Proton Knight Shift in Lithium-Methylamine Solutions

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Alkali-metals can be dissolved in liquid methylamine (CH_3NH_2) as in liquid ammonia. We have reported[1,2] that the volume expansion and viscosity of the Li–CH_3NH_2 system can be interpreted by the presence of anion-like solvated electrons trapped by 'cavities', as in alkali metal-ammonia solutions.[3] In this communication we describe the experimental results on the proton Knight shift in the Li–CH_3NH_2 system over a wide range of Li concentration.

The method of preparation of Li–CH_3NH_2 solutions has been described.[1] Solutions were sealed in measuring cells in a vacuum. Nuclear resonance was observed with a JEOL-3H-60 external lock NMR spectrometer in a magnetic field in the vicinity of 14,092G. The Knight shift k is defined[4] as $k=(H_r-H_s)/H_r$, where H_r is the magnetic field for which resonance occurs in the reference solution, and H_s is the magnetic field in sample solution at a fixed frequency. The Knight shift of protons in CH_3- and NH_2-group in CH_3NH_2 was measured as a function of Li concentration. The pure solvent was taken as a reference. Measurements were carried out at 21°C.

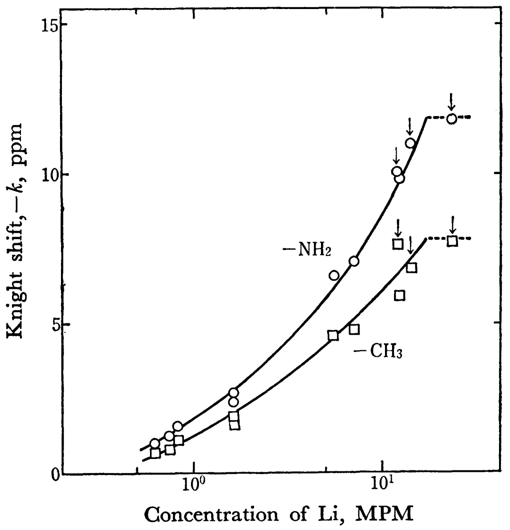

Fig. 1. Proton Knight shift for Li solutions in CH_3NH_2 at 21°C.

The results are shown in Fig. 1. The concentration of the metal is expressed by MPM or mol percentage of metal. The observed Knight shift increases with increasing metal concentration, as for proton and nitrogen in alkali metal-ammonia solutions.[4–6] The shifts are larger for the NH_2-group than for the CH_3-group, which may indicate that the CH_3NH_2 molecules are oriented at the edge of a cavity so that an ammonia-like trap is produced.[7] The values of k for the NH_2-group are of the same order of magnitude as those found in liquid ammonia.[5] It is interesting to see that the observed curve is continuous from low concentration (electrolytic region) to high concentration (metallic region) exhibiting no anomalies at the transition region, which is also in accordance with the observations in ammonia solutions.[5] The broken lines in the figure indicate the saturated solution range determined previously by electrical conductivity measurements.[2] Linewidths were generally around 15 Hz.

It should be noted that the resonance peaks both for CH_3- and NH_2-groups split into unsymmetrical doublets for three samples with high Li concentration, as indicated by arrows in Fig. 1. The width of the split was 8 Hz for the 12.0 MPM solution and almost independent of the metal concentration. Whether this corresponds to two different states of the solvated electrons[3] will be the subject of further investigation. It is also noted that at lower concentrations the sign of k seems to be inverted, though it is negative for the concentration range studied. A supplementary measurement with a saturated solution of the K metal ($\sim 4.7\times10^{-2}$ MPM) shows a positive value of k, +0.07 ppm, for protons in NH_2. A similar result has been observed for the Na-saturated solution, the concentration being about 2×10^{-2} MPM.

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