Dielectric Relaxation and Molecular Structure. XI. Dielectric Behavior of Various Polar Molecules in the Supercooled *o*-Terphenyl Solution

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The dielectric constants and losses of dilute solutions of anthrone, xanthone, phenothiazine, 9-fluorenone, benzophenone, diphenylnitrosamine, 1,8-dinitronaphthalene, *p*-nitrotoluene and *m*-nitrophenol in *o*-terphenyl have been measured in the supercooled state in the frequency range 1—100 MHz and temperature range 15—30 °C. The results have been analyzed by Davidson-Cole's skewed-arc method to calculate the relaxation times, the distribution parameters, the activation enthalpies and entropies for the dielectric relaxation processes.

Davidson and Cole[1] found that glycerol and propylene glycol in the supercooled liquid state show the skewed-arc behavior and introduced the empirical equation

$$\varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1+j\omega\tau_0)^\beta} \tag{1}$$

where ε_0 and ε_∞ are the limiting low and high frequency dielectric constants, respectively, ω is the angular frequency, τ_0 the characteristic relaxation time and β the distribution parameter. When β is equal to unity, the locus becomes a Debye-type semicircle.

Recently Shears and Williams made dielectric measurements on various polar molecules in supercooled *o*-terphenyl solution.[2] The absorption curves were found to be unsymmetrical and broader than expected for any Debye relaxation process; large activation energies were obtained in agreement with the cooperative process.

The present study has been conducted since little information is available on the dielectric behavior of the supercooled state in this particular solvent. *o*-Terphenyl provides a medium having viscosity so high that the region of dielectric absorption is in the range 1—100 MHz at room temperature.

Experimental

Materials. Commercial chemicals were carefully purified by recrystallization before use. The melting and glass transition points of *o*-terphenyl are 58 and −29 °C, respectively. The measurements were carried out not in a glassy state, but in the state of so-called metastable equilibrium.[3] Crystallization in the solution was prevented either by examining visually or by checking its dielectric constant and loss.

Apparatus. Dielectric constants and losses were measured in the frequency range 1—100 MHz with a twin-T bridge of type DLB-1101D (Fujisoku Electric Co., Ltd.). This bridge consists essentially of a circuit for impedance measurement divised by Sinclair and Woods, the detailed description of which was given by S. Okamoto.[4] Temperature was kept constant within ±0.2 °C by thermistors.

Results and Discussion

Dielectric constants and losses are plotted against the logarithm of the frequency (*e.g.*, *cf.* Fig. 1 for anthrone in *o*-terphenyl). In all the solutions the dispersion and absorption of solute molecules were observed in the frequency range 1—100 MHz and temperature range 15—30 °C. Dielectric constants and losses are also plotted in a complex plane; normalized Davidson-Cole

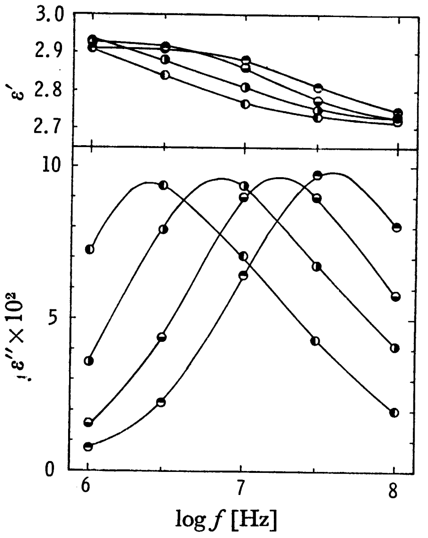

Fig. 1. Dielectric constant and loss curves for anthrone (Mole fraction, f_2=0.028) in *o*-terphenyl solution.
◐: 15 °C, ◑: 20 °C, ◒: 25 °C, ◓: 30 °C.

