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The Dipole Moments of the Oligomer of Ethylenediamine

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The dipole moments of ethylenediamine ($N=1$), diethylenetriamine ($N=2$), triethylenetetramine ($N=3$), and tetraethylenepentamine ($N=4$) were measured in a benzene solution at 25°C and 45°C. The observed dipole moments of $N=1$, $N=2$, $N=3$, and $N=4$ are 1.89 D, 2.22 D, 2.37 D, and 2.56 D respectively at 25°C, and 1.84 D, 2.22 D, 2.36 D, and 2.58 D respectively at 45°C. The dipole moments were theoretically calculated on the assumptions that; (i) the dipole moments of these chain molecules are given by the vector sum of the dipole moments of the polar groups of amine, and (ii) all internal rotations about single bonds are free. The calculated values of $N=1$, $N=2$, $N=3$, and $N=4$ are 1.84 D, 2.15 D, 2.43 D, and 2.68 D respectively. The agreement between the observed values and the calculated values is satisfactory. It may, therefore, be expected that the molecular chains will be in the random coil state. The intramolecular hydrogen-bonding is very weak, as there is no temperature dependence of the observed dipole moments.

The study of the electric dipole moments of the oligomer of ethylenediamine in solutions is important from the point of view of thermodynamic property of solutions as well as from that of the molecular structure. The dipole moments of oligomers such as those of ethylene glycol and oxymethylene have been measured and discussed by some authors[1] in terms of their molecular structures. This paper will present a similar study of the dipole moments of ethylenediamine, diethylenetriamine, triethylenetetramine, and tetraethylenepentamine in a benzene solution, and will give some information about the molecular configurations in solutions. Unfortunately, this oligomer is not dissolved in any nonpolar solvent other than benzene. The temperature dependence of dipole moments will be discussed in connection with the intramolecular hydrogen bond.

Experimental

The oligomer (a product of the Tokyo Kasei Chemicals Co., Ltd.) was dried over fresh sodium and distilled several times under a nitrogen atmosphere. The benzene was purified by shaking it with concentrated sulfuric acid, dried over phosphorus pentoxide, and distilled through a 100-cm. column packed with stainless steel helices.

1) T. Uchida, Y. Kurita and M. Kubo, *J. Polymer Sci.*, **19**, 365 (1956); T. Uchida, Y. Kurita, N. Koizumi and M. Kubo, ibid., **21**, 313 (1956); J. Marchal and H. Benoit, ibid., **23**, 223 (1957); K. Kimura and R. Fujishiro, This Bulletin, **39**, 608 (1966).

The measurements of the dielectric constants, ε, and the specific volumes, v, were carried out with an apparatus devised by Le Fevre and his collaborators.[2]

Results

The observed values of ε and v are expressed by equations linear in solute concentrations; they and the w values (the weight fraction of solutes) are summarized in Table I. The range of w values used in the present measurements ranged up to about 0.025. Measurements were carried out at 25°C and 45°C. The calculation of the molecular polarizations, P, from these experimental data was performed according to the standard method.[3] Molecular refractions, R_D, for the sodium D line were calculated on the assumption of the additivity of bond refractions, and distortion polarizations were assumed to be equal to $1.05 \times R_D$. The polarization values and the observed dipole moments, μ, are tabulated in Table II, together with the theoretically-calculated dipole moments, which will be discussed in the next section.

Discussion

The dipole moment of a chain molecule (N-mer), consisting of $(n+1)$ polar units, is given by:

$$\vec{\mu} = \sum_{i=0}^{n} \vec{\mu}_{3i} = \vec{\mu}_0 + \sum_{k=1}^{n-1} \vec{\mu}_{3k} + \vec{\mu}_{3n} \qquad (1)$$

where $\vec{\mu}_{3i}$ is the dipole moment of amine, and the suffix "$3i$" indicates the location of a dipole in the chain schematically shown in Fig. 1. The

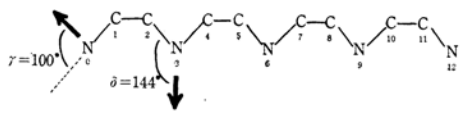

Fig. 1. Numbering of a chain of tetraethylenepentamine.

