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The Dipole Moments of α,ω-Alkanediols

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The electric dipole moments of α,ω-alkanediols such as HO–$(CH_2)_n$–OH (n being varied from 2 to 5) were measured both in dioxane and in a mixed solvent of dioxane with carbon tetrachloride at 25°C. The observed dipole moments increase with the increasing n until $n=4$, and then decrease for $n=5$, while the calculated dipole moments based on the vector addition of group moments on the assumption of the random coil model for alkane chains increase monotonously as n increases from 2 to 5. It is concluded that for both propanediol and butanediol the conformations forming the intramolecular hydrogen-bond which have the larger dipole moments contribute appreciably to the observed dipole moments. The dipole moment of pentanediol is close to the calculated one for the random coil model, whereas that of ethylene glycol suggests the existence of the intramolecular hydrogen-bond. Population analysis of the hydrogen-bonded species in solutions is also given.

The electric dipole moments of molecules with multiple degrees of freedom of internal rotation were already discussed.[1] Recently, the anomalous dipole moments of 1,4-dichlorobutane or 1,4-dibromobutane were reported by Thompson and Hanson,[2] and led to the conclusion that the steric hindrance between two halogen atoms attached at the end positions of the aliphatic chain excludes some of the conformations which have larger dipole moments. The dipole moments of these compounds are, therefore, anomalously small.

When the two halogen atoms in 1,4-dihalogenobutane are replaced by hydroxy groups, the intramolecular hydrogen-bond may be formed. Study of the intramolecular hydrogen-bonding in solutions is carried out extensively by help of the infrared absorption spectra, but α,ω-alkanediols dissolve scarcely in solvents commonly used in the infrared absorption study. Nevertheless, the formation of the intramolecular hydrogen-bond for some of α,ω-alkanediols in solutions is inferred from the infrared absorption[3] or from NMR spectra[4] by making suitable device. It is interesting and valuable to investigate the intramolecular hydrogen-bond in mixed solvents from the view point of dipole moments.

In this paper, the electric dipole moments of α,ω-alkanediols such as HO–$(CH_2)_n$–OH (n being varied from 2 to 5) are measured and discussed in connection with the intramolecular hydrogen-bonding.

Experimental

All the alkanediols used in this work were purified by the fractional distillation through a 100 cm column packed with stainless-steel helices, dried over molecular sieves and distilled in vacuum. Dioxane used as a solvent was refluxed over fresh sodium for a few days and distilled through the same column as that just mentioned. A mixed solvent of dioxane with carbon tetrachloride was also used, when necessary. Carbon tetrachloride was purified by shaking it with alcoholic sodium hydroxide, dried, and then distilled through

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1) C. P. Smyth, "Dielectric Behavior and Structure, McGraw Hill, New York, N. Y. (1955), p. 368; J. W. Smith, "Electric Dipole Moments" Butterworths Scientific Publications, London (1955), p. 292.

2) H. B. Thompson and S. L. Hanson, *J. Phys. Chem.*, **65,** 1005 (1961).

3) L. P. Kuhn, *J. Amer. Chem. Soc.*, **74,** 2492 (1952).

4) K. Fukui, T. Yonezawa, H. Saito and S. Matsuoka, This Bulletin, **38,** 1431 (1965).

the same column.[5]

Measurements of the dielectric constants, ε's and the specific volumes, ρ's were carried out by the same apparatus and method as in the previous work.[6] All the data were obtained at 25±0.02°C. In the present investigation, the weight fractions, w's of solutes range over from zero to about 0.02.

Results

The observed values of ε's and of ρ's are fairly well expressed by the linear equations of w's. The molecular polarizations, p's were obtained from these experimental data according to Halverstadt-Kumler's method.[7] The molecular refractions, R_D's 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's are tabulated in Table 1, together with the linear equations of ε's and ρ's to w's. Data for ethyl alcohol are also given in Table 1.

