[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MARYLAND]

The Dipole Moment of Carbowax 4000[1]

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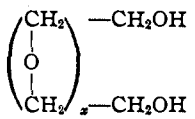
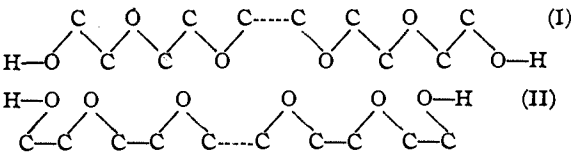
Carbowax 4000, a polyethylene glycol, can be represented by the following general formula[2]



Two of the simplest structures which can be based on the general formula are



In formula I the symmetry of the structure would eliminate any resultant link moment except that due to the end hydroxyl groups, giving zero moment or at most the moment of ethylene glycol, namely, 2.24 *D*. If formula II were correct, an extremely large moment for such a high molecular weight compound of the order of 150 *D* would result. The dipole moment of Carbowax 4000 was measured in benzene in order to determine whether the material was polar or non-polar and thus allow one to decide between or to reject completely both formulas I and II.

Materials and Experimental Procedure

Benzene.—The benzene was purified and the measurements were made by means of the heterodyne beat apparatus and methods previously described.[3]

Carbowax 4000.—This material, a product of Carbide and Carbon Chemicals Co., was purified as follows: 100 g. was dissolved in about 400 ml. of carbon tetrachloride. The solution was warmed and Norite was added. The resulting mixture was boiled and filtered through a large preheated Buchner. The solution was then chilled in a refrigerator for about two hours and filtered. The crystals were dried in air. The above procedure, omitting however the use of Norite, was repeated twice. The final product was dried in a vacuum desiccator. No ash was obtained on the slow ignition of the final product indicating complete removal of any inorganic salts as an impurity.

Index of refraction measurements were made at room temperature with an Abbe refractometer using a sodium vapor lamp.

Experimental Results

The dielectric constant, ϵ, the densities, d, the molar polarizations, P_2, the indices of refraction, n, of the various benzene solutions containing mole fractions,[4] N_2, of the solute and the extrapolated value of P_∞ for the solute are given in Table I. A value of the molar refraction MR_D of

TABLE I

SUMMARY OF DATA IN BENZENE AT 44°

$N_2 \times 10^3$	d	ϵ	P_2	$n_{D,30}$
0.000	0.85208	2.2298	P_∞ = 2861	(1.4964)
.4765	(.85700)	2.2888	2859	1.4960
.7141	.85940	2.3183	2856	1.4958
.9499	(.86180)	2.3472	2857	1.4957
1.1915	.86400	2.3776	2872	1.4954

Data in parentheses have been picked off a corresponding mole-fraction plot.

carbowax 4000, namely, 927, was calculated from the atomic and molecular refractions given in Landolt–Börnstein assuming the molecule to be a polymer of ethylene oxide with hydroxyl groups on each end of the molecule and using an average molecular weight[4] of 3750. The index of refraction measurements given in Table I, after the densities of the solutions were reduced to 27.3° led to a calculated value of 897 ± 2 for MR_D in each of the solutions. Since the agreement between the two results is quite satisfactory (3% variation), the value of MR_D obtained experimentally was selected for further calculations. Using the value of $P_E + P_A$ equal to 1.05 MR_D, one calculates in the usual fashion a value of 9.91 *D* for the dipole moment[5] of carbowax.

Discussion

It is well known that the higher polyethylene glycols are actually mixtures of a large number of polymers. Although the range of molecular weights present in carbowax 4000 has never been experimentally determined,[4] nevertheless, it has been found for the lower molecular weight polyethylene glycols that the experimental distribution curve follows[2] the one calculated by Flory's method.[6] We have therefore determined the theoretical distribution curve for carbowax 4000 using Flory's method. This is shown in Fig. 1. As can be seen from Fig. 1, 90% by weight of carbowax 4000 is made up of polymers varying in molecular weight from 3098 to 4418. It follows therefore that carbowax 4000 should be made up

(1) Presented in part at the spring meeting of the Washington Section of the American Chemical Society held at the University of Maryland, College Park, Maryland, May, 1945.

(2) McClelland and Bateman, *Chem. Eng. News*, **23**, 247 (1945), recently published an excellent article on the "Technology of the Polyethylene Glycols."

(3) Lander and Svirbely, THIS JOURNAL, **67**, 322 (1945).

(4) In all calculations involving molecular weight, a value of 3750 was assumed for Carbowax 4000. Private communication from C. P. McClelland Fine Chemicals Division, Carbide and Carbon Chemicals Co. "The molecular weight of this compound has been determined using the acetic anhydride pyridine reagent and has been found to lie in the range of 3500 to 4000. This method as applied to the carbowax compounds is considered to be accurate within about ±2%."

