© 1991 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 64, 2030—2031 (1991) [Vol. 64, No. 6

Dielectric Relaxation Studies of Oligether of Ethylene Glycol at Microwave Frequencies

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(Received September 19, 1990)

Synopsis. Dielectric relaxation studies of dialkyl ethers of ethylene glycol and of diethylene glycol have been carried out at microwave frequencies in benzene solutions. Dipole moment and relaxation times corresponding to overall and group rotations and their weight factors have been determined. The configuration of these molecules and the mechanism of the rotation of end alkoxyl groups have been discussed.

Several[1–3] attempts have been made to study the configuration of oligethers of ethylene glycol by carrying out measurements of dipole moments in solutions. So far these studies have been made with ethers, R–$(OCH_2CH_2)_m$–OR with different values of *m* but keeping same end alkoxyl groups. All these studies concluded the preference of the trans positions in the chain.

In this paper dipole moments of dialkyl ethers of ethylene glycol and of diethylene glycol with different end alkoxyl groups in benzene solutions have been determined, using Higasi[4] equation (Table 1). The dielectric measurements of these molecules in benzene solutions have also been carried out at microwave frequencies with a view to study the group rotations of the end alkoxyl groups and configurations of these molecules.

Experimental

The dielectric permittivity ε' and dielectric loss ε'' at four microwave frequencies viz. 9.83, 18.26, 24.50, and 30.20 GHz and static permittivity ε_0 at 1 MHz and permittivity at high frequency $\varepsilon_\infty = n_D^2$ in benzene solutions were determined using the method described in an earlier paper.[5] All measurements were made at 35 °C.

Linear slopes a_0, a', a'', and a_∞ (ε_0, ε', ε'', and ε_∞ vs. wt fraction of solute) have been used for complex plane plots (a'' vs. a') and analysis of data. Average relaxation time τ_0 and distribution parameter α have been calculated from these plots.[6] Data have been analyzed for the relaxation time of overall rotation τ_1, group rotation τ_2 and their corresponding weight factors, using Budo[7] equation (Table 2).

The compounds were obtained from Riedel-de Haën, E. Merck, Germany and Messrs Fluka A.G., Switzerland of purum grade and used as such. Benzene Analar (B.D.H., India) was used as solvent after double distillation.

Results and Discussion

The dipole moment of these compounds are in good agreement with those reported earlier[1–3] (Table 1). The dipole moment of the molecule decreases with increase in the size of two end alkoxyl groups. This is the characteristic behavior of all homologous series in which increase in the size of the alkoxyl groups decreases the polarity at the two ends of the chain, hence there is a decrease in the dipole moment. The dipole moment of dialkyl ether of diethylene glycol is greater than the corresponding dialkyl ether of ethylene glycol because of the increase in the separation of the end polar alkoxyl groups resulting in an increase in the dipole moment. Dipole moment of monoalkyl ether[8,9] is greater than the corresponding dialkyl ether because of the higher group moment of the hydroxyl group in comparison to that of the alkoxyl group (Table 1).

The complex plane plots obeyed the Cole–Cole arcs which show the symmetrical distribution of relaxation time in these molecules. The value of τ_0 increases with increase in the size of the molecule which is in agreement with that of the other homologous series.[8,9] Small values of τ_0 and large values of α indicate that besides

Table 2. Relaxation Times τ_0, τ_1, and τ_2, Distribution Parameter α, and Weight Factor C_2 for Group Rotation in Benzene Solutions at 35 °C

Compound	τ_0/ps	α	τ_1/ps	τ_2/ps	C_2
	Dialkyl ethers of ethylene glycol				
Dimethyl	1.8	0.25	24.8	1.6[a)]	0.90
Diethyl	3.0	0.23	16.8	2.3	0.82
	Dialkyl ethers of diethylene glycol				
Dimethyl	2.0	0.34	21.7	1.5[a)]	0.80
Diethyl	3.5	0.29	18.1	2.0	0.75
Dibutyl	4.5	0.25	14.6	2.7	0.66

a) 1,4-Dimethoxybenzene[10,11] in benzene, τ_1=11.55 τ_2=1.65 C_2=0.20. Anisole[10,11] in benzene, τ_1=9.90 τ_2=1.65 C_2=0.16. Ethylene glycol monomethyl ether[8] in benzene, τ_1=16.26 τ_2=1.54 C_2=0.75.

