

ELECTRIC DIPOLE MOMENT OF AMINES AND SOLUTE-SOLVENT INTERACTION

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In an infinitely dilute solution, the solute molecules are so far apart from one another that an interaction amongst them is not possible. Consequently, at approximate zero concentration of the solute, the only interaction present is the one which occurs between the molecules of solute and solvent. Since electric dipole moment values are determined from the polarization at zero concentration, any deviation in the value of the moment in solution from that in the vapour state, or a change from one solvent to another, must be ascribed to solute-solvent interaction.

The most successful amongst many theories put forward to this effect was that of Higasi.^{1,2} This theory has been tested with success for the amine molecules in benzene and cyclohexane, showing a positive solvent effect in these cases.³ The present study has been made to ascertain the same concept for some more amine molecules. The experimental electric dipole moment values for these compounds are new, except for isopropylamine⁴ which has been studied only in heptane.

Experimental

The techniques for the measurement of static dielectric constants and densities of the solutions have been described elsewhere.^{5,6} The solution moments were evaluated by Halverstadt and Kumler's standard method.⁷ The constants appearing in the rectilinear expressions governing the variations of dielectric constant and specific volume with the change of concentration (at low range), were evaluated by the method of least squares. The distortion polarization ($P_e + P_a$) has been taken to be the same as the molar refraction values for the sodium-D line.

Benzene (E. Merck, G. R.), carbon tetrachloride (E. Merck, G. R.), and cyclohexane (B.D.H.) were redistilled and the fractions boiling at 79°, 75°, and 80°, respectively, were collected and kept in a desiccator before use. Isopropylamine (K. Light), diisopropylamine (Fluka, Switzerland), diisobutylamine (B.D.H.), and furfurylamine (K. Light) were also purified by distillation.

Results and Discussion

The electric dipole moments in benzene, carbon tetrachloride, and cyclohexane have been summarized in Table 1. Higasi's theory has been found valid for the amines

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¹ Smith, J. W., "Electric Dipole Moments." Ch. 6. (Butterworths: London 1955.)

² Higasi, K., *Bull. Inst. phys. chem. Res. Japan*, 1935, **14**, 146; *Sci. Pap. Inst. phys. chem. Res., Tokyo*, 1936, **28**, 284.

³ Krishna, B., and Srivastava, A. N., *Aust. J. Chem.*, 1966, **19**, 1847.

⁴ Shirai, M., *Sci. Pap. Coll. gen. Educ. Tokyo*, 1958, **8**, 5.

⁵ Krishna, B., Srivastava, S. C., and Mahadane, S. V., *Tetrahedron*, 1967, **23**, 4801.

⁶ Prakash, B., D.Phil. Thesis, University of Allahabad, 1968.

⁷ Halverstadt, I. F., and Kumler, W. D., *J. Am. chem. Soc.*, 1942, **64**, 2988.

under investigation, as their moment values in benzene are greater than those in carbon tetrachloride or cyclohexane.

TABLE 1
ELECTRIC DIPOLE MOMENTS OF AMINES

At 25°. The concentration range of the solutes used in the present case was 0.003–0.080 by weight fraction. A linear variation of dielectric constant and specific volume with concentration was found

Compound	In Benzene (ϵ 2.274)	In Carbon Tetrachloride (ϵ 2.228)	In Cyclohexane (ϵ 2.015)
Isopropylamine	1.45	—	—
Diisopropylamine	1.26	1.15	1.20
Diisobutylamine	1.10	—	1.03
Furfurylamine	1.74	1.48	1.56

The electric dipole moment values of diisopropylamine and furfurylamine in carbon tetrachloride are, however, lower than the moment values in cyclohexane. To explain the greater moment values for certain amines in carbon tetrachloride than in benzene, Sharpe and Walker⁸ suggested a donor-acceptor type of interaction existing between the amine and carbon tetrachloride molecules, where the latter serves as an acceptor. This interaction mostly depends on the basicity of amine and the steric factors governing the approach of carbon tetrachloride molecule to the amino nitrogen atom.

In the case of diisopropylamine, a compound possessing low basicity, the presence of alkyl groups and the amino hydrogen atom shields the amino nitrogen atom for the approach of carbon tetrachloride molecules. In furfurylamine, the similar effect is due to the presence of an intramolecular hydrogen bond between the oxygen atom of the nucleus and one of the amino hydrogen atoms. Thus, the formation of any complex involving the lone pair of electrons of the nitrogen atom is not feasible; hence furfurylamine and diisopropylamine have the lowest moment values in carbon tetrachloride.

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⁸ Sharpe, A. N., and Walker, S., *J. chem. Soc.*, 1961, 2974.