Table 1. Dipole moment data

	Dioxane	A mixed solvent*
$n = 2$	$\varepsilon=2.2079+10.61w$	$\varepsilon=2.2470+14.48w$
	$\rho=0.9729-0.08w$	$\rho=0.7123+0.20w$
	$p=124.5$ cc	$p=123.0$ cc
	$R_D=14.4$ cc	$R_D=14.4$ cc
	$\mu=2.31$ D	$\mu=2.30$ D
$n = 3$	$\varepsilon=2.2090+10.53w$	$\varepsilon=2.2480+15.60w$
	$\rho=0.9726-0.03w$	$\rho=0.7126+0.29w$
	$p=152.6$	$p=163.0$
	$R_D=19.1$	$R_D=19.1$
	$\mu=2.55$	$\mu=2.65$
$n = 4$	$\varepsilon=2.2061+9.10w$	$\varepsilon=2.2470+13.68w$
	$\rho=0.9726+0.01w$	$\rho=0.7127+0.29w$
	$p=160.7$	$p=172.6$
	$R_D=23.7$	$R_D=23.7$
	$\mu=2.58$	$\mu=2.69$
$n = 5$	$\varepsilon=2.2083+7.46w$	$\varepsilon=2.2476+10.48w$
	$\rho=0.9725+0.04w$	$\rho=0.7117+0.31w$
	$p=158.4$	$p=160.3$
	$R_D=28.3$	$R_D=28.3$
	$\mu=2.51$	$\mu=2.53$
C_2H_5OH**	$\varepsilon=2.2095+9.40w$	$\varepsilon=2.2725+6.83w$
	$\rho=0.9726+0.04w$	$\rho=1.14619+0.19w$
	$p=77.8$	$p=77.7$
	$R_D=12.9$	$R_D=12.9$
	$\mu=1.77$	$\mu=1.77$

* A mixed solvent is composed of one volume of dioxane and two volumes of carbon tetrachloride.

** Measurements were carried out not in the mixed solvent but in both dioxane (the left column) and benzene (the right column).

Discussion

The mean square dipole moment, $\overline{\mu^2}$ of α,ω-disubstituted alkanes can be written on the assumption of the vector addition as

$$\overline{\mu^2} = \mu_1^2 + \mu_n^2 + 2(\vec{\mu}_1\cdot\vec{\mu}_n) \tag{1}$$

where $\vec{\mu}_1$ and $\vec{\mu}_n$ mean moment vecotrs of polar groups located at the both ends, and μ_1 and μ_n scalar quantities of $\vec{\mu}_1$ and of $\vec{\mu}_2$, respectively. The third term of Eq. (1) in the right hand side may be easily calculated by the use of transformation matrix.[8] The coordinate system is chosen as follows, which is depicted in Fig. 1: the x_i axis of the origin C_i is taken in the direction of C_i-C_{i+1} bond of a chain, the z_i axis in the direction of the vector product of C_i-C_{i+1} and C_{i-1}-C_i, and the y_i axis in the direction to constitute the right-handed coordinate system. The coordinate system of the origin C_{i+1} is chosen in the same way as already mentioned. The transformation from the coordinate system$(x_{i+1}, y_{i+1}, z_{i+1})$ to (x_i, y_i, z_i) is carried out by help of the following transformation matrix:

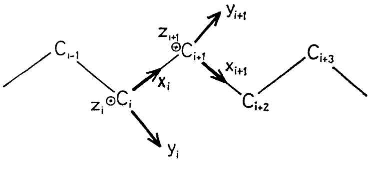

Fig. 1. The coordinate system.
⊕ Upwards from the plane
⊙ Downwards from the plane

$$T_{i,i+1} = \begin{pmatrix} \cos\chi & \sin\chi & 0 \\ \sin\chi\cos\varphi_i & -\cos\chi\cos\varphi_i & -\sin\varphi_i \\ -\sin\chi\sin\varphi_i & \cos\chi\sin\varphi_i & -\cos\varphi_i \end{pmatrix} \tag{2}$$

where the valence angles$(\pi-\chi)$ are assumed to be tetrahedral, and φ_i is an angle of the internal rotation measured from the *trans*-form about C_i-C_{i+1} bond. The successive operation of this transformation on the third term of Eq. (1) gives

$$\overline{\mu^2} = \mu_1^2 + \mu_n^2 + 2\overrightarrow{\mu_1(T_{1,2}\cdots\cdots T_{n-1,n})}\vec{\mu}_n. \tag{3}$$

