BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 608—610 (1966)

The Dipole Moments of the Oligether of Ethylene Glycol

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(Received July 31, 1965)

The dipole moments of ethylene glycol dimethyl ether ($N=1$), diethylene glycol dimethyl ether ($N=2$), triethylene glycol dimethyl ether ($N=3$), and tetraethylene glycol dimethyl ether ($N=4$), were measured in *n*-hexane or benzene at 25°C and 45°C. The observed dipole moments of $N=1$, $N=2$, $N=3$, and $N=4$ are 1.59 D, 1.92 D, 2.16 D, and 2.44 D, respectively, in *n*-hexane at 25°C, 1.71 D, 1.97 D, 2.22 D, and 2.45 D, respectively, in benzene at 25°C, and 1.72 D, 1.98 D, 2.27 D, and 2.50 D, respectively, in benzene 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 polar groups of ether whose group moment is 1.20 D, and (ii) all the internal rotations of a chain molecule are free. The calculated values of $N=1$, $N=2$, $N=3$, and $N=4$ are 1.67 D, 2.03 D, 2.33 D, and 2.60 D, respectively. The agreement between the observed and the calculated values is satisfactory. The solvent effect and the temperature dependence of the observed dipole moments have also been discussed in terms of chain flexibility.

The study of the electric dipole moments of the oligomer of ethylene glycol in solutions from the point of view of thermodynamic behavior is important as well as from that of the molecular structure. The molecular structure of the oligomer of ethylene glycol in dioxane had been discussed,[1] but there is some difficulty in analyzing the experimental results because of the intra- and intermolecular hydrogen-bonding between hydroxyl groups of the solutes and the solvent. The hydrogen-bonding of the end groups may determine the configuration of chain molecules when their chain lengths are as short as those in oligomers. This paper, therefore, will present a study of the dipole moments of the dimethyl ether of monomer (ethylene glycol), dimer, trimer, or tetramer in solvents such as benzene and *n*-hexane, and will describe their correlation with their molecular configurations.

Experimental

Dimethyl ethers of the oligomer (products of the Tokyo Kasei Chemicals Co., Ltd.) were dried over calcium chloride and distilled under nitrogen several times. Benzene was purified by shaking it with concentrated

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[1] T. Uchida, Y. Kurita, N. Koizumi and M. Kubo, *J. Polymer Sci.*, **21**, 313 (1956); J. Marchal and H. Benoit., ibid., **23**, 223 (1957).

TABLE I. OBSERVED VALUES OF ε AND v EXPRESSED BY LINEAR EQUATIONS OF w

	H* 25°C	B* 25°C	B 45°C
Monomer (N=1)	$\varepsilon=1.8929+1.98w$ $v=1.49776-0.272w$	$\varepsilon=2.2725+3.21w$ $v=1.14508+0.050w$	$\varepsilon=2.2331+2.95w$ $v=1.17444+0.014w$
Dimer (N=2)	$\varepsilon=1.8867+2.01w$ $v=1.50969-0.427w$	$\varepsilon=2.2725+3.00w$ $v=1.14465-0.084w$	$\varepsilon=2.2331+2.95w$ $v=1.17458-0.098w$
Trimer (N=3)	$\varepsilon=1.8912+1.98w$ $v=1.50126-0.483w$	$\varepsilon=2.2725+2.91w$ $v=1.14475-0.115w$	$\varepsilon=2.2331+2.73w$ $v=1.17442-0.134w$
Tetramer (N=4)	$\varepsilon=1.8877+2.01w$ $v=1.50946-0.499w$	$\varepsilon=2.2725+2.87w$ $v=1.14481-0.147w$	$\varepsilon=2.2331+2.69w$ $v=1.17451-0.161w$

* B and H are abbreviations of benzene and hexane, respectively. Values of w's used in these measurements are from zero to about 0.03.

sulfuric acid and by fractional distillation through a 100 cm. column packed with stainless-steel helices. Hexane was purified by letting it stand with fuming sulfuric acid for a few months and by fractional distillation.

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 linear equations of the solute concentrations, w (the weight fraction of solutes); they are summarized in Table I. 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 the distortion polarizations were assumed to be equal to $1.1\times R_D$.[1] The observed dipole moments, μ, are tabulated in Table II, together with the polarization values.

TABLE II. OBSERVED DIPOLE MOMENTS

		H 25° C	B 25° C	B 45°C
N=1	p_∞	0.8682 cc.	0.9600	0.9262
	P	78.25 cc.	86.52	83.48
	$1.1\times R_D$	26.64 cc.		
	μ	1.59 D	1.71	1.72
N=2	p_∞	0.8496	0.8802	0.8485
	P	114.0	118.1	113.8
	$1.1\times R_D$	38.83		
	μ	1.92	1.97	1.98
N=3	p_∞	0.8222	0.8540	0.8398
	P	146.5	152.1	149.6
	$1.1\times R_D$	51.0		
	μ	2.16	2.22	2.27
N=4	p_∞	0.8329	0.8371	0.8242
	P	185.1	186.1	183.2
	$1.1\times R_D$	63.2		
	μ	2.44	2.45	2.50

* p_∞ stands for the specific polarization.

