MODERN DIELECTRIC THEORY APPLIED TO POLYMETHYLDISILOXANE MOLECULES

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INTRODUCTION

The dielectric behavior of materials has provided a method for investigating the structure of matter. Molecular structure influences the net dipole moment of the molecule. The dipole moment is the electric moment produced when the centers of gravity of the positive and negative charges of the molecule do not coincide. The presently accepted interpretation of the dielectric behavior is based upon the work of Debye and refinements by others.

Debye (1929) considered the permanent dipole moment of a polar molecule as one of the major contributors to the polarization of a dielectric in an electric field. He arrived at equation number 1, in which the symbols are: μ_o, permanent dipole moment; k, Boltzman constant; M, molecular weight; T, absolute temperature; N, Avogadro's number; d, density; ϵ, static dielectric constant; and ϵ_{oo}, optical dielectric constant. However, he assumed that neighboring molecules would not cause orientation in the absence of an external field.

Onsager (Smyth, 1955) added to Debye's work by considering the problem of the internal field of the molecule and its effect upon neighboring molecules during polarization. His equation, number 2, was derived on the assumption that molecules are spherical. The influence of neighboring molecules upon orientation was neglected.

1.

$$\mu_o = 3/2 \sqrt{\frac{kMT}{\pi N d}} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{\epsilon_{oo} - 1}{\epsilon_{oo} + 2} \right]$$

2.

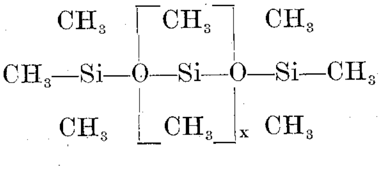
$$\mu_o = 3/2 \sqrt{\frac{kMT}{\pi N d} \; \frac{(2\epsilon + \epsilon_{oo})\ (\epsilon + 2)}{3\epsilon\ (\epsilon_{oo} + 2)} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{\epsilon_{oo} - 1}{\epsilon_{oo} + 2} \right]}$$

3.

$$\sqrt{g}\;\mu_0 = 3/2\sqrt{\frac{kMT}{\pi N d}\left[\frac{(\epsilon-1)\;(2\epsilon+1)}{9\epsilon} - \frac{\epsilon_{00}-1}{\epsilon_{00}+2}\right]}$$

Kirkwood (Smyth, 1955) included the hindrance to molecular orientation in determining the dielectric polarization for polar liquids. The dipole moment by his determination is (number 3), where g is a correlation factor relating the molecular dipole moment and the moment induced by hindered rotation as a result of the field of the neighboring molecules. The correlation factor, g, is a function of the angle between dipole moments of a neighboring pair of molecules and is very difficult to determine.

The polymethyldisiloxanes (silicone oils) make excellent sample molecules to compare the dipole moments calculated from the Debye, Onsager, and Kirkwood equations. The molecules have a small permanent dipole moment caused by the Si—O—Si bond angle, and data for their physical and chemical properties are available from the published literature. The polymethyldisiloxanes are a chain-type molecule. The chemical formula (Rochow, 1951) is



$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_x-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

where x represents the number of inner structural units.

ANALYSIS OF DATA

The values of ϵ, ϵ_{00}, d, and M are listed in Table 1 for 8 polymethyldisiloxanes at 20°C. The data for hexamethyldisiloxane ($x = 0$) were measured by Holland and Smyth (1955) and those for polymers $x = 1$, 2, 3, 4, 5, 6, and 48 were measured by Baker, Barry, and Hunter (1946); the densities were obtained from the Dow-Corning Silicone Notebook (1948). The large polymer, $x = 48$, was included to test the results of Debye, Onsager, and Kirkwood equations for a molecule that has a comparatively large dipole moment and thus a large internal field. Polarization produced by orientation is temperature dependent. The data discussed here were taken at 20°C; however, corresponding data are available for —20°C.

