Dielectric Polarization of Some Aliphatic Amines in the Liquid State

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Introduction

The relation between the dielectric constant of a liquid and the properties of its individual molecule is a complicated problem. Debye[1] derived the well-known formula,

$$\frac{M}{d}\frac{\varepsilon-1}{\varepsilon+2}=\frac{4\pi N}{3}\left(\alpha+\frac{\mu^2}{3kT}\right),$$

based on Mosotti's hypothesis, where M is the molecular weight, d the density, ε the dielectric constant, N Avogadro's number, α the polarizability, μ the dipole moment, k Boltzmann's constant, and T the absolute temperature. Debye's formula was found to be in agreement with the experimental results for gases and dilute solutions in nonpolar solvents. In this formula the intermolecular interactions are neglected. But, when any effect of interactions between polar molecules exists, some modifications of this theory are required.

Onsager[2] worked out this problem by taking into account the so-called reaction field as well as the cavity field. The formula derived by him is as follows:

$$\frac{M}{d}\frac{(\varepsilon-n)^2(2\varepsilon+n^2)}{\varepsilon(n^2+2)^2}=\frac{4\pi N}{3}\frac{\mu^2}{3kT}$$

where n is the refractive index for optical region. Onsager's formula accounts for the dielectric constants of all substances except a few highly associated liquids, and can be used to calculate dipole moments from the dielectric constants of several polar liquids.

Previously, Estermann[3] found that in pure liquids of diethyl ether, diphenyl ether, and ethylamyl ether, the molecular polarization calculated from the dielectric constant of the pure liquid by means of Debye's formula was in good agreement with that measured with the dilute solution in non-polar solvent, in spite of the considerable polarity of its molecule. Recently, the author has found that the same rule also holds for some aliphatic amines.

Experimental

Method of Measurement.—The measurement of dielectric constant was carried out at a frequency of 2 Mc./sec. by means of resonance method, the details of which were described elsewhere[4]. The density was measured with a pycnometer.

Materials.—Diethylamine was purified from a commercial sample by drying over caustic soda and distillation. b. p. 55.5°C.

Triethylamine was purified from a commercial sample by the method given for diethylamine. b. p. 88.8°C.

i-Propylamine was purified from a commercial sample by distillation. b. p. 33.0–33.5°C.

n-Heptane was purified from a commercial sample by shaking with sulfuric acid, washing with water, drying over metallic sodium, and fractional distillation. b. p. 97.5°C.

Cyclohexane was purified from a commercial sample by the method given for *n*-heptane. b. p. 81.0°C.

Results and Discussion

Dipole Moment.—The mole fraction of the solute x, the dielectric constant ε, and the density d are indicated in Table I, together with the molecular polarization P_2, calculated from them. The molecular polarization was calculated by the following formula;

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[1] P. Debye, "Polare Molekeln", S. Hirzel Press, Leipzig (1929), p. 33.

[2] L. Onsager, *J. Am. Chem. Soc.*, 58, 1486 (1936).

[3] I. Estermann, *Z. physik. Chem.* B 1, 134 (1928).

[4] M. Yasumi and M. Shirai, This Bulletin, 28, 193 (1955).

$$P_2=P_1+\frac{P_{12}-P_1}{x}$$

where P_1, P_2, P_{12} are the molecular polarization of the solvent, solute, and solution, respectively.

The molecular polarization at infinite dilution $P_{2\infty}$ and the dipole moment μ calculated from it are also shown in Table I. The dipole moment is given by

$$\mu=0.0128\sqrt{(P_2-P_E-P_A)T}=0.0128\sqrt{P_0T}$$

where P_E, P_A, and P_0 are the electronic, atomic, and orientation polarization, respectively. P_E+P_A for diethylamine and that for triethylamine were taken to be 25.7 cc. and 33.0 cc., respectively. These were determined by the temperature dependence of their molecular polarization in the gaseous state[5]. For *i*-propylamine, P_E was taken to be equal to the molar refraction for sodium D line, and P_A was assumed to be 5% of the electronic polarization.

The dipole moment of diethylamine and that of triethylamine measured in different solvents are nearly the same, but they are a little greater than those in the gaseous state. This fact is interpreted in terms of solvent effect[6].

TABLE I

DIELECTRIC CONSTANT, DENSITY, MOLECULAR POLARIZATION, AND DIPOLE MOMENT

Diethylamine (P_E+P_A=25.7 cc.)

n-Heptane Solution (−25°C)

x	ε	d	P_2 (cc.)
0.00000	2.0167	0.7229	(58.0)
0.03235	2.0590	0.7233	58.0
0.05199	2.0855	0.7235	57.9
0.07101	2.1123	0.7238	58.2
0.09068	2.1399	0.7241	58.0

$P_{2\infty}$=58.0 cc. P_0=32.3 cc. μ=1.14 D

(25°C)

x	ε	d	P_2 (cc.)
0.00000	1.9529	0.6824	(50.0)
0.03235	1.9816	0.6826	49.9
0.05199	1.9997	0.6827	50.1
0.07101	2.0178	0.6828	50.3
0.09068	2.0361	0.6829	50.2

$P_{2\infty}$=50.0 cc. P_0=24.3 cc. μ=1.09 D

Cyclohexane Solution (25°C)

x	ε	d	P_2 (cc.)
0.00000	2.0309	0.7735	(50.6)
0.03079	2.0672	0.7710	50.6
0.05106	2.0905	0.7691	50.4
0.07069	2.1153	0.7675	50.6
0.09052	2.1391	0.7655	50.7

$P_{2\infty}$=50.6 cc. P_0=24.9 cc. μ=1.10 D

i-Propylamine (P_E+P_A=20.6 cc.)

n-Heptane Solution (−25°C)

x	ε	d	P_2 (cc.)
0.00000	2.0167	0.7229	(56.3)
0.03214	2.0624	0.7229	56.3
0.05110	2.0907	0.7229	56.5
0.07577	2.1292	0.7230	56.5
0.09341	2.1564	0.7220	56.4

$P_{2\infty}$=56.3 cc. P_0=35.7 cc. μ=1.20 D

(25°C)

x	ε	d	P_2 (cc.)
0.00000	1.9529	0.6824	(50.0)
0.03214	1.9863	0.6820	50.1
0.05110	2.0067	0.6818	50.0
0.07577	2.0337	0.6815	50.1
0.09341	2.0531	0.6813	49.8

$P_{2\infty}$=50.0 cc. P_0=29.4 cc. μ=1.20 D

Triethylamine (P_E+P_A=33.0 cc.)

n-Heptane Solution (−25°C)

x	ε	d	P_2 (cc.)
0.00000	2.0167	0.7229	(47.8)
0.03179	2.0344	0.7240	48.0
0.05113	2.0459	0.7247	48.3
0.07319	2.0584	0.7252	48.4
0.09115	2.0690	0.7258	48.4

$P_{2\infty}$=47.8 cc. P_0=14.8 cc. μ=0.78 D

(25°C)

x	ε	d	P_2 (cc.)
0.00000	1.9529	0.6824	(45.8)
0.03179	1.9665	0.6836	45.9
0.05113	1.9745	0.6840	46.0
0.07319	1.9852	0.6849	46.2
0.09115	1.9921	0.6853	46.0

$P_{2\infty}$=45.8 cc. P_0=12.8 cc. μ=0.79 D

Cyclohexane Solution (25°C)

x	ε	d	P_2 (cc.)
0.00000	2.0309	0.7735	(46.5)
0.03090	2.0473	0.7716	46.5
0.05119	2.0578	0.7700	46.6
0.07103	2.0676	0.7687	46.5
0.09195	2.0778	0.7672	46.4

$P_{2\infty}$=46.5 cc. P_0=13.5 cc. μ=0.81 D

Dielectric Polarization in Pure Liquid State.—Dielectric constant and density measured at different temperatures are shown in Table II. The molecular polarization and the dipole moment calculated from them according to Debye's formula and Onsager's formula, respectively, are also listed there. The refractive index which is to be inserted into Onsager's formula should contain the atomic polarization, so that it was calculated by the following formula:

$$\frac{M}{d}\frac{n^2-1}{n^2-2}=P_E+P_A$$

assuming that Lorentz field is valid for the electronic and atomic polarization.

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[5] G.A. Barcley. R.J.W. Le Fèvre and B.M. Smyth, *Trans. Faraday Soc.*, **46**, 812 (1950).

[6] K. Higashi, *Sci. Pap. I.P.C.R.*, **31**, 311 (1937).

TABLE II

DIELECTRIC CONSTANT, DENSITY, MOLECULAR POLARIZATION, AND DIPOLE MOMENT IN THE LIQUID STATE

Diethylamine ($P_E+P_A=25.7$ cc.)

Temp.	ε	d	Debye		Onsager	
(°C)			P_0 (cc.)	μ (D)	P_0 (cc.)	μ (D)
−45	7.2301	0.7684	38.5	1.20	66.0	1.57
−40	6.8079	0.7665	37.2	1.19	61.5	1.53
−30	6.1119	0.7534	35.5	1.19	55.0	1.48
−25	5.8220	0.7508	34.3	1.18	51.8	1.45
−20	5.5797	0.7484	33.3	1.18	49.1	1.43
−10	5.1246	0.7382	31.6	1.17	44.5	1.38
0	4.7734	0.7286	30.2	1.16	41.0	1.36
10	4.4575	0.7183	28.8	1.16	37.9	1.34
20	4.1823	0.7070	27.5	1.15	35.2	1.30
25	4.0656	0.7016	27.0	1.15	32.8	1.28
30	3.9639	0.6964	26.5	1.15	33.1	1.27
40	3.7615	0.6856	25.4	1.14	31.0	1.25
50	3.6063	0.6754	24.6	1.14	29.7	1.25

i-Propylamine ($P_E+P_A=20.6$ cc.)

Temp.	ε	d	Debye		Onsager	
(°C)			P_0 (cc.)	μ (D)	P_0 (cc.)	μ (D)
−60	9.5531	0.7732	37.0	1.14	75.0	1.61
−50	8.8388	0.7630	36.4	1.15	70.1	1.60
−40	8.1835	0.7497	36.0	1.17	65.9	1.58
−30	7.5819	0.7401	35.2	1.18	61.5	1.56
−25	7.2929	0.7354	34.8	1.19	59.2	1.55
−20	7.0448	0.7308	34.4	1.19	57.4	1.54
−10	6.5882	0.7216	33.7	1.20	53.9	1.52
0	6.2176	0.7098	33.3	1.22	51.5	1.52
10	5.9490	0.7012	32.9	1.23	49.6	1.51
20	5.6268	0.6900	32.4	1.24	47.4	1.51
25	5.4656	0.6843	32.1	1.25	46.2	1.50

Triethylamine ($P_E+P_A=33.0$ cc.)

Temp.	ε	d	Debye		Onsager	
(°C)			P_0 (cc.)	μ (D)	P_0 (cc.)	μ (D)
−60	3.0238	0.7923	18.4	0.80	21.7	0.87
−50	2.9387	0.7812	17.8	0.80	19.0	0.83
−40	2.8552	0.7739	16.9	0.80	18.1	0.83
−30	2.7795	0.7678	16.0	0.80	17.4	0.83
−25	2.7470	0.7651	15.6	0.80	16.9	0.82
−20	2.7161	0.7626	15.3	0.80	15.9	0.82
−10	2.6550	0.7549	14.6	0.79	15.7	0.82
0	2.5922	0.7472	13.9	0.79	14.9	0.82
10	2.5348	0.7379	13.4	0.79	14.2	0.82
20	2.4886	0.7280	13.1	0.79	13.8	0.82
25	2.4651	0.7229	13.0	0.80	13.6	0.82
30	2.4492	0.7181	12.9	0.80	13.6	0.82
40	2.3910	0.7097	12.1	0.79	12.7	0.81
50	2.3161	0.7007	11.0	0.76	11.5	0.78

As shown in Tables I and II, both for diethylamine and for *i*-propylamine the dielectric polarization calculated from the dielectric constant and the density of a pure liquid by Debye's formula is in fairly good agreement with that measured in solution at 25°C and −25°C. And, the dipole moment measured by the solution method agrees well with that calculated from the dielectric constant and the density of a pure liquid by Debye's formula throughout the range of temperature −50°C–50°C at which the measurement was performed. On the other hand, the molecular polarization and the dipole moment calculated by Onsager's formula are considerably greater than those in dilute solutions both for diethylamine and *i*-propylamine. Of course, ambiguity about the estimation of the atomic polarization exists, but the contribution of the atomic polarization to the dielectric constant is so small that it has little effect on the value of molecular polarization or dipole moment. For triethylamine, it is impossible to determine whether Debye's formula or any other formula holds, on account of its low dielectric constant. Dielectric polarizations of some other aliphatic amines such as ethylamine, *n*-propylamine, *n*-butylamine, etc. have been measured both in dilute solutions and in pure liquids by Barcley et al[5]. All of them show a considerable departure from Debye's formula and are rather consistent with Onsager's formula.

The difference between the derivation of Debye's formula and that of Onsager's formula may be described as follows: in deriving the former formula, the polarizing effect of the molecule on the surrounding medium is assumed to have average rather than its instantaneous value whereas the latter formula is derived for the instantaneous orientation of each molecule. In other words, in Onsager's field it is taken into account that the field due to the permanent moment polarizes the surrounding medium and produces a reaction field to the dipole. Accordingly, whether Debye's formula or Onsager's formula is valid, depends upon the existence of dipolar interaction.

In this way, it is reasonable to say that the reason why Debye's formula is valid in these pure liquids is the absence of a dipolar interaction. In fact, for these molecules the permanent dipole is screened by non-polar groups and has little effect on the surrounding medium. The result obtained in this work will be useful for the discussion of dipolar interaction in the liquid state, such as micelle formation in organic solvent. The latter problem will be discussed later.

Summary

For diethylamine, *i*-propylamine, and triethylamine, Debye's formula holds as the relation between dielectric constant and dipole moment over a wide range of temperature. This fact can be attributed to the absence of the dipolar interaction on account of the screening of the permanent dipole by non-polar alkyl groups.

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