(5) The value of the dipole moment using MR_D equal to 927 is 9.83*D*.

(6) Flory, THIS JOURNAL, **62**, 1561 (1940).

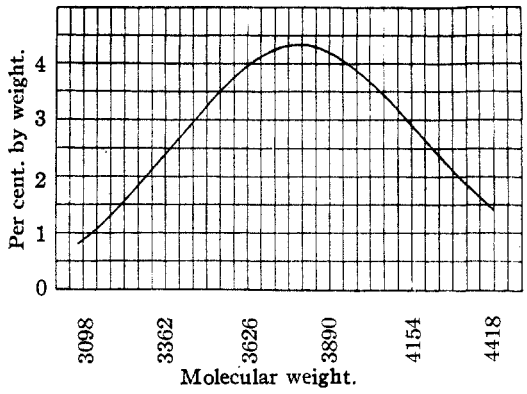


Fig. 1.—Calculated distribution of polyethylene glycols in carbowax 4000.

of polymers with different dipole moments. The average dipole moment reported here, namely 9.91*D*, is based on the assumption that carbowax 4000 can be treated as a pure polyethylene glycol of molecular weight 3750. The fact that polyethylene glycol 400 is very similar[2] in most respects to pure nonaethylene glycol seems to indicate that our assumption in the case of carbowax 4000 is allowable.

Using the experimental value of 9.91*D* one calculates an average moment of 0.117*D* for a glycol unit as it exists in the pure polyethylene glycol of molecular weight 3750. This in turn leads to calculated moments of 8.2*D* and 11.7*D* for the pure materials of molecular weights 3098 and 4418, respectively. We conclude, therefore, that 90% of carbowax 4000 will be made up of polymers having a dipole moment greater than 8.2*D* but less than 11.7*D*. It is thus evident that carbowax 4000 is quite polar and the magnitude of the moment is such that the linear structural formula I and II are definitely eliminated. Qualitatively the structure of the polymer could be explained by at least two other linear pictures, one in which there is a spiral-like rotation of the structure II so that some cancelling of link moments takes place and in the other there would be an irregular configuration of monomers giving a combination of structures I and II.

Studies by Wyman and others[7] indicate that the usual Debye equation for calculation of dipole moments cannot be applied in media of high dielectric constant and that a relation

$$h = (D - D^0 - j)/p$$

holds in binary mixtures where h and j are constants, p is the volume polarization, D and D^0 are the dielectric constants of solution and solvent, respectively. The evaluating of h and j has been done both empirically and theoretically leading to values of h varying between 4.5 and 8.5. Our experimental data for carbowax 4000 also permits an empirical evaluation of h. Figure 2 shows a plot of dielectric constant *versus* concentrations of carbowax 4000 in moles/liter. The slope of this curve gives a dielectric increment value (δ) of 11.06. Using the equation[8] where P_s is the molal

$$\delta = hp_s/1000$$

polarization of the solute which in this case can be determined from the P_∞ value and the MR_D value to be 1919, one obtains a value of h equal to 5.77. This value of h is in very good agreement with the empirical value of 5.8 obtained[9] from data for the glycine molecule.

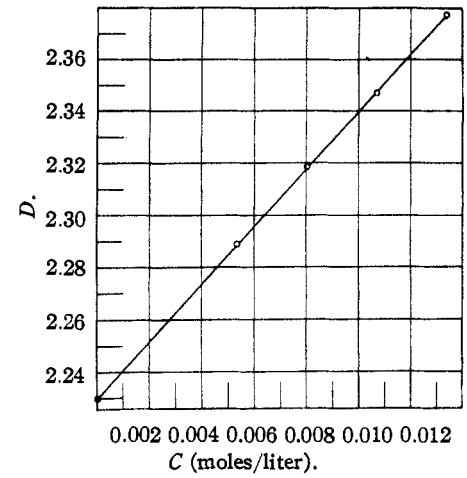


Fig. 2.—Dielectric constants of solutions of carbowax 4000 in benzene.

Summary

1. The dipole moment of carbowax 4000, a mixture of polyethylene glycols, has been determined in benzene yielding an average value of 9.91*D* on the assumption that the material can be treated as a compound of average molecular weight 3750.

2. The two simplest linear structures are not compatible with observed dipole moment.

3. The value of h, a constant of Wyman's equation, is empirically found to be 5.77 and is in good agreement with a previous empirical value of 5.8.

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(7) (a) Wyman, THIS JOURNAL, **58**, 1482 (1936); (b) Onsager, *ibid.*, **58**, 1486 (1936); (c) Cohn and Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corp., New York, N. Y., 1943; Chapters 6, 12, and 22 discuss the work on dipole moments of dipolar ions very thoroughly.

(8) Ref. 7c, equation 10, page 151.

(9) Oncley, THIS JOURNAL, **60**, 1117 (1938); ref. 7c, page 547.