If all the internal rotations are free, the mean square dipole moment of α,ω-alkanediol becomes independent on φ_i's, and is given by[1]

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[5] A. Weissberger *et al.*, "Organic Solvents," Interscience Publishers, New York, N. Y. (1955).

[6] K. Kimura and R. Fujishiro, This Bulletin, **39,** 608 (1966).

[7] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, **64,** 2988 (1942).

[8] 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, N. Y. (1963).

$$\overline{\mu^2} = 2\mu_1^2(1-\cos^2\theta\cos^n\chi) \tag{4}$$

where μ_1 is the magnitude of the moment vector $\vec{\mu}_1$ for a HO-C group and is assigned to be 1.77D[1),9)] and θ is an angle between the moment vector $\vec{\mu}_1$ and the position vector, $\overrightarrow{\text{C-O}}$ bond and is equal to 62°. Dipole moments calculated by the use of Eq. (4) are summarized in Table 2, together with those obtained from Eq. (3) by assigning appropriate angles to φ_i's, which are determined by the intramolecular hydrogen-bonded conformations. Tables 1 and 2 show that the observed dipole moments increase with the increasing n until $n=4$, and then decrease for $n=5$, whereas the calculated moments on the assumption of the random coil model increase monotonously, as is expected from Eq. (4), when n increases from 2 to 5. This phenomenon is observed remarkably in the mixed solvent of dioxane with carbon tetrachloride, as is shown in Table 1. Agreement between the observed value and the calculated average one is good only for $n=5$ irrespective of solvents used in this research. If it is assumed that the vector addition of group moments is valid even for the hydrogen-bonded system, a pentanediol molecule forms no intramolecular hydrogen-bond at all in solutions. This result is supported by the infrared absorption spectra,[3)] and also by NMR spectra.[4)] On the contrary, the observed dipole moments for 1,3-propanediol and for 1,4-butanediol are larger than the calculated average moments. Difference between the calculated average moment and the calculated moment for the intramolecular hydrogen-bonded conformation amounts to about 1D for the former and to about 0.5D for the latter. Small but not negligible increase of the observed dipole moments over the calculated average moments is due to the appreciable contribution of the intramolecular hydrogen-bonded conformations to the observed dipole moments. The same kind of research as mentioned above was carried out recently by Toshiyasu and Fujishiro[10)] both for 1,3-dimethoxypropane or 1,4-dimethoxybutane and for monomethyl ether of 1,3-propanediol or 1,4-butanediol, although the former corresponds to the case of α, ω-dihalogenoalkane reported by Thompson *et al.*,[2)] and the latter to the present research. Hence, it is possible to infer the existence of the intramolecular hydrogen-bond in solutions from measurements of dipole moments together with the calculations of dipole moments based on the vector addition of group moments both for the random coil model and for the intramolecular hydrogen-bonded conformations. The intramolecular hydrogen-bond for ethylene glycol in solutions was confirmed by the infrared absorption spectra, but any information can not be obtained from dipole moment data, as is seen from Table 2.

TABLE 2. CALCULATED DIPOLE MOMENTS

	The average moment μ_r (the random coil model)	The moment for the intramolecular hydrogen-bond conformations* μ_h	
$n=2$	2.47D	TGG′ (TG′G)	2.51D
$n=3$	2.48	TGG′G (TG′GG′)	3.54
$n=4$	2.49	TGG′GG′ (TG′GG′G) GGG′GG′ (G′G′GG′G)	3.06
$n=5$	2.50		

* T and G represent *trans*- and *gauche*-form, respectively.