end groups of $\vec{\mu}_0$ and $\vec{\mu}_{3n}$ are primary amine. Its group moment is assumed to be 1.30 D.[4] This moment lies in the bisecting plane of the H–N–H valence angle, and it is directed along an arrow which makes an obtuse angle, $\gamma = 100°$, with the $\vec{CN}$ bond, as is shown in Fig. 1. In the middle part of a chain, there is secondary amine. Its group moment is assumed to be 1.10 D.[4] This moment lies in the bisecting plane of the C–N–C valence angle, and it is directed along an arrow which makes obtuse angles, $\delta = 144°$ with the $\vec{NC}$ bond and $\delta = 146°$ with the $\vec{NH}$ bond of secondary amine, as is also shown in Fig. 1. The average value of μ^2 over all the angles of internal rotation is given by:

$$\overline{\mu^2} = \mu_0^2 + \sum_{k=1}^{n-1} \mu_{3k}^2 + \mu_{3n}^2 + 2(\overline{\vec{\mu}_0 \cdot \vec{\mu}_{3n}}) + 2\sum_{k=1}^{n-1}(\overline{\vec{\mu}_0 \cdot \vec{\mu}_{3k}}) + 2\sum_{k=1}^{n-1}(\overline{\vec{\mu}_{3k} \cdot \vec{\mu}_{3n}}) + 2\sum_{\substack{k,k'=1 \\ k<k'}}^{n-1}(\overline{\vec{\mu}_{3k} \cdot \vec{\mu}_{3k'}}). \qquad (2)$$

In order to calculate the fourth term in the right hand side of Eq. 2, two vectors, $\vec{\mu}_0$ and $\vec{\mu}_{3n}$ must be expressed with reference to the same coordinate system. This procedure has been used by many authors.[5] The x axis is chosen in the direction of each bond axis of a chain. For example, the coordinate system (x_2, y_2, z_2) of the C_2 origin is fixed as follows: the x_2 axis is taken in the direction of the $\vec{C_2N_3}$ vector, the z_2 axis is directed along the

Table I. Observed values of ε and v expressed by linear equations of w

	25°C	45°C
$N=1$	$\varepsilon = 2.2725 + 6.33\,w$	$\varepsilon = 2.2331 + 5.64\,w$
	$v = 1.14490 + 0.014\,w$	$v = 1.17302 + 0.004\,w$
$N=2$	$\varepsilon = 2.2725 + 5.16\,w$	$\varepsilon = 2.2331 + 4.67\,w$
	$v = 1.14490 - 0.068\,w$	$v = 1.17293 - 0.088\,w$
$N=3$	$\varepsilon = 2.2725 + 4.24\,w$	$\varepsilon = 2.2331 + 3.76\,w$
	$v = 1.14502 - 0.119\,w$	$v = 1.17275 - 0.126\,w$
$N=4$	$\varepsilon = 2.2725 + 3.84\,w$	$\varepsilon = 2.2331 + 3.55\,w$
	$v = 1.14500 - 0.133\,w$	$v = 1.17295 - 0.147\,w$

Tablf II. Polarization values and dipole moments

		25°C	45°C	The theoretically calculated dipole moment
$N=1$	p_∞*	1.536 cc.	1.392	
	P	92.31 cc.	83.67	
	$1.05 \times R_D$	19.10 cc.		
	μ	1.89 D	1.84	1.84
$N=2$	p_∞	1.291	1.234	
	P	133.19	127.29	
	$1.05 \times R_D$	32.66		
	μ	2.22	2.22	2.15
$N=3$	p_∞	1.103	1.044	
	P	161.28	152.62	
	$1.05 \times R_D$	46.22		
	μ	2.37	2.36	2.43
$N=4$	p_∞	1.024	0.996	
	P	193.82	188.46	
	$1.05 \times R_D$	59.77		
	μ	2.56	2.58	2.68

* p stands for the specific polarization.

