Fluorescence Depolarization Study of Hydrogen Bonded 1-Anthrol

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Rotaional depolarization of 1-anthrol fluorescence was studied in liquid paraffin. The molecular volume of 1-anthrol becomes large when it forms a hydrogen bonded complex. The molecular volume of the complex depends on the concentration of acceptor as well as the kind of acceptor. The molecular volume obtained by extrapolation to nil acceptor concentration increases with increasing size of acceptor molecule and is appreciably larger for amines than for ethers. The emitting species in the case of amines is 1-anthrolate ion pair whose strong dipolar nature may cause further interaction with excess amine molecules. It is probable that more than one molecule of amine participate in the rotating unit, leading to a large molecular volume. The rotational relaxation time was evaluated and found to depend on acceptor concentration. Two competitive effects occur by the increase in acceptor concentration, one shortening the relaxation time because of reduction of viscosity, and the other lengthening it because of molecular volume enlargement.

Fluorescence from the viscous solution is more or less polarized. The degree of polarization P depends on viscosity η and temperature T. For linearly polarized excitation light, the degree of polarization is given by the following equation derived by Perrin[1] assuming a spherical molecular shape of fluorescent solute.

$$\frac{1}{P}-\frac{1}{3}=\left(\frac{1}{P_0}-\frac{1}{3}\right)\left(1+\frac{kT}{V\eta}\tau\right) \quad (1)$$

where P_0, V, and τ stand for the limiting polarization, the molecular volume, and the mean fluorescence lifetime respectively.

From the measurements of the degree of polarization as a function of T/η aided by the lifetime determination, it is possible to obtain the molecular volume as well as the rotational relaxation time ρ, which is defined as $\rho=3V\eta/kT$. Depolarization studies have been made so far mostly in alcoholic solutions such as glycerol and cyclohexanol.[2] However, a molecular volume obtained from these highly associative solutions involves the solvated shell and becomes extremely large in some cases.[2] In order to minimize the solvation effect, liquid paraffin was employed as a viscous solvent. Since liquid paraffin consists of mainly alkyl naphthenes, the interaction between solute and solvent is expected to be small enough to prevent the solvation shell formation.

As a fluorescent solute, 1-anthrol (1-A) was selected. The molecular volumes, the rotational relaxation times and the activation energies of rotational motion were determined for the liquid paraffin solutions of 1-A containing various kinds of proton acceptor.

Experimental

Apparatus and Procedure. Absorption spectra were measured with a Hitachi EPS-3T spectrophotometer. Fluorescence polarization measurements were made with an apparatus similar to that of Weber.[3] A Polacoat PL-40 polarizing plate and a Polaroid KN-36 were employed as polarizer and analyzer, respectively. A sheet of pergament paper as a depolarizer was placed in front of a photomultiplier. Excitation light was obtained by combining a Xe arc lamp and a Hitachi G-3 grating monochromator. 0–0 absorption band was excited in every case.

Fluorescence lifetime was measured with a phase fluorometer similar to that described elsewhere.[4] Fluorescence spectra were recorded on a modified Hitachi EPU spectrophotometer equipped with an EMI 9558QB photomultiplier. Excitation light source was the same type as in the polarization measurements. The spectral calibration factors of this photometer were obtained by the method of Lippert *et al.*[5]

Viscosity was measured with an Ostwald viscometer.

Material. Scintillator grade anthracene was employed. 1-A was synthesized and recrystallized 5 times from a water–ethanol mixture.[6] Triethylamine (Wako G.R.) was dried with calcium chloride or alumina, and fractionally distilled under reduced pressure. *N,N*-Dimethylbenzylamine (Tokyo Kasei G.R.) was passed through a column of activated alumina.

Ethyl ether, *n*-butyl ether, *n*-hexyl ether, and *p*-dioxane (Wako G.R.) were distilled over sodium wire. Benzyl ether (Wako G.R.) was distilled over sodium wire under reduced pressure.

Liquid paraffin (Merck) was treated with columns of silica gel until the optical density for the 1 cm path around 270—280 nm became less than 0.02. Glycerol was distilled under reduced pressure. *n*-Hexane was purified by the standard method.

Results and Discussion

Molecular Volume. Absorption and fluorescence spectra of 1-A in liquid paraffin are given in Fig. 1.

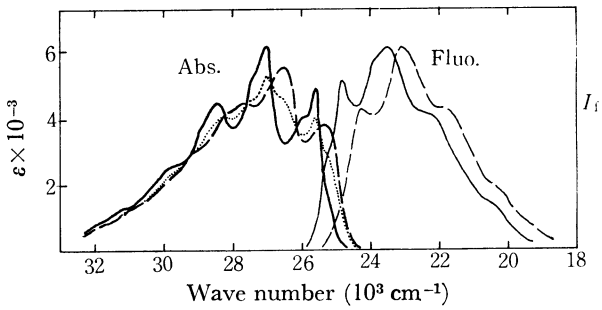

Fig. 1. Absorption and fluorescence spectra of 1-A in liquid paraffin.
Absorptoin; [1-A]$=1.41\times10^{-4}$M
——: [ethyl ether]$=0.0$ M, ----: [ethyl ether]$=9.62\times10^{-2}$M, — —: [ethyl ether]$=4.81\times10^{-1}$M
Fluorescence;
——: 1-A, — —: hydrogen bonded 1-A with ethyl ether.

The mirror image relationship between absorption and fluorescence spectra is rather poor. The excitation spectra at several points in the fluorescence band agree well with absorption spectrum. Thus, the observed fluorescence is intrinsic for 1-A and not an artifact such as impurity. $1/P$ *vs.* T/η plots for 1-A and for anthracene are shown in Fig. 2 for the sake of comparison. T/η varied with temperature. The solute concentrations were sufficiently low to prevent undesirable depolarizing effects such as reabsorption and concentration quenching.

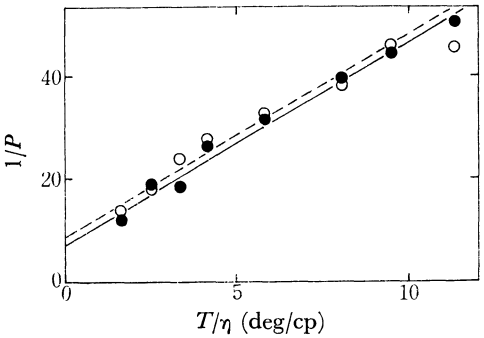

Fig. 2. Perrin plots for anthracene (—○—) and 1-A (—●—) in liquid paraffin.

Fluorescence lifetimes of anthracene and 1-A were determined respectively as 5.1 and 6.9 ns. They did not change within the experimental error in the temperature range studied. The molecular volume of anthracene was thus found to be 138 Å^3. This value corresponds to the radius of 3.21 Å assumed to be a sphere. Assuming one half of the length of the long axis, 4.6 Å, for the radius we obtain the volume 408 Å^3. The experimental value is much smaller and is close to the value of 120 Å^3 estimated for a prolate shape.

The molecular volume of 1-A was found to be 172 Å^3 which corresponds to the radius 3.43 Å. It may be due to volume expansion by the substituent that the molecular volume is larger for 1-A than for anthracene. Rather small molecular volumes obtained suggest that there is no participation of the solvation shell in the solute–liquid paraffin system.

1-A forms a hydrogen bonded complex with many acceptors. The absorption spectrum of 1-A in liquid paraffin containing various amount of ethyl ether is shown in Fig. 1. A similar result to that of Suzuki and Baba was obtained.[7] At ether concentration higher than ~0.5 M, the complexing seems to be almost complete in the ground state. The fluorescence spectrum of this solution is less structured than that of free 1-A as shown in Fig. 1. Beyond ether concentration of ~0.2 M, the fluorescence spectrum becomes a single component which is attributed to the hydrogen bonded 1-A. 1-A becomes a stronger hydrogen bond donor upon excitation to the first singlet excited state as expected from the spectral shifts by hydrogen bond formation. For other ethers absorption and fluorescence spectra are similar to the case of ethyl ether except for slight changes in shape and band positions.

Depolarization studies for hydrogen bonded 1-A were performed in liquid paraffin containing various amounts

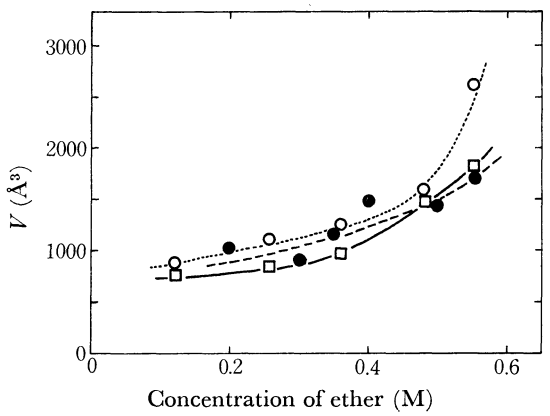

Fig. 3. Change of the molecular volume for various concentrations of ether.
—□—: *n*-butyl ether, ---○---: *n*-hexyl ether,
—●—: benzyl ether.

of ether. Linear $1/P$ *vs.* T/η plots were obtained for all the solutions studied. Fluorescence lifetimes of hydrogen bonded 1-A with ethers were found to be 14—15 ns and did not differ appreciably from each other. It was found that the molecular volume increased with the increase of acceptor concentration. As a typical example, Fig. 3 shows the molecular volume changes as a function of ether concentration. The increase of the molecular volume might be attributed to the formation of the solvation shell around the hydrogen bonded 1-A by excess ether molecules. This view is supported by the fact that the fluorescence spectrum changes in shape slightly at higher acceptor concentration in the case of benzyl ether. Solvent effect on the fluorescence spectrum of hydrogen bonded complex was found in the case of acridone–acetic acid in benzene.[8]

An empirical equation which fits the dependence of molecular volume on the concentration of ether added at a given temperature was found to be:

$$V = V_0 + A\frac{[C]^2}{\eta}$$

where V_0 is the molecular volume of the hydrogen bonded complex free from the solvation and [C] the ether concentration. V *vs.* $[C]^2/\eta$ plots for several

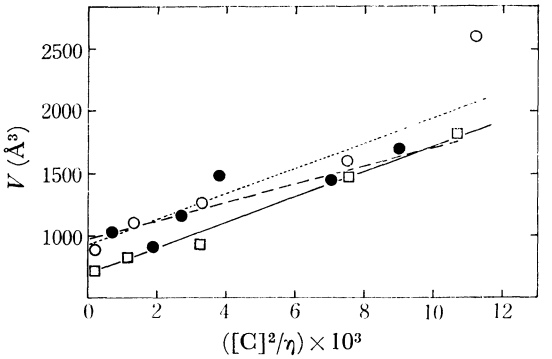

Fig. 4. Plots according to the empirical formula at 15 °C: $V = V_0 + A \cdot [C]^2/\eta$.
—□—: *n*-butyl ether, ---○---: *n*-hexyl ether,
—●—: benzyl ether.
[C] is the concentration of ether.

Table 1.

Proton acceptor	V_0 (Å^3)
Ethyl ether	~200
p-Dioxane	~500
n-Butyl ether	700
n-Hexyl ether	920
Benzyl ether	960
Triethylamine	1720
N,N-Dimethylbenzylamine	2300

ethers are shown in Fig. 4. The V_0 values thus obtained are summarized in Table 1. There is a clear tendency for the molecular volume to increase with the increase in size of acceptor molecule.

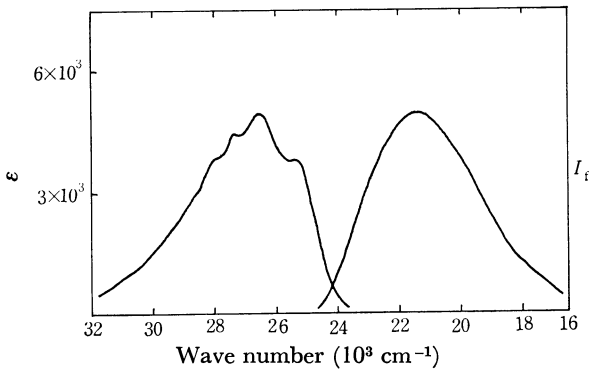

Fig. 5. Absorption and fluorescence spectra of 1-A in glycerol–water (9:1).

As a different kind of solvent, a glycerol–water mixture (9: 1) was employed. Absorption and fluorescence spectra in this solution are shown in Fig. 5. Due to hydrogen bonding and strong solvent effects, structures in the spectra are considerably blurred, the spectrum showing no structure particularly for fluorescence.

The molecular volume of 1-A was obtained from the slope of Perrin's plot and the measured lifetime of 18.6 ns as 688 Å^3. This volume is considerably larger than the molecular volume of free 1-A in liquid paraffin, but smaller than that of hydrogen bonded 1-A with some larger ethers. This might suggest that the solvated shell of 1-A water–glycerol mixture is smaller than that expected from the highly associative nature of solvent. However, the evaluation of molecular volume is not based on the 'micro' viscosity, but on the measured 'macro' viscosity. Furthermore, the shape of rotating unit may differ for liquid paraffin and glycerol–water. A straightforward comparison of the results obtained for different solvents may lead to an erroneous conclusion.

Triethylamine and *N,N*-dimethylbenzylamine were employed as stronger proton acceptors than ethers. The absorption spectrum in liquid paraffin containing various amounts of triethylamine is shown in Fig. 6. At 0.4 M of amine concentration, the hydrogen bond formation seems almost complete. Absorption maxima of hydrogen bonded complex lie in a slightly smaller wavenumber compared to the case of ethers. In contrast to absorption, the fluorescence spectrum