Population analysis of rotational isomers in solutions is performed by the help of the theory of chemical equilibrium. According to the statistical thermodynamic treatment of associated solutions by Saroléa-Mathot,[11)] the partition function Ω is given by

$$\Omega = \phi_a^{N_a}\phi_d^{N_d}\phi_c^{N_c}\frac{(x-z-u+N_d+N_c)!}{x!y!z!u!v!(N_d-y-2\cdot z-v)!N_c!} \times \exp[-1/\boldsymbol{k}T\{x_1f_1+x_2f_2+x_3f_3 + (y+2\cdot z+v)\Delta E_{\text{I}} + (u+v)\Delta E_{\text{II}}\}] \tag{5}$$

where ϕ_a, ϕ_d, and ϕ_c represent the internal partition functions of alkanediols, dioxane and carbon tetrachloride, respectively, and N_a, N_d, and N_c are the number of molecules corresponding to each suffix. The total number of molecules for alkanediols, N_a is divided into five molecular species, that is,

$$N_a = x+y+z+u+v$$

where x is the number of molecules with the free hydroxy groups without any hydrogen-bond, y the number of molecules with one free hydroxy group and the other hydrogen-bonded with dioxane, z the number of molecules with both hydrogen-bonded with dioxane, u the number of molecules with one free hydroxy group and the other forming the intramolecular hydrogen-bond, and v the number of molecules with one hydrogen-bonded with dioxane and the other forming the intramolecular hydrogen-bond. Interaction parameters f_1, f_2, and f_3 are defined as follows:

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9) In order to confirm the value assigned by Smyth, the dipole moment measurement for ethyl alcohol was carried out in the same condition as that for α, ω-alkanediols. The observed value is fairly close to that given by Smyth, as is shown in Table 1.

10) Y. Toshiyasu and R. Fujishiro, to be published.

11) L. Saroléa-Mathot, *Trans. Faraday Soc.*, **49**, 8 (1953).

$$\left.\begin{aligned} f_1 &= f_{cd} - 1/2(f_{cc}+f_{dd}) \\ f_2 &= f_{ad} - 1/2(f_{dd}+f_{aa}) \\ f_3 &= f_{ac} - 1/2(f_{cc}+f_{aa}) \end{aligned}\right\} \tag{6}$$

where f_{ij} is the interaction energy due to dispersion force between two contact molecules i and j. The quantities x_1, x_2, and x_3 represent the number of contact pairs corresponding to each suffix. $\varDelta E_{\mathrm{I}}$ and $\varDelta E_{\mathrm{II}}$ are energies of the intermolecular hydrogen-bond and of the intramolecular hydrogen-bond, respectively. Equality of the chemical potentials of all species in the equilibrium state gives equilibrium concentrations of all species as functions of $\varDelta E_{\mathrm{I}}$, $\varDelta E_{\mathrm{II}}$, and $C=N_d/(N_d+N_c)$. On the assumption ($N_a \ll N_d$ or N_c) in dilute solutions, one obtains

