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Dielectric Relaxation and Molecular Structure. XII. Dipole Moments and Dielectric Relaxation Times of Rigid Molecules in Solutions

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Synopsis. Dielectric constants and losses of anthrone, xanthone, fluorenone and ten other rigid and almost rigid organic molecules were measured at the frequency of about 100 GHz in benzene at 25 °C. The dielectric relaxation times $\tau(1)$ and $\tau(2)$ and the dipole moments μ of these molecules were obtained and discussed.

Two sets of dielectric relaxation times for thirteen rigid molecules were obtained in benzene from measurements at the frequency of 96.5 GHz at 25 °C and discussion is presented on the results.

Experimental

Dielectric measurements at the frequency of 96.5 GHz were made by use of the apparatus and techniques described previously.[1] Symbols employed in this note have the same definition as that given in the preceding paper.[2]

Purchased materials of the best grade (for solutes) were purified by the usual method. Benzene for solvent was carefully purified in the usual way. All the experimental data are collected in Table 1 including those for optical and dielectric (static) measurements.

TABLE 1. SLOPES a', a'' (100 GHz), a_0 (STATIC) AND a_D (OPTICAL) IN BENZENE, 25 °C

Compound	a'	a''	a_0	a_D
Anthrone	0.847	0.551	7.877	0.417
Xanthone	0.843	0.357	5.373	0.421
Benzophenone	0.852	0.444	5.780	0.277
Fluorenone	0.766	0.549	7.181	0.362
Acetone	4.144	4.932	13.736	−0.473
Methyl ethyl ketone	2.623	3.489	10.973	−0.415
Nitrobenzene	1.077	1.805	14.194	0.109
Chlorobenzene	0.298	0.433	2.465	0.066
Dibenzofuran	0.390	0.046	0.768	0.331
Dibenzothiophene	0.495	0.037	0.803	0.434
Toluene	−0.011	0.030	0.127	−0.036
o-Xylene	0.021	0.057	0.322	0.006
m-Xylene	−0.009	0.021	0.105	−0.025

Discussion

Two dielectric relaxation times $\tau(1)$ and $\tau(2)$ were calculated from

$$\tau(1) = \frac{1}{\omega}\frac{a''}{a'-a_\infty} \tag{1}$$

$$\tau(2) = \frac{1}{\omega}\frac{a_0-a'}{a''} \tag{2}$$

(See Table 2). The first relaxation times $\tau(1)$ calculated on the assumption $a_\infty = a_D$ are found to be much smaller than the second ones $\tau(2)$. This is partly due to the neglect of atomic polarization; a_∞ is expected to be larger than a_D. Besides, the dielectric system considered here is possibly of multi-relaxation times rather than of a single relaxation time. For instance, it was found by Hassel and Walker[3] that even toluene has two relaxation times in cyclohexane. If these molecules in benzene solution are provided with a small but appreciable absorption* in the extremely

TABLE 2. DIPOLE MOMENTS μ (UNITS: 10^{-30} C m) AND RELAXATION TIMES $\tau(1)$ AND $\tau(2)$ (UNITS: ps) 25° C

Compound	μ	$\tau(1)$	$\tau(2)$	τ(lit.)
Anthrone	12.17	2.1	21.0	24.8*[a]
Xanthone	9.96	1.4	21.0	—
Benzophenone	10.12	1.3	18.3	20.4[b,**c]; 17.4*[d]
Fluorenone	11.21	2.2	19.3	19.9*[a]
Acetone	9.18	1.8	3.2	3.2***[e]; 3.3**[c]; 3.3***[f]
Methyl ethyl ketone	9.16	1.9	3.9	3.7*****[k]
Nitrobenzene	13.31	3.1	12.0	12.0[b,g]; 14.9[h]
Chlorobenzene	5.25	3.1	8.3	8.3*[i,*d]; 9.7[h]
Dibenzofuran	2.74	1.3	13.5	—
Dibenzothiophene	2.63	1.0	13.6	—
Toluene	1.24	2.0	7.5	7.58****[j]; 5.6[l]
o-Xylene	1.85	6.4	8.7	—
m-Xylene	1.18	2.1	9.0	—

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* 20 °C ** 23 °C *** 19 °C **** 18.5 °C ***** 30 °C

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* The above-mentioned absorption includes the Poley absorption[5] which differs from the real relaxation phenomenon. We shall assume this small absorption to have a pseudo-relaxation time in order to examine the present dielectric system by use of the method of analysis for the system with two Debye dispersions.[6]

high frequency region[4,5] (for submillimeter wavelengths) and a large and dominant absorption in the lower frequency range, $\tau(1)$ and $\tau(2)$ will give average values with different weights of the two relaxation times. An analysis in the preceding paper[6] shows that the second relaxation times $\tau(2)$ will be fairly close to the relaxation times for the main absorption of molecular rotation.[6] In fact, the literature values obtained from lower frequency measurements compare favorably with $\tau(2)$. Exception may occur, however, if the molecule has a very small polarity.

The dipole moment μ is calculated from $\mu=B(a_0-a_D)^{1/2}$ and $B=(0.3197\times10^{-30}\ \text{Cm})M_2^{1/2}$ in benzene at 25 °C[2], in which a_0 and a_D are slopes for concentrations expressed in weight fraction[2] and M_2 is the molecular weight of the solute. The results of calculation are shown in Table 2. The dipole moment for dibenzofuran is probably a new value and those for the other molecules compare favorably with literature values.[7]

Literature

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