The Mobility of the Hydrogen Ion in Liquid Ammonia

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THE work of Franklin and Cady[1] indicates that the transference number of the ammonium ion (the hydrogen ion) in liquid ammonia at −34°C lies between 0·42 and 0·44. In the present work the transference numbers of ammonium and potassium ions in nitrate solutions have been determined by a moving boundary method at various concentrations up to 0·2M and temperatures between

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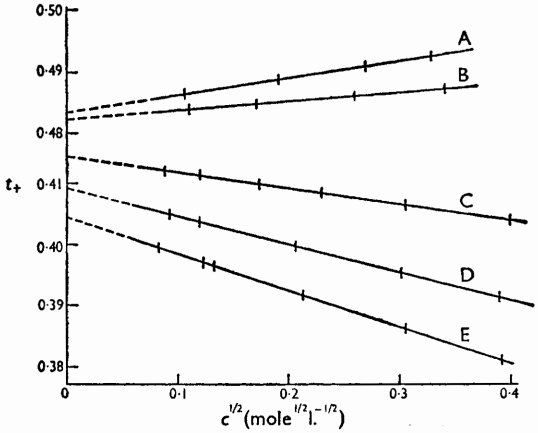
[1] E. C. Franklin and H. P. Cady, *J. Amer. Chem. Soc.*, 1904, **26**, 499.

−45° and −65°. The results are shown in the Figure.

It is seen that, within the limits of the experimental error (±1 part in 1000), the transference numbers of both ammonium and potassium ions in liquid ammonia show a linear variation with $c^{\frac{1}{2}}$.



Variation of transference numbers of potassium and ammonium ions at various temperatures with the square root of concentration.

A, K^+ at −65°; B, K^+ at −48°; C, NH_4^+ at −45°; D, NH_4^+ at −55°; E, NH_4^+ at −65°.

Assuming that the nitrate ion behaves similarly in both ammonium and potassium solutions at the same concentrations and temperatures it follows that the hydrogen ion in liquid ammonia has a significantly lower ionic mobility than the potassium ion at all temperatures. Thus the phenomenon of the anomalously high ionic mobility of hydrogen ion is absent in liquid ammonia. Further the values of the transference numbers of the hydrogen ion decrease as the temperature decreases. This is exactly the opposite situation to that observed for the limiting values for the hydrogen ion in water which increase from 0·764 at 100°, to 0·830 at 25°, to 0·850 at 0°.[2] This is attributed to the increasing degree of order within the solvent's structure which allows a greater contribution towards the total mobility to come from the proton-transfer mechanism[3,4] as the temperature is lowered. The properties of molecular association within liquid ammonia are well established and in the same way an increasing degree of ordering is to be expected as the temperature decreases though not to the same extent as in water because of weaker hydrogen bonding and the inability to form three-dimensional arrangements. Thus if a proton-transfer mechanism contributes appreciably towards the ionic mobility of the hydrogen ion in liquid ammonia then an increase in the transference number relative to the nitrate ion is to be expected as the temperature is lowered. The opposite effect is observed and it is inferred, therefore, that the ionic mobility of the hydrogen ion in liquid ammonia is composed mainly of the normal mobility contribution corresponding to the diffusion of the ammonium ion and its associated solvent molecules. If a proton-transfer mechanism occurs then it must be regarded as contributing only to a minor extent towards the total ionic mobility.

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[2] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworth's Scientific Publications, 1959, p. 465.

[3] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, 1933, 1, 515.

[4] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill Book Co, Inc., 1941, Ch. 10.