable estimate of the ionic size will give roughly the same value of K_F or K_{Bj}. In low-dielectric media, q becomes much larger than the ionic dimensions. The estimated ionic size will then be in a region where either K varies very rapidly with a.

Since K_1 cannot be estimated *via* K_0, an alternate means must be applied. Consider the two extreme cases where the ion pairs are virtually all contact or all solvent separated. In the latter case the bonding within the pair is solely electrostatic and thus insensitive to the nature of the intervening solvent molecule. Providing the size of the solvated ion remains the same, the value of K_p will be unchanged as one type of solvating molecule in the first coordination sphere of the cation is replaced by another. In the extreme case of extensive contact pairing, the anion itself is in the first coordination sphere of the cation. Addition of strong solvating agents may displace the anion and produce a solvent-separated ion pair. The value of K_p is then expected to be very sensitive to the addition of such solvating agents since the value of K_1 in eq 2 will be dramatically lowered by such addition.

In order to apply this principle it is necessary that the added solvating agent be quantitatively incorporated into the first coordination sphere of the cation. For lithium ion in THF it seems[10] that dimethyl sulfoxide and 1,2-dimethoxyethane both approximate this condition. Hence stock solutions were prepared which contained lithium nitrate and DMSO or DME in the mole ratio 1:2. This solution is then added to pure solvent. The assumption of quantitative incorporation of solvating agent into the coordination sphere of the cation means that the dielectric constant of the solvent is unaltered by this procedure. The results of such conductance runs were analyzed by eq 1 to give the values reported in Table I.

It is evident that rather than decreasing as would be expected for nearly complete inner sphere association, the actual values of K increase. From these data it appears that the lithium nitrate ion pair is essentially solvent separated. Quantitative estimation of K_1 is impossible due to the possible variations of Λ_0 with solvating agents. It seems that the slope of the plot based on eq 1 is rather sensitive to additions of solvating agents. There are a number of possible explanations for this. The triple ion formation constant can be altered or the ratio λ_0/Λ_0 may vary with solvating agents. In addition, small changes in the quadrupole formation constant can cause a change of slope.

Using theoretical equations for ion pairing,[7,8] triple ion formation,[3] and quadrupole formation,[11] it is easily seen that the values of the formation constants are in the order $K_p \gg k_T > k_Q$, where k_Q is the quadrupole formation constant

$$k_Q = [M_2L_2]/[ML]^2$$

Nevertheless, a simple calculation shows that at reasonably high total concentrations beyond the minimum of conductance the concentration of the various species is in the order pairs > quadrupoles > triplets > free ions. If the two types of ion triplets (M_2L^+ and ML_2^-) are formed equally, the conductance is given by the equation

$$\Lambda C_T = \Lambda_0[M^+] + \lambda_0[M_2L^+]$$

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(7) R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958).

(8) N. Bjerrum, *Kon. Danske Vedensk. Selskab*, 7 (1926).

(9) S. Petrucci, P. Hemmes, and M. Battistini, *J. Amer. Chem. Soc.*, **89**, 5552 (1967).

(10) T. E. Hogen-Esch and J. Smed, *ibid.*, **88**, 307 (1966).

(11) R. M. Fuoss and C. A. Kraus, *ibid.*, **57**, 1 (1935).

The following equations also apply

$$K_p = [ML]/([M][L])$$

$$k_T = [M_2L^+]/([ML][M])$$

$$k_Q = [M_2L_2]/[ML]^2$$

$$C_T = [M^+] + [ML] + 2[M_2L^+] + [ML_2^-] + 2[M_2L_2]$$

Since the concentration of ions is very small[3]

$$C_T \cong [ML] + 2[M_2L_2]$$

or

$$[ML] = C_T - 2[M_2L_2] = C_T - 2k_Q[ML]^2$$

as a zeroth approximation, the value of [ML] in the second term can be replaced by C_T to give

$$[ML] \cong C_T - 2k_QC_T^2$$

Then

$$[M^+] = \frac{1}{K_p^{1/2}}(C_T - 2k_QC_T^2)^{1/2}$$

$$[M_2L^+] = \frac{k_T}{K_p^{1/2}}(C_T - 2k_QC_T^2)^{3/2}$$

Using the approximation $(1 - x)^{1/2} \cong 1 - {}^1/_2x$ gives to order C_T

$$\Lambda C_T^{1/2} = \frac{\Lambda_0}{K_p^{1/2}} + \left[\frac{\lambda_0 k_T}{K_p^{1/2}} - \frac{\Lambda_0 k_Q}{K_p^{1/2}}\right]C_T \qquad (3)$$

This is the modification of eq 1 which applies when quadrupole formation occurs and activity coefficients can be neglected and also when the concentration dependence of mobility can be neglected ($g(C) = 1$).

The consequence of eq 3 is *that the first effect of quadrupole formation is to lower the slope of the plot based on eq 1 and thus lower the apparent triple ion formation constant.* Curvature will occur only at higher concentrations. The k_Q term in eq 3 is the first term in the conductance equation including quadrupoles. The effect is significant; the k_Q term may be 10% of the k_T term.

Since media where quadrupoles form to a moderate extent also make difficult the evaluation of Λ_0 to say nothing of λ_0, it is evident that eq 3 cannot be used to evaluate k_Q.

The shapes of the conductance curves shown in Figures 1 and 2 show a marked curvature at higher concentrations. This is also a consequence of quadrupole formation. The effect is more pronounced for the tetrabutylammonium nitrate than for lithium nitrate. This reflects the larger size of the tetrabutylammonium ion. The formation of quadrupoles is strongly dependent upon the dipole moment of the ion pair from which it forms. Hence increasing the size of one ion will enhance k_Q but will decrease K_p. Ultrasonic absorption results also show that k_Q for tetrabutylammonium nitrate is significantly larger than for the lithium salt. The present conductance results reveal the lower value of K_p for the ammonium salt compared with the lithium value.

It will require additional experimental techniques, capable of determining the formation constants of the various species or of the ionic mobilities, in order to successfully interpret the conductance curve. The greatest need at the moment is a means of evaluating the ratio λ_0/Λ_0. All evidence seems to indicate that quadrupole formation is much more extensive for the tetrabutylammonium nitrate than for lithium nitrate. However, the triple ion formation constant seems to be lower. This may very easily be an indication that the assumed value of λ_0/Λ_0 for the former salt is greater than for the latter.

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