2) R. J. W. Le Fevre, I. G. Ross and B. M. Smythe, *J. Chem. Soc.*, **1950**, 276.
3) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).
4) C. P. Smythe, "Dielectric Behavior and Structure," McGraw Hill, New York (1955), pp. 253, 311.
5) S. Oka, *Proc. Phys. Math. Soc. Japan*, **24**, 657 (1942); J. Marchal and H. Benoit, *J. Chim. Phys.*, **52**, 818 (1955); M. V. Volkenstein, "Configurational Statistics of Polymer Chains," Interscience Publishers, New York (1963).

vector product of $\overrightarrow{C_2N_3}$ and $\overrightarrow{C_1C_2}$, and the y_2 axis is determined by the x_2 axis and z_2 axis in order that the three axes may constitute a right-handed coordinate system. The same procedure is taken for the coordinate system (x_1, y_1, z_1) of the C_1 origin. The transformation of (x_2, y_2, z_2) to (x_1, y_1, z_1) is easily carried out by the help of the following transformation matrix, $\boldsymbol{T}_{12}$:

$$\boldsymbol{T}_{12} = \begin{pmatrix} \cos\omega & \sin\omega & 0 \\ -\sin\omega\cos\varphi_1 & \cos\omega\cos\varphi_1 & -\sin\varphi_1 \\ -\sin\omega\sin\varphi_1 & \cos\omega\sin\varphi_1 & \cos\varphi_1 \end{pmatrix}$$

where the valence angles $(\pi-\omega)$ are assumed to be tetrahedral about nitrogen atoms of amine as well as carbon atoms, and where φ_1 is an angle of the internal rotation about the C_1—C_2 bond (or an angle between the z_1 axis and the z_2 axis). Then the transformation of (x_2, y_2, z_2) to (x_0, y_0, z_0) is performed by the successive operation of $\boldsymbol{T}_{01}$ on $\boldsymbol{T}_{12}$. For example, the two vectors of $\vec{\mu}_0$ and $\vec{\mu}_3$ for $N=1$ are thus represented by the (x_0, y_0, z_0) coordinate system. If all the internal rotations are free, the average value of the scalar product $(\vec{\mu}_0\cdot\vec{\mu}_3)$ becomes independent of both φ_0 and φ_1, and is given by:

$$\cos^2\omega\cos^2\gamma\,\mu_0\mu_3 \qquad (4)$$

for $N=1$. The same procedure is applied to $N\geqq 2$. The calculated result may be summarized as follows:

$$\overline{\mu^2} = 2\mu^2_p(1-\xi^2\lambda^2) \quad \text{for} \quad N=1,$$

$$\overline{\mu^2} = 2\mu^2_p(1-\xi^2\lambda^5)+\mu^2_s+2\mu_p\mu_s\xi\eta(\lambda^2-\lambda^3) \quad \text{for} \quad N=2,$$

$$\overline{\mu^2} = 2\mu^2_p(1-\xi^2\lambda^{3N-1}) + \mu^2_s\left[N-1+\frac{2\eta^2\lambda^3}{1-\lambda^3}\left\{N-2-\frac{\lambda^3(1-\lambda^{3N-6})}{1-\lambda^3}\right\}\right] + 2\mu_p\mu_s\xi\eta(\lambda^2-\lambda^3)\frac{1-\lambda^{3N-3}}{1-\lambda^3} \quad \text{for} \quad N\geqq 3, \qquad (5)$$

where μ_p and μ_s are 1.30 D and 1.10 D respectively, and λ, ξ, and η are $\cos\omega$, $\cos\gamma$, and $\cos\delta$ respectively. The calculated dipole moments for $N=1$, $N=2$, $N=3$, and $N=4$ are 1.84 D, 2.15 D, 2.43 D, and 2.68 D respectively. The agreement between the calculated dipole moments and the observed ones is satisfactory in view of the model used in the above calculation. Strictly speaking, the effect of the excluded volume on dipole moments must be taken into consideration, but this effect may make only a minor contribution to dipole moments for such short chains as those considered here. It may, therefore, be inferred that the oligomer of ethylenediamine in a benzene solution is in the random coil state. This is also supported by the fact that the observed dipole moments do not show any temperature dependence. This suggests that the intramolecular hydrogen-bonding is very weak or that it does not occur at all in this case.