TABLE III. COMPARISON BETWEEN THE CALCULATED DIPOLE MOMENTS AND THE OBSERVED ONES

		$\mu_{\text{obs.}}$		
N	$\mu_{\text{calc.}}$	H 25°C	B 25°C	B 45°C
1	1.67D	1.59	1.71	1.72
2	2.03	1.92	1.97	1.98
3	2.33	2.16	2.22	2.27
4	2.60	2.44	2.45	2.50

Discussion

The dipole moment of a chain molecule consisting of n polar units is equal to:

$$\vec{\mu}=\sum_{i=1}^{n}\vec{\mu}_i \tag{1}$$

where $\vec{\mu}_i$ is the dipole moment of each unit. In the present case, it is a group moment of ether, which is directed along the bisectrix of the C–O–C valence angle with the positive center at the side of carbon atoms. Its value, μ_0, is assumed to be 1.20 D. As a monomer consists of two units, n is equal to $N+1$. The scalar product of $\vec{\mu}$ gives:

$$\overline{\mu}^2=\sum_{i=1}^{n}\mu_i^2+2\sum_{i=1,\ i<j}^{n}\overline{(\vec{\mu}_i\cdot\vec{\mu}_j)} \tag{2}$$

where $\overline{\mu^2}$ is the average μ^2 value over the angles of all internal rotations. The second term on the right hand side of (2) can be easily calculated if all the internal rotations are free.[4] The calculated results of (2) are as follows:

$$\overline{\mu^2}=(2-2\lambda^2\eta^2)\mu_0^2 \qquad \text{for } N=1$$

$$\overline{\mu^2}/2=(3/2-2\lambda^2\eta^2-\lambda^5\eta^2)\mu_0^2 \qquad \text{for } N=2$$

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[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] S. Oka, *Proc. Phys. Math. Soc. Japan*, **24**, 657 (1942); M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," Interscience Publishers, New York (1963), p. 301; J. Marchal and H. Benoit, *J. Chim. Phys.*, **52**, 818 (1955).

Table IV. Distances between two methyl groups in the case of $N=1$, when a molecule is fixed at the gauche configuration about the central bond

GG	GT	GG′	TG	TT	TG′	G′G	G′T	G′G′
(1.32Å)	(3.06)	(3.36)	(3.06)	4.67	3.97	(1.83)	3.97	(3.20)

$$\overline{\mu^2}/3 = (4/3-2\lambda^2\eta^2-4/3\cdot\lambda^5\eta^2-2/3\cdot\lambda^8\eta^2)\mu_0{}^2 \qquad \text{for } N=3$$

$$\overline{\mu^2}/4 = (5/4-2\lambda^2\eta^2-3/2\cdot\lambda^5\eta^2-\lambda^8\eta^2 -1/2\cdot\lambda^{11}\eta^2)\mu_0{}^2 \qquad \text{for } N=4$$

$$\overline{\mu^2}/N = [1+1/N-2\lambda^2\eta^2\{1/(1-\lambda^3) -\lambda^3(1-\lambda^{3N})/N(1-\lambda^3)^2\}]\mu_0{}^2 \qquad \text{for } N$$

$$= \{(1-2\lambda^2\eta^2/(1-\lambda^3))\}\mu_0{}^2 = 12/13\cdot\mu_0{}^2 \qquad \text{for } N\to\infty$$

where λ and η are $\cos\omega$ and $\sin\omega/2$, respectively. For the sake of simplicity, the valence angle $(\pi\text{-}\omega)$ is assumed to be tetrahedral about the oxygen atoms as well as about the carbon atoms of ether. The calculated dipole moments are tabulated in Table III, together with the observed moments. From a comparison of the calculated dipole moments with the observed ones, we can see that the former agrees satisfactorily with the latter. It may, therefore, be suggested that the oligether of ethylene glycol in non-polar solvents is in a random coil state. For $N=1$, the solvent effect makes a considerable contribution to the dipole moment compared with the temperature effect, but for $N=4$, two effects are reversed, as is shown in Table III. This result may be expected if the steric effect of the rotational isomers is taken into consideration. The distances between two methyl groups for $N=1$ are estimated for nine configurations in Table IV, when the *gauche* configuration is kept about the central bond. Only three rotational isomers among the nine are possible as a result of the overlapping of two methyl groups. This means that chain flexibility is not expected for $N=1$. Therefore, no temperature dependence of its dipole moments was observed. On the contrary, the observed dipole moments at 25°C are constant for $N=4$ within the range of experimental errors, irrespective of the solvents used, but their temperature dependence was observed. The observed moments at 45°C approach the calculated moments more closely than those at 25°C. It may, therefore, be expected that the temperature effect rather than the solvent effect will become important as a result of the increase in chain flexibility when the chain length is lengthened.

Raman spectra at low frequencies (250 cm^{-1} to 600 cm^{-1}) corresponding to the skeletal deformation show the feature already described, although measurements of Raman spectra[5] were carried out for pure liquids. Only four sharp lines are observed for $N=1$. However, as N increases, broader bands are observed at these frequencies.

Summary

The dipole moments of the oligether of ethylene glycol have been measured in *n*-hexane and benzene at 25°C and 45°C. The observed values have been compared with the calculated values derived on the assumption that all internal rotations are free. The agreement between them is satisfactory. The solvent effect and the temperature dependence of the observed dipole moments have also been discussed.

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[5] K. Kimura and R. Fujishiro, unpublished work.