$$\left.\begin{aligned} x &= N_a/[1+\exp(-\varDelta E_{\mathrm{II}}/\boldsymbol{k}T) + C\cdot\exp(-\varDelta E_{\mathrm{I}}/\boldsymbol{k}T) \\ &\quad \times \{1+\exp(-\varDelta E_{\mathrm{II}}/\boldsymbol{k}T)\} + C^2\cdot\exp(-2\cdot\varDelta E_{\mathrm{I}}/\boldsymbol{k}T)] \\ y &= N_a/[1+\exp(-\varDelta E_{\mathrm{II}}/\boldsymbol{k}T) + 1/c\cdot\exp(\varDelta E_{\mathrm{I}}/\boldsymbol{k}T) \\ &\quad \times \{1+\exp(-\varDelta E_{\mathrm{II}}/\boldsymbol{k}T)\} + c\cdot\exp(-\varDelta E_{\mathrm{I}}/\boldsymbol{k}T)] \\ z &= N_a/[1+1/c\cdot\exp(\varDelta E_{\mathrm{I}}/\boldsymbol{k}T)\{1+\exp(-\varDelta E_{\mathrm{II}}/\boldsymbol{k}T)\} \\ &\quad + 1/c^2\cdot\exp(2\cdot\varDelta E_{\mathrm{II}}/\boldsymbol{k}T)\{1+\exp(-\varDelta E_{\mathrm{II}}/\boldsymbol{k}T)\}] \\ u &= N_a/[1+\exp(\varDelta E_{\mathrm{II}}/\boldsymbol{k}T)+c\cdot\exp(-\varDelta E_{\mathrm{I}}/\boldsymbol{k}T) \\ &\quad \times \{1+\exp(\varDelta E_{\mathrm{II}}/\boldsymbol{k}T)\} \\ &\quad + c^2\cdot\exp\{(\varDelta E_{\mathrm{II}}-2\cdot\varDelta E_{\mathrm{I}})/\boldsymbol{k}T\}] \\ v &= N_a/[1+\exp(\varDelta E_{\mathrm{II}}/\boldsymbol{k}T) + 1/c\cdot\exp(\varDelta E_{\mathrm{I}}/\boldsymbol{k}T) \\ &\quad \times \{1+\exp(\varDelta E_{\mathrm{II}}/\boldsymbol{k}T)\} \\ &\quad + c\cdot\exp\{(\varDelta E_{\mathrm{II}}-\varDelta E_{\mathrm{I}})/\boldsymbol{k}T\}] \end{aligned}\right\} \tag{7}$$

Then, the observed dipole moments are approximately given by

$$\mu_{\mathrm{obs}}^2 = (x+y+z)\mu_r^2 + (u+v)\mu_h^2 \tag{8}$$

where μ_r and μ_h represent the average dipole moment for the random coil model and that for the intramolecular hydrogen-bonded conformation, respectively, which are given in Table 2. When $\varDelta E_{\mathrm{I}}$ is assigned to be -4 kcal/mol,[12] a value of $\varDelta E_{\mathrm{II}}$ for $n=3$ and that for $n=4$ are -2.2 kcal/mol and -2.9 kcal/mol, respectively, each of which is close to already reported value[13], *i.e.*, -2.1 kcal/mol for $n=3$ and -2.7 kcal/mol for $n=4$. Population analysis in solutions was performed by using these energy values. Table 3 gives the equilibrium concentrations of all species present in solutions. This table is suggestive in giving information about what kind of molecular species is predominant in a solvent: for $n=3$, the species v is scarcely present in pure dioxane, but for $n=4$, it amounts to about 13% even in pure dioxane, and the amount of species v becomes significant in a mixed solvent (1 volume dioxane to 2 volumes carbon tetrachloride) both for $n=3$ and for $n=4$.

TABLE 3. MOLE FRACTIONS OF SPECIES PRESENT IN SOLUTIONS

		x	y	z	u	v
$n=3$	Dioxane	0	0.001	0.953	0	0.046
	A mixed solvent	0	0.003	0.880	0	0.117
$n=4$	Dioxane	0	0.001	0.865	0	0.134
	A mixed solvent	0	0.002	0.696	0.001	0.301

In conclusion, dipole moment study makes it possible in some cases of α,ω-alkanediols to confirm the existence of the intramolecular hydrogen-bonded species and to do population analysis of all species in solutions.

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[12] G. C. Pimentel and A. L. McClellan, "Hydrogen Bonding," W. H. Freeman and Company, Reinhold Publishing Corp., New York N. Y. (1960).

[13] L. P. Kuhn and R. A. Wires, *J. Amer. Chem. Soc.*, **86**, 2161 (1964).