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PARAMAGNETIC RESONANCE IN ALKALI METAL SOLUTIONS AT LOW FIELDS*

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We have made an investigation of paramagnetic resonance in some alkali metal solutions at low magnetic fields. Measurements involving one of these solutions have been reported by Hutchison and Pastor,¹ and Garstens and Ryan.² The principal experiments were performed at a frequency of 49.0 mc in a precession field of approximately 17.5 gauss. The apparatus consisted of a pair of Helmholtz coils and a conventional nuclear induction system, the latter having a tuned probe into which the various samples could be inserted. A brief summary describing a few of the media investigated follows:

1. Solutions of Sodium in Liquid Ammonia. A sealed Faraday tube capable of withstanding a pressure in excess of 10 atmospheres was fabricated containing a fixed quantity of liquid ammonia and metallic sodium. The concentration of the solution could be varied at will by simple distillation techniques, and temperature effects could be observed by placing

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¹ Clyde A. Hutchison, Jr., and Ricardo C. Pastor, Phys. Rev. 81, 282 (1951)

² Martin A. Garstens and Alden H. Ryan, Phys. Rev. 81, 888 (1951)

the tube in several calibrated baths ranging between dry ice-acetone temperature (-78 deg. C.) and room temperature. Equipment limitations made it necessary to estimate concentrations from visual color observations, and therefore the behavior of these solutions with respect to concentration variations must be considered somewhat qualitative.

The signal amplitude was found to be dependent upon concentration, being barely visible at approximately 0.0001 M, growing until a maximum amplitude was reached at 0.1 M, and decreasing in amplitude with further increase in concentration. The ratio of signal amplitude to concentration decreased as the concentration changed from 0.0001 M to 0.1 M. It is entirely possible that the optimum concentration effect may not have been due completely to a decrease in the susceptibility for high concentrations, but may have been due partially to the increase in electrical conductivity of metal-ammonia solutions at high concentrations. Such large conductivities would lower the sensitivity of the system by reducing the Q of the resonant circuit and simultaneously preventing the penetration of the sample by the radio-frequency field.

An experiment was performed with 0.3 cc, 0.1 M, sealed sodium ammonia sample to determine the effect of temperature on signal width and amplitude. The results appear below:

Table I. Temperature dependence of signal width and amplitude

<u>Temperature</u>	<u>Full-width at half-max. amplitude</u>	<u>Signal amplitude</u>
-78 deg. C.	0.13 gauss	8 (% of amplitude
0	0.08	79 at room temp.)
+21	0.08	100

The table demonstrates that the signal amplitude from sodium-ammonia exhibits a temperature-amplitude effect opposite to that of the nuclear induction proton signal, the latter behaving in accordance with the temperature dependence of the Curie Susceptibility Law.

At concentrations above the 0.1 M optimum amplitude concentration, signal widths up to 0.7 gauss were observed, but at smaller concentrations than 0.1 M, no narrowing to less than 0.08 gauss was observed. The ratio of signal amplitude at room temperature to that at dry ice-acetone temperature was dependent upon concentration, being greater for high concentrations (~ 0.1 M) than for low (~ 0.001 M).

A sealed sample of sodium in liquid ammonia, kept at -78 deg. C. during the intervals of non-use, has not deteriorated in the eight weeks since its fabrication. The signal amplitude from this sample has not changed measurably in that period.

2. Solutions of Lithium in Methylamine. Faraday tube observations of signals from lithium in methylamine (CH_3NH_2) indicated that the functional dependence of width and amplitude on temperature and concentration was generally similar to that of the metal-ammonia solutions. Compared to these metal-ammonia solutions, an increase of width and an approximately proportional increase in amplitude was observed. The amplitude reached an optimum value at approximately 1 M. Lithium-methylamine showed a less pronounced temperature effect on amplitude than was shown by the metal-ammonia solutions. The ratio of amplitude at room temperature to amplitude at dry ice-acetone temperature was 1.3. The narrowest observed full-width was 0.4 gauss. A 0.3 cc, 1.2 M, sealed sample deteriorated rather suddenly after being at room temperature continuously for five hours.

3. Solutions of Lithium in Ethylenediamine. Paramagnetic resonance was observed in an open test tube solution and a sealed Faraday tube solution of lithium in ethylenediamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$). Signal widths of approximately 0.6 gauss (full-width) were seen. Chemical deterioration proved to be so rapid as to render impractical further studies of these solutions.