Table 1. Values of Dipole Moments in Benzene Solutions at 35 °C[e)]

Ethers of ethylene glycol				Ethers of diethylene glycol			
Compound	μ/Debye	Compound	μ/Debye	Compound	μ/Debye	Compound	μ/Debye
Monomethyl	2.24	Dimethyl[a)]	1.81	Monomethyl	2.75	Dimethyl[c)]	2.09
Monoethyl	2.26	Diethyl[b)]	1.76	Monoethyl	2.78	Diethyl[d)]	1.98
Monobutyl	2.24			Monobutyl	2.65	Dibutyl	1.88

a) 1.71 Debye[1)] at 25 °C. b) 1.61 Debye[3)] at 20 °C. c) 1.97 Debye[1)] at 25 °C. d) 1.99 Debye[2)] at 20 °C, 1.93 Debye[3)] at 25 °C. e) 1 Debye=3.3356×10^{-30} C m.

the overall rotation, there is considerable contribution of group rotations. It has been observed that the presence of polar end alkoxyl groups in the polymers of lower molecular weight results in proportionately higher rigidity in the polymer chain, consequently there is practically no twisting or coiling of the chain. In case of these molecules central portion may be regarded as a rigid rod, at the two ends of which the alkoxyl groups rotate. The situation can be compared with 1,4-dimethoxybenzene[10)] in which there is internal rotation of the alkoxyl groups about the C–O axes, the angle of rotation of two groups at the upper and lower end being different and hence these molecules have two distinct relaxation processes viz., due to overall rotation as well as to internal rotations. The weight factor for group rotations C_2 is considerably large indicating the possibility of the trans positions of the end groups. In this model if the two alkoxyl groups would have been in gauche form with respect to the central portion of the chain, the freedom of rotation of end groups would have been restricted. Value of C_2 decreases with increase in the size of the alkoxyl group in the same series which indicates that the freedom of the rotation of alkoxyl groups decreases and hence τ_2 increases. The values of C_2 for dialkyl ethers of diethylene glycol are less as compared to the dialkyl ethers of ethylene glycol because with the increase in the size of the chain, the flexibility of the chain increases causing the end alkoxyl groups to be closer thereby decreasing the freedom of rotation of the end alkoxyl groups. The values of τ_2 of methoxyl group presented in this paper compares favorably with that reported earlier.[8,10,11)] The value of τ_1 is found to decrease with the increase in the size of the alkoxyl groups because of the decrease in the dipole moment with increase in the size of the alkoxyl group.

The authors wish to express their appreciation to Professor N. K. Mathur, Department of Chemistry of this University for many fruitful discussions. One of the authors (R. J. S.) is also thankful to Council of Scientific and Industrial Research, New Delhi for providing financial assistance.

References

1) K. Kimura and R. Fujishiro, *Bull. Chem. Soc. Jpn.*, **39**, 608 (1966).

2) J. Marchal and H. Bênoit, *J. Chim. Phys.*, **52**, 818 (1955); *J. Polym. Sci.*, **23**, 223 (1957).

3) A. Kotera, K. Suzuki, K. Matsumura, T. Nakano, T. Oyama, and U. Kambayashi, *Bull. Chem. Soc. Jpn.*, **35**, 797 (1962).

4) K. Higasi, *Denki Kenkyusho Iho,* **4**, 231 (1952).

5) H. D. Purohit, H. S. Sharma, and A. D. Vyas, *Bull. Chem. Soc. Jpn.*, **48**, 327 (1975).

6) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

7) A. Budo, *Z. Physik.*, **39**, 706 (1938).

8) H. D. Purohit and R. J. Sengwa, *J. Mol. Liq.*, **39**, 43 (1988).

9) H. D. Purohit and R. J. Sengwa, *J. Mol. Liq.*, **40**, 237 (1989).

10) K. Chitoku, K. Higasi, M. Nakamura, Y. Koga, and H. Takahashi, *Bull. Chem. Soc. Jpn.*, **44**, 992 (1971).

11) K. Higasi, Y. Koga, and M. Nakamura, *Bull. Chem. Soc. Jpn.*, **44**, 988 (1971).