933. *Dipole Moment Studies on Polyethylene and Polypropylene Glycols of Low Molecular Weight.*

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Dipole-moment measurements, on the pure solute and on benzene solutions, of polypropylene glycols are reported, as are measurements on some polyethylene glycols. These are compared with theoretical dipole moments calculated by using the equations of Uchida *et al.* and Marchal and Benoit. The dipole moments obtained from the measurements of the pure solute in both glycol series are discussed with reference to the Kirkwood g factor.

DIPOLE-MOMENT measurements of polymer molecules can be used to obtain information on the relative orientation of the polar groups in the molecule and sometimes the ability of these groups to rotate. Polyethylene and polypropylene glycols, $HO\cdot[CH_2\cdot CH_2\cdot O]_n\cdot H$ and $HO\cdot[CH_2\cdot CHMe\cdot O]_n\cdot H$, respectively, have a large degree of molecular freedom; rotation of the ether linkage can take place giving rise to an absorption in the radio-wave region.[1] In initiating these dipole-moment studies it was hoped to ascertain the ease of rotation by comparing the experimental values of the dipole moments with those calculated for a free-rotation model[2] and for a model involving some steric hindrance.[3] The Kirkwood correlation factor g is a valuable measure of both inter- and intra-molecular forces in a polymer, and in the present investigation this factor has been evaluated, enabling dipole moments obtained from the solution to be compared with those for the pure solute.

EXPERIMENTAL AND RESULTS

Polyethylene glycols of molecular weight 200—4000 were obtained from Oxirane Ltd. Polypropylene glycols of molecular weight 1000—4000 were obtained from the Union Carbide Chemicals Company, except that of molecular weight 400 which was supplied by the Dow Chemical Company.

Dielectric constants of the polyethylene glycols were measured on an N.P.L. calibrated Hartshorn–Ward dielectric test set;[4] those of the polypropylene glycols were made on the Cole–Gross bridge mark II.[5] Refractive indexes were measured with an Abbé refractometer. Benzene was purified as described by Prosskauer *et al.*[6]

Results.—Dipole moments were evaluated for the pure solute from the dielectric constant and refractive index by using Kirkwood's equation:[7]

$$\frac{(2\varepsilon_0 + n^2)(\varepsilon_0 - n^2)9\boldsymbol{k}TV}{\varepsilon_0(n^2+2)^2} = g\mu^2, \qquad (1)$$

where ε_0 is the static dielectric constant of the solute, n is the refractive index, g is the Kirkwood correlation factor, and μ is the dipole moment of the molecule.

For solutions the dipole moment was calculated by Guggenheim's method:[8]

$$\frac{9\boldsymbol{k}T}{4\pi N}\cdot\frac{3}{(\varepsilon_1+2)(n_1^2+2)}\cdot\frac{\Delta}{C} = \mu^2, \qquad (2)$$

where Δ is $(\varepsilon_0 - n_0^2) - (\varepsilon_1 - n_1^2)$, ε_0 is the static dielectric constant of the solution, n_0 is its

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[1] Davies, Williams, and Loveluck, *Z. Elektrochem.*, 1960, **64**, 575; Stockmayer and Bauer, personal communication; Koizumi, *J. Chem. Phys.*, 1957, **27**, 625.

[2] Uchida, Kurita, Koizumi, and Kubo, *J. Polymer Sci.*, 1956, **21**, 313.

[3] Marchal and Benoit, *J. Polymer Sci.*, 1957, **23**, 223.

[4] Hartshorn and Ward, *J. Inst. Elect. Engineers*, 1936, **79**, 597.

[5] Cole and Gross, *Rev. Sci. Instr.*, 1949, **20**, 252.

[6] Prosskauer, Weissberger, Riddick, and Toops, " Organic Solvents," 2nd Edition, Interscience Publishers Inc., New York.

[7] Kirkwood, *J. Chem. Phys.*, 1939, **7**, 911.

[8] Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714; 1951, **47**, 573.

refractive index, ε_1 is the static dielectric constant of the benzene, and n_1 is its refractive index. C is the concentration of the solute in moles per c.c. of solution.

TABLE 1.

Polyethylene glycols at 20°.

		Solute alone					In C_6H_6	
M	n	ε	$g\mu^2/n$ from eqn. 1	$g\mu^2$	g‡ from eqn. 3	μ (D)	μ (D)	μ^2/n
62	1	41·82 *	13·0	13·0	1·31	3·2	2·0	4·0
106	2	31·69 *	6·1	12·3	1·35	3·0	2·3	2·6
150	3	23·69 *	5·8	17·3	1·50	3·4	2·5	2·1
200	4	21·1	4·9	20·1	1·61	3·5	2·8	1·9
238	5	18·16 *	4·1	20·8	1·69	3·5	3·0	1·8
282	6	16·00 *	3·6	21·4	1·74	3·5	3·2	$1{\cdot}7_6$
300	6·4	15·9	3·4	22·0	1·75	3·5	3·3	1·7
326	7	14·85 *	3·3	22·9	1·77	3·6	3·4	$1{\cdot}6_7$
400	8·7	13·7	2·9	25·7	1·81	3·8	3·7	1·6
800	17·7	11·2	2·5	44·7	1·90	4·8	4·9	1·3
1000	22·2	10·9	2·4	54·4	1·92	5·3	5·3	$1{\cdot}2_6$
1500	33·6	10·8	2·4	80·3	1·94	6·4	6·4	1·2

* By use of values given by Koizumi and Hanai (*J. Phys. Chem.*, 1956, **60**, 1496). † By use of values from ref. 3. ‡ Calculated by using $2\theta = 110°$.

TABLE 2.

Polypropylene glycols at 25°.

		Solute alone					In C_6H_6			
M	n	ε	$g\mu^2/n$ from eqn. 1	$g\mu^2$	g ‡ from eqn. 3	μ (D)	μ (D) from eqn. 2	μ^2/n	μ^{2*}/n	μ^2/n †
400	6·6	8·86	2·66	17·6	1·40	3·5	3·6	$1{\cdot}9_6$	$1{\cdot}9_6$	$2{\cdot}2_6$
1000	17·2	6·16	1·6	27·7	1·56	4·2	4·8	$1{\cdot}3_4$	$1{\cdot}3_5$	$1{\cdot}9_4$
2000	34·5	5·51	1·4	47·2	1·61	5·4	6·3	$1{\cdot}1_4$	$1{\cdot}1_4$	$1{\cdot}8_0$
3000	51·7	5·27	1·3	66·2	1·63	6·4	7·6	$1{\cdot}1_1$	$1{\cdot}0_8$	$1{\cdot}7_8$
4000	69·0	5·27	1·3	88·3	1·65	7·3	8·5	$1{\cdot}05_5$	$1{\cdot}0_7$	$1{\cdot}7_8$

* By use of Marchal and Benoit's equation.[3]. † By use of Uchida *et al.*'s equation.[2] ‡ By using $2\theta = 120°$ (cf. text).

Table 1 contains the results for pure polyethylene glycol and Marchal and Benoit's results [3] for benzene solutions. Table 2 contains results, for both solute and solution, for polypropylene glycols.

DISCUSSION

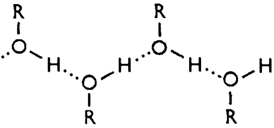
Solution Measurements.—Marchal and Benoit [3] and Uchida and his co-workers [2] put forward theoretical expressions whereby the dipole moments of polyethylene glycols and closely related structures may be calculated. Uchida *et al.* used a free-rotation model; Marchal and Benoit used a model incorporating a steric-hindrance factor which takes short-range interactions into account. In their work on the polyethylene glycols in dioxan, Uchida *et al.* measured the dipole moments of the polymers up to the heptamer, but even this comparatively small increase in molecular weight caused divergence between their experimental and theoretical values of the dipole moment, this being attributed to the "excluded volume effect." On the other hand, Marchal and Benoit measured the dipole moments of the polyethylene glycols in benzene up to a degree of polymerisation of 230 and found that their theoretical expression reproduced the experimental results very well. They also concluded that the "excluded volume effect" does not refer to polymer chains of this type.

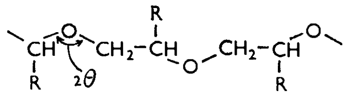
In the present study the measured dipole moments agreed extremely well with Marchal and Benoit's theoretical expression, as shown in the last three columns of Table 2. This expression also reproduces the experimental values obtained by Uchida *et al.* for some polyethylene glycols in dioxan better than the expression which they themselves proposed (these calculations are not reported here).

Although the dielectric absorption data[1] indicate a remarkable freedom of rotation, the fact that a steric hindrance factor must be introduced to obtain agreement between the calculated and the experimental dipole moments indicates that freedom of rotation is not complete. This agrees with recent viscosity measurements[9] which show that polyethylene glycol maintains, in toluene solution, a very close configuration involving considerable hindrance to rotation. The value of 0·33 used for the steric-hindrance factor is a little larger than that (0·3) used by Marchal and Benoit in their work on the polyethylene glycols in benzene: it can be reasonably understood on the assumption that the methyl side chain in the polypropylene glycols hinders rotation about the ether linkage.

Measurements for Solutes.—Values of the dipole moment have been obtained from the measurement of the dielectric constants of the pure glycols by using equation 1, which gives values of the product $g\mu^2$ (see the fifth column of Tables 1 and 2). Kirkwood's correlation factor g is a measure of the degree of interaction between the many dipoles present in the dielectric. In the present context it is a measure of the interaction between the dipoles forming the randomly orientated polymer chain. To obtain values of the dipole moment μ from the product $g\mu^2$, values of g must be assumed.

In relatively simple cases, g can sometimes be successfully evaluated from *X*-ray data, but in such complex cases as liquid polymers this is not feasible. Oster and Kirkwood[10] adopted a rough model for the calculation of g for infinite chains of hydrogen-bonded aliphatic alcohols. This model was subsequently modified by Dannhauser and Cole[11] who adopted a model (A) composed of finite chains and obtained an expression for g in the following manner. The value of g is different for different members i of a finite chain and a mean value is obtained and defined as $ng = \sum_i g_i$, where n is the number of alcohol molecules in the chain. If 2θ is the bond angle, which is assumed equal to the angle between the hydrogen bonds, then


(A)



(B)

$$g = 1 + 2f\cos^2\theta - \frac{2f\cos^2\theta\,.\,(1-\cos^{2n}\theta)}{n\sin^4\theta},$$

where $f = (\mu_H + \mu_R)(\mu_H + \mu_R\cos 2\theta)/(\mu_H{}^2 + \mu_R{}^2 + 2\mu_H\mu_R\cos 2\theta)$; here μ_H and μ_R are the group moments.

This treatment has been used to evaluate g in the present investigation. In the place of fluctuating hydrogen-bonded chains we have permanent polymer entities involving covalent bonds. The model is thus (B), where R is a hydrogen atom in the polyethylene glycols and is methyl in the polypropylene glycols. 2θ is taken as the bond angle of the ether linkage. The values assumed for 2θ are given in Tables 1 and 2. The value of f is unity since the group moments corresponding to μ_H and μ_R are both μ_{C-O}.

The values of g calculated in this way are tabulated in the sixth column of Tables 1 and 2. From these and the values of $g\mu^2$, values of μ are obtained and may be compared with the dipole moments obtained from the solution measurements. This comparison is made in the seventh and the eighth column of the Tables. The agreement between the solution and solute dipole moment is striking, especially in the polyethylene glycol series. The poorer agreement for polypropylene glycols could be due to neglect of the definite contribution of the methyl side chain to the dipole moment of the polymer molecule.

[9] Thomas and Charlesby, *J. Polymer Sci.*, 1960, **42**, 195.
[10] Oster and Kirkwood, *J. Chem. Phys.*, 1943, **11**, 175.
[11] Dannhauser and Cole, *J. Chem. Phys.*, 1955, **23**, 1762.

However, the good agreement between the dipole moments from the two series of measurements indicates that the relatively simple model assumed for the polymer molecule is capable of giving realistic values of g.

Conclusion.—Marchal and Benoit's model, involving hindered rotation in the polymer chain, accurately represents the behaviour of both series of glycols in solution while the model given by Uchida *et al.* is in error. Reasonable values of the Kirkwood correlation parameter are obtained from a simple model of the polymer molecule, enabling values of the dipole moment to be obtained which are in good agreement with those for solutions.

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