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Abstract

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DIPOLE MOMENTS OF HEXAALKYL DERIVATIVES OF DISILOXANE

In the present communication we give the values of the dipole moments for four hexaalkyl derivatives of disiloxane: hexamethyldisiloxane, hexaethyldisiloxane, hexapropyldisiloxane, and hexabutyldisiloxane, obtained by hydrolysis of the corresponding trialkylhalide (ethoxy) silanes (^{1}).

The dipole moment of hexamethyldisiloxane has been measured by a number of authors (^{2,3}), whereas the dipole moments of the other hexaalkyl derivatives of disiloxane have been measured by us for the first time. We calculated the dipole moments from the values of the dielectric constants of dilute solutions of these substances in the nonpolar solvent—*n*-hexane.

The dielectric constants were measured in an apparatus operating by the beat method. The stabilization of the instrument was piezoquartz, with a frequency of 7.95×10^5 Hz. The measuring capacitor consisted of three concentric platinum cylinders. The outer and inner cylinders were connected to one another at several points by platinum wire, and this electrode was grounded, whereby the middle electrode was shielded.

The interelectrode capacitance of this capacitor, as measured with benzene, proved to be 12.363 pF. Using this value and the results of experimental data on the measurement of the capacitance of the capacitor filled with substance, we calculated the dielectric constants of toluene, *n*-hexane, and hexamethyldisiloxane at 25°. The values obtained and the literature data are given in Table 1. Comparison of these data indicates the very high accuracy of the instrument.

Table 1

Dielectric constants of toluene, *n*-hexane, and hexamethyldisiloxane at 25°

Substance	Our data (ε_1)	Lit. data (ε_2)	$\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_2} \cdot 100$
Toluene	2.3744	2.3738 (^{4})	+0.03
n-Hexane	1.8854	1.8867 (^{5})	−0.07
Hexamethyldisiloxane	2.1719	2.17* (^{6})	–

* For $t = 20°$.

The measurement of the dielectric constant ε, density d, and refractive index n_D was carried out at $25 \pm 0.05°$. The dielectric constant was determined with an accuracy of 0.02%. The density of the solutions was determined with a pycnometer with an accuracy of 0.02%, and the refractive index on an IRF-23 refractometer with an accuracy of 0.01%.

The dipole moments of the hexaalkyl derivatives of disiloxane were calculated by the method of Hedestrand (^{7}) from the formula:

$$\mu = 0.012813 \cdot 10^{-18} \sqrt{P_{\text{op}} T} \tag{1}$$

where μ is the dipole moment, P_{op} is the orientational polarization, and T is the absolute temperature.

Orientational polarization is related to the total polarization of the dissolved substance P_∞ and to the deformation polarization $P_{D\infty}$, taken as equal to the molar refraction, by the relation

$$P_{\text{op}} = P_\infty - P_{D\infty}. \tag{2}$$

The subscript ∞ indicates that the values P_∞ and $P_{D\infty}$ have been extrapolated to infinite dilution by the Hedestrand method.

The total polarization at infinite dilution was calculated by the following formulas, in which subscript 1 refers to the pure solvent and subscript 2 to the dissolved substance; the dielectric constant ε, density d, and refractive index n_D without subscripts are quantities characterizing the solution; C_2 is the mole fraction of the dissolved substance, and M_1 and M_2 are the molecular weights of the solvent and the dissolved substance.

Total polarization of the dissolved substance:

$$P_\infty = A\left(M_2 - \beta d_1 \frac{M_1}{d_1}\right) + B\alpha\varepsilon_1, \tag{3}$$

where

$$A = \frac{\varepsilon_1 - 1}{\varepsilon_2 + 2}\frac{1}{d_1}, \qquad B = \frac{3M_1}{d_1(\varepsilon_1 + 2)^2}, \qquad \beta d_1 = \frac{d - d_1}{c_2} \quad \text{and} \quad \alpha\varepsilon_1 = \frac{\varepsilon - \varepsilon_1}{c_2}.$$

Deformation polarization of the dissolved substance:

Table 2

Constants of *n*-hexane

Constants for calculating P_∞	Constants for calculating P_∞	Constants for calculating P_∞	Constants for calculating P_∞	Constants for calculating P_∞	Constants for calculating P_∞
M_1	d_4^{25}	ε_{25}	$\frac{M_1}{d_1}$	A	B
86.18	0.6549	1.8854	131.593	0.3480	26.151

Constants for calculating $P_{D\infty}$	Constants for calculating $P_{D\infty}$	Constants for calculating $P_{D\infty}$	Constants for calculating $P_{D\infty}$
$n_1\,(25^\circ)$	n_1^2	A'	B'
1.3724	1.8835	0.3474	26.176

$$P_{D\infty} = A'\left(M_2 - \beta d_1 \frac{M_1}{d_1}\right) + B'\gamma n_1^2, \tag{4}$$

where

$$A' = \frac{n_1^2 - 1}{n_1^2 + 2}\frac{1}{d_1}; \qquad B' = \frac{3M_1}{d_1(n_1^2+2)^2}$$

and

$$\gamma n_1^2 = \frac{n^2 - n_1^2}{c_2}.$$

Table 2 gives the constants of the pure solvent for calculating P_∞ and $P_{D\infty}$.

Table 3 gives the results of measurements of the dielectric constant (ε), density (d), and refractive index (n_D) of solutions of hexaalkyl derivatives of disiloxane in n-hexane for different concentrations of the dissolved substance, expressed in mole fractions (C_2).

From the data of Tables 2 and 3, the constants necessary for calculating dipole moments by the Hedestrand method were calculated. These constants are given in Table 4.

For a number of compounds, $\alpha\varepsilon$, βd_1, and γn_1^2 depend nonlinearly on concentration; therefore, extrapolation to zero concentration was necessary. For this purpose the curves $\varepsilon = f_1(c_2)$, $d = f_2(c_2)$, and $n_2 = f_3(c_2)$ were constructed, and tangents were drawn at the point $c_2 = 0$. The tangent of the angle of inclination of the tangent to the concentration axis gave the desired value.

As indicated above, the literature contains data only on the dipole moment of hexamethyldisiloxane. The dipole moment of this compound, measured in benzene, proved to be $0.80\,D$ (^{2}). According to other data (^{3}), the dipole moment of hexamethyldisiloxane, measured in benzene at 30°, is $0.79\,D$. These values agree well with the value obtained by us, equal to $0.78\,D$.

Table 3

Experimentally found values of ε, d, and n_D for solutions of hexaalkyl derivatives of disiloxane in n-hexane

C_2	ε_{25}	d_4^{25}	n_D^{25}	C_2	ε_{25}	d_4^{25}	n_D^{25}
Hexamethyldisiloxane in n-hexane				Hexapropyldisiloxane in n-hexane			
0	1.8854	0.6549	1.3724	0	1.8854	0.6549	1.3724
0.0206	1.8956	0.6585	1.3726	0.0197	1.9032	0.6659	1.3767
0.0353	1.9029	0.6607	1.3727	0.0346	1.9182	0.6725	1.3799
0.0499	1.9076	0.6633	1.3728	0.0496	0.9334	0.6788	1.3824
Hexaethyldisiloxane in n-hexane				Hexabutyldisiloxane in n-hexane			
0	1.8854	0.6549	1.3724	0	1.8854	0.6549	1.3724
0.0201	1.9010	0.6635	1.3755	0.0196	1.9108	0.6684	1.3781
0.0351	1.9107	0.6699	1.3776	0.0348	1.9294	0.6770	1.3822
0.0499	1.9210	0.6755	1.3795	0.0486	1.9381	0.6858	1.3856

Table 4

Constants for calculating the dipole moments of hexaalkyl derivatives of disiloxane by the Hedestrand method

Substance	M_2	$\alpha\varepsilon_1$	βd_1	$P\infty$	γn_1^2	$P_D\infty$	P_{or}	$\mu\cdot 10^{18}$
$(CH_3)_3SiOSi(CH_3)_3$	162.30	0.4958	0.168	61.8	0.022	49.3	12.5	0.78
$(C_2H_5)_3SiOSi(C_2H_5)_3$	246.55	0.772	0.427	86.4	0.434	77.5	8.9	0.66
$(C_3H_7)_3SiOSi(C_3H_7)_3$	330.71	0.948	0.640	110.6	0.599	101.3	9.3	0.67
$(C_4H_9)_3SiOSi(C_4H_9)_3$	414.88	1.215	0.6775	145.1	0.830	134.9	10.2	0.71

The values of the dipole moments of the hexaalkyl derivatives of disiloxane given in Table 4 show that the Si–O bond is strongly polar. This is due to the considerable difference in the electronegativities of Si and O.

The observed decrease in the dipole moment of molecules containing ethyl, propyl, and butyl radicals in comparison with molecules containing methyl radicals can apparently be explained by an increase in the valence angle caused by repulsion of bulky groups.

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