Sauer and Meade (1946) established the following empirical equation for the dipole moments of polymethyldisiloxanes:

$$\mu_0 = C\sqrt{n}$$

where C is a constant and n is the number of oxygen atoms in the molecule. Holland and Smyth (1955) found the dipole moment of hexamethyldisiloxane ($x = 0$) to be 0.54 Debye units. This value was obtained by the benzene-solution method and was regarded as the most reliable figure available for determining C in the Sauer and Meade equation. Values from this empirical equation are included in Table 2

TABLE 1.—Dielectric Constants of Eight Polymethyldisiloxanes at 20°C.

	x=0	x=1	x=2	x=3	x=4	x=5	x=6	x=48
M	162	236	310	384	458	532	606	3714
d	.764	.823	.854	.876	.891	.902	.910	.954
ϵ	2.18	2.31	2.40	2.48	2.52	2.55	2.57	2.79
ϵ_{∞}	2.06	2.08	2.33	2.22	2.20	2.27	2.34	2.43

for comparison with those of Deybe, Onsager, and Kirkwood. It should be pointed out that the Kirkwood values in this table are for $\sqrt{g}\ \mu_0$.

All three equations predict an increase in the dipole moment as the size of the molecule increases, and a decrease of the moment as the temperature is lowered. The average deviation of the Debye, Onsager, and Kirkwood moments from the Sauer and Meade empirical moments are about 13, 10, and 18%, respectively. However, the average deviation for the Kirkwood equation is not too meaningful as the Kirkwood results include the $\sqrt{g}$, although g is often chosen as 1.

The correlation factor, g, is the ratio μ/μ_0, where μ is the sum of the permanent dipole moment and the moment induced as a result of hindered rotation in the spherical region surrounding the molecule. Therefore, it is reasonable to expect g to decrease as the distance separating the centers of the force fields of the neighboring molecules increases. This suggests a relation between g and the size of the molecule. We have proposed the relation

$$g = \frac{K}{\log V}$$

to supply the unknown factor in Kirkwood's equation. K is a constant and V is the molecular volume. The molecular volume is proportional to M/d, and this ratio was used in place of V to determine K. The constant K was determined from the most reliable value of μ_0, namely,

TABLE 2.—Comparison of Dipole Moments (Debye Units) Calculated from Debye, Onsager, Kirkwood, and Empirical Equations at 20°C.

	Debye μ_0	Onsager μ_0	Kirkwood $\sqrt{g}\ \mu_0$	Sauer and Meade μ_0	g	μ_0^*
x=0	0.46	0.47	0.68	0.54	1.59	0.54
x=1	0.73	0.74	0.99	0.76	1.51	0.81
x=2	0.44	0.44	1.05	0.84	1.45	0.87
x=3	0.91	0.92	1.16	1.08	1.40	0.99
x=4	1.11	1.12	1.71	1.20	1.36	1.46
x=5	1.12	1.13	1.80	1.32	1.33	1.56
x=6	1.07	1.08	1.86	1.43	1.31	1.57
x=48	4.08	4.25	4.32	3.78	1.03	4.25

0.54 Debye units, and was found to be 3.70. New values of g were calculated from

$$g = \frac{3.70}{\log M/d}$$

and are listed in column 6 of Table 2. These coefficients were then applied to the Kirkwood values of Table 2 (column 4) to find μ_o^*. Thus, the results (last column of Table 2) are obtained by adjustment of Kirkwood's equation as suggested by the authors. The true dipole moments are probably nearer those calculated from the empirical equation suggested by the authors, or those calculated from the Sauer and Meade equation. Additional experimental work will be required to find the correct equation.

CONCLUSIONS

From this evaluation of existing equations for dielectric properties, some conclusions regarding their application may be made.

1. The Debye equation should not be used to determine the dipole moments of pure polar liquids as the results will show considerable error. If the dipole moment is extremely small and the molecules could be isolated from each other as in a gas or in a very dilute solution, the error would be reduced as the effect of the hindered rotation would be at a minimum. However, the Onsager equation will give more accurate results as it accounts for the effect of the internal field on molecular orientation. When the Onsager equation is used for a pure polar liquid, the error is increased again because of the hindered rotation.
2. The Kirkwood equation takes into account the effects of the hindered rotation. Refinements of this equation offer the best means to account for dielectric behavior. Unless the correlation factor is known, however, the error is likely to be greater than with the Onsager equation. A modification of Kirkwood's equation has been suggested.
3. The most accurate method for determination of the molecular dipole moments at the present time entails use of the Onsager equation on measurements in dilute solutions of polar molecules in a liquid known to be non-polar. This minimizes the effect of the hindered rotation upon the orientation polarization, as the internal field for a non-polar molecule is zero. Then the dipole moments obtained from this method may be used to evaluate the correlation factor in the Kirkwood equation.

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