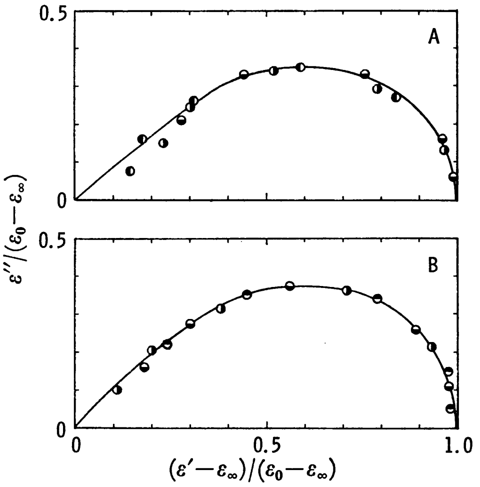

Fig. 2. Normalized Davidson-Cole plots for solutions in *o*-terphenyl.
A: Anthrone (f_2=0.028), B: 1,8-Dinitronaphthalene (f_2=0.010).
◐: 15 °C, ◑: 20 °C, ◒: 25 °C, ◓: 30 °C.

Table 1. Values of the characteristic relaxation time (τ_0)

Substance	τ_0 (ns) 15°C	20°C	25°C	30°C	τ (ps) (in benzene)
Anthrone	106	41.7	18.7	11.2	24.8(20°C)[5] 18.4(40°C)
Phenothiazine	115	45.0	21.0	11.4	
Xanthone	94.9	40.0	18.2	9.1	21.0(25°C)[6]
9-Fluorenone	80.4	37.1	15.3	7.6	19.9(20°C)[5] 14.9(40°C)
Diphenyl-nitrosamine	76.4	32.8	14.2	7.1	
1,8-Dinitronaphthalene		65.0	32.0	14.6	
p-Nitrotoluene	48.4	22.7	10.1	5.6	19 (22°C)[7]
Benzophenone	52.9	24.2	12.4		16.2(20°C)[8]
m-Nitrophenol	53.4	26.2	11.7	6.3	

diagrams are shown in Fig. 2. The values of ε_0 and ε_∞ are obtained by extrapolation at each temperature.

The characteristic relaxation times τ_0 obtained in this experiment are shown in Table 1 together with literature values in benzene. The decrease in the relaxation times in benzene with a rise of 20 °C is 6.4 ps for anthrone and 5.0 ps for 9-fluorenone. In the supercooled state the decrease for 15 °C becomes almost ten times for anthrone, 9-fluorenone and other compounds.

According to Eyring the relaxation time τ_0 is expressed in terms of thermodynamic parameters as follows.

$$\tau_0 = \frac{h}{kT}\exp\left(\frac{\Delta H^*}{RT}\right)\exp\left(-\frac{\Delta S^*}{R}\right). \qquad (2)$$

where ΔH^* is the activation enthalpy, ΔS^* the activation entropy and k, h, and R are the Boltzmann, Planck and gas constants, respectively. The activation enthalpy obtained from temperature dependence of τ_0 (Table 2) is much greater than that obtained in ordinary non-polar solvents; ΔH^*s for anthrone and 9-fluorenone in benzene are 8.8 and 8.4 kJ mol^{-1}, respectively.[5] We see that ΔS^* increases with ΔH^* so that an apparently linear relationship exists between these parameters.

$$\Delta S^*(\text{J deg}^{-1}\,\text{mol}^{-1}) = 3.44\Delta H^*(\text{kJ mol}^{-1}) - 106 \qquad (3)$$

Equations similar to Eq. (3) have been obtained for other dielectric relaxation processes,[9] *e.g.*, for polar polymers[10] and for nonrigid molecules in the polystyrene matrix.[11]

Table 2. Values of the distribution parameter (β), the activation enthalpy (ΔH^*) and entropy (ΔS^*)

Substance	β	ΔH^* $\left(\frac{\text{kJ}}{\text{mol}}\right)$	ΔS^* $\left(\frac{\text{J}}{\text{deg mol}}\right)$
Anthrone	0.47	122	313
Phenothiazine	0.49	119	302
Xanthone	0.49	116	293
9-Fluorenone	0.35	114	289
Diphenylnitrosamine	0.49	113	282
1,8-Dinitronaphthalene	0.52	108	261
p-Nitrotoluene	0.40	102	249
Benzophenone	0.27	101	246
m-Nitrophenol	0.29	101	245

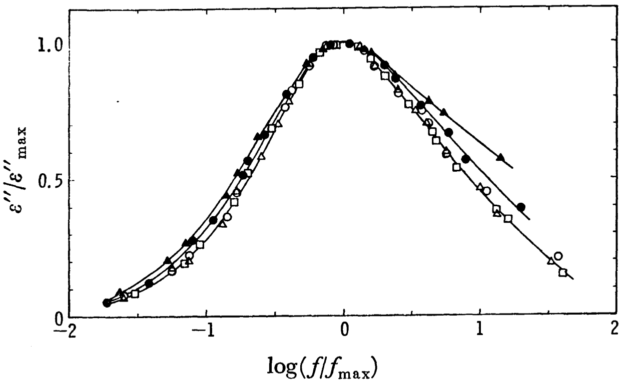

Fig. 3. Normalized plots of $\varepsilon''/\varepsilon''_{\max}$ against $\log(f/f_{\max})$ for solutions in *o*-terphenyl at 15°, 20°, 25°, and 30 °C.
○: Anthrone (f_2=0.028), △: Xanthone (f_2=0.028),
□: Phenothiazine (f_2=0.040),
●: 9-Fluorenone (f_2=0.028),
▲: Benzophenone (f_2=0.030).

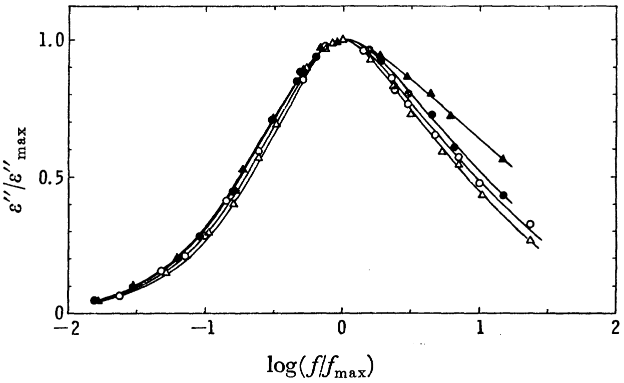

Fig. 4. Normalized plots of $\varepsilon''/\varepsilon''_{\max}$ against $\log(f/f_{\max})$ for solutions in *o*-terphenyl at 15°, 20°, 25°, and 30 °C.
△: 1,8-Dinitronaphthalene (f_2=0.010),
○: Diphenylnitrosamine (f_2=0.028),
●: *p*-Nitrotoluene (f_2=0.020),
▲: *m*-Nitrophenol (f_2=0.020).

Normalized absorption curves, shown in Figs. 3 and 4, are unsymmetrical in shape and broader than the pure Debye curves. All the points measured at different temperatures are reasonably close to a single curve for each sample. The above feature differs from one for polar molecules dispersed in the polystyrene matrix, where a symmetrical distribution of relaxation times occurs;[11] it also differs from that for rigid molecules in Nujol[12,13] or decalin (normal[13] and supercooled[14] liquids), where the absorption curves become broader with decreasing temperature.

The abosorption curves of anthrone, xanthone and phenothiazine have almost the same shape with nearly the same values of β (Fig. 3 and Table 2). This might arise from the similarity in the size and shape of these molecules. The absorption curve of benzophenone (▲ in Fig. 3) is, however, broader than that of its related molecules 9-fluorenone (● in Fig. 3) in the higher frequency side. Possibly an extra absorption occurs in the higher frequency region on account of the intramolecular rotation of the phenyl groups of benzophenone.[15)]

Figure 4 shows the normalized absorption curves of four remaining molecules whose size and shape are not similar. The curve for *m*-nitrophenol (▲ in Fig. 4) is far broader in the higher frequency side than curves of other molecules. The deviation might originate from the high frequency absorption due to rotation of the OH group.

Denny[16)] made skewed-arc plots for several supercooled, branched hydrocarbon halides including isobutyl bromide which is known to have a single relaxation time in the normal liquid state.[17)] In order to explain the unsymmetrical distribution of relaxation times of those nonassociated molecules, Glarum[18)] proposed a defect diffusion model, in which the shape of the distribution function becomes very little dependent upon temperature (Figs. 3 and 4). High activation energies obtained indicate the difficulty of diffusion of defects through solvent molecules. The results of this experiment seem to support Glarum's mechanism.

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