Feigl's reagent, *viz.*, detection of 1 part in 5,000,000. It is suggested that this might be considerably increased if the substance can be condensed with substituted benzaldehydes.

4. Under conditions of highest sensitivity (weak acidity), the reagent is more selective for silver than Feigl's reagent.

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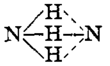
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AND THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA]

The Dipole Moment of Ammonia in Solution

BY W. D. KUMLER

The ammonia molecule is one of the rare cases in which one of the vibrations of the molecule causes an inversion of the dipole moment. Evidence for this vibration was obtained from the spectrum.[1] The period of the vibration is about 10^{-10} seconds and the movement responsible for the effect is a shifting of the nitrogen atom with respect to the plane of the hydrogen atoms.[1,2] 1  2. When the nitrogen is in position 2 the molecule will have a moment equal to but just opposite in direction to the moment when the nitrogen is in position 1. This inversion of the moment will have an effect on the dipole moment as measured in solution depending on whether the inversion time is greater or less than the relaxation time τ of the orientation in the electric field. The polarization due to dipole orientation reaches a maximum τ seconds later than the field so if the time of inversion is less than τ, the molecule will invert before the maximum polarization is obtained and the field will tend to give the inverted molecule angular momentum opposite in direction to that given it originally. Before the new orientation can reach a maximum the inversion again takes place, etc. As the time of inversion decreases with respect to τ, the limiting condition is one in which the molecule virtually stands still, in which case it would give no evidence of possessing a dipole moment.

Some of the earlier work seemed to indicate a time of relaxation in the usual organic solvents of about 10^{-7} second,[3] in which case ammonia should have a very small or zero moment in solution. More recently Debye[4] has determined the time of relaxation in organic solvents by means of high frequency energy absorption and finds it to be of the order of 10^{-12} second, in which case ammonia would be expected to have a dipole moment in solution differing from that in the gas by only a small amount, due to the solvent effect.[5]

I have measured the dipole moment of ammonia in benzene and in *n*-heptane and find it to be 1.38×10^{-18} e. s. u. in benzene and 1.43×10^{-18} e. s. u. in *n*-heptane. The average value of five determinations taken from the literature of the dipole moment of ammonia in the gaseous state is 1.47×10^{-18} e. s. u.[6] The moment in solution is less than in the gas but the discrepancy is not of a greater magnitude than can be accounted for by the solvent effect. The value of the moment in benzene and *n*-heptane is evidence that the time of relaxation in these solvents is less than the time of inversion of the molecule.

Results

In Table I the symbols are: ω the weight fraction of the solute, d the density of the solution, ϵ the dielectric constant of the solution, P_2 the polarization of the solute, P_{E_2} the electronic polarization of the solute, μ the dipole moment.

TABLE I

AMMONIA IN BENZENE

ω	d	ϵ	P_2
0.00	0.87212	2.26700	
.0008799	.87154	2.27685	46.19
.0015437	.87116	2.28473	46.77
.0024244	.87068	2.29459	46.17
.0039526	.87003	2.31281	46.29

AMMONIA IN *n*-HEPTANE

ω	d	ϵ	P_2
0.00	0.679306	1.90936	
.0003859	.679264	1.91281	50.67
.0012537	.678932	1.92020	50.81
.0020071	.678536	1.92468	46.44

	P_{E_2}	$\mu \times 10^{18}$
Ammonia in benzene	6.5	1.38
Ammonia in *n*-heptane	6.7	1.43

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[1] Dennison and Hardy, *Phys. Rev.*, **39**, 938 (1932).

[2] Rodebush, *Trans. Faraday Soc.*, **30**, 783 (1934).

[3] Ebert, Leipziger Vorträge, Leipzig, 1929, p. 55.

[4] Debye, *Trans. Faraday Soc.*, **30**, 679 (1934).

[5] Müller, *ibid.*, **30**, 729 (1934).

[6] Table of Dipole Moments, *ibid.*, **30**, XI (1934).

The polarizations P_2 were calculated by use of the equations

$$p_1 = \frac{\epsilon - 1}{\epsilon + 2}\frac{1}{d}$$

$$p_{12} = \frac{\epsilon - 1}{\epsilon + 2}\frac{1}{d} = (1 - \omega)p_1 + \omega p_2$$

$$P_2 = M_2\left(p_1 + \frac{p_{12} - p_1}{\omega}\right)$$

where p_1 is the specific polarization of the solvent, p_2 the specific polarization of the solute and p_{12} the specific polarization of the solution. The P_{E_2} values were calculated from the refractive index for the D sodium line. The dipole moments were obtained by taking an average of the P_2 values and substituting in the equation $\mu = 0.0127 \times 10^{-18}\sqrt{(P_2 - P_{E_2})T}$.

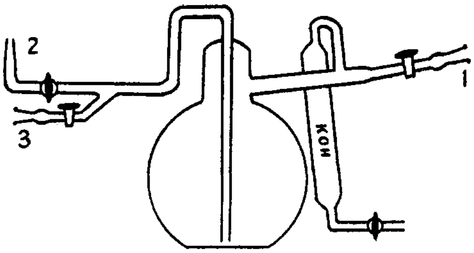

Fig. 1.

Experimental

Apparatus.—Due to the volatility of the solute precautions had to be taken to prevent its escape while the measurements were being made. The vessel of about 500-cc. capacity, shown in the diagram, was used as a reservoir for the solution. In making a run the vessel was connected to the fractionating column by means of ground glass joint 1 and the desired amount of solvent distilled into the flask. Then the vessel was connected to the ammonia purification apparatus by ground glass joint 2 and ammonia bubbled through the solvent until the desired concentration was obtained. The solution was forced into a 5-cc. pipet, attached at 3 by a ground glass joint, and the contents of the pipet run immediately into an Erlenmeyer flask containing an excess of 0.1 or 0.01 *N* hydrochloric acid. The amount of ammonia was determined by titration, using methyl orange as an indicator. The air used in forcing the solution out of the vessel was passed through two tubes, one containing calcium chloride, the other pellets of potassium hydroxide. The density of the solution was obtained by forcing the solution into a pycnometer attached at 3 with a ground glass joint. The vessel was attached to the condenser by means of ground glass joint 2 and the solution forced into it by air pressure. The condenser had a stopcock at the top which was open while the solution was being forced in but was always closed while the measurements were being made. The stopcocks with which the solution came in contact were all used without lubricant.

The procedure was to first make measurements on the solvent alone, then on the most concentrated solution. The solutions of lower concentration were all obtained from the one of higher concentration by blowing air, which had passed over calcium chloride and potassium hydroxide, through the solution. At the end of each series of runs the ammonia was completely blown out of the solvent and the dielectric constant, density and refractive index again determined to see whether any contamination had occurred during the course of the measurement. In each case the properties of the solvent were the same as they were originally.

The dielectric constants were measured with the same apparatus described previously.[7] Densities were measured in a pycnometer of approximately 26-cc. capacity. Refractive indices were taken with a Pulfrich refractometer. Temperatures were controlled to within 0.05° by electrically regulated thermostats. All measurements were made at 25°.

Materials

Ammonia.—Tank ammonia was passed through a tube about a meter long containing calcium oxide, pellets of potassium hydroxide and cotton. It was solidified in a liquid air trap and distilled into a second liquid air trap from which it was distilled into the solvent. The last portion was discarded in both distillations.

Benzene.—Benzene was shaken several times with concentrated sulfuric acid until it no longer gave a color with isatin, washed with dilute sodium hydroxide and water, dried over calcium chloride, refluxed over sodium, distilled from a 35-cm. fractionating column packed with glass helices and stored over fresh sodium from which it was distilled into the vessel as needed; b. p. 80.1–80.2° corr. at 753 mm.

***n*-Heptane.**—Eastman *n*-heptane was refluxed over sodium and distilled from the above fractionating column. It was stored over fresh sodium and distilled as needed into the vessel; b. p. 98.4–98.5° corr. at 762 mm.

Summary

The dipole moment of ammonia was found to be 1.38 × 10^{-18} e. s. u. in benzene and 1.43 × 10^{-18} e. s. u. in *n*-heptane. The value of the moment indicates that the time of relaxation in these solutions is less than the time of inversion of the molecule.

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[7] Kumler and Porter, THIS JOURNAL, **56**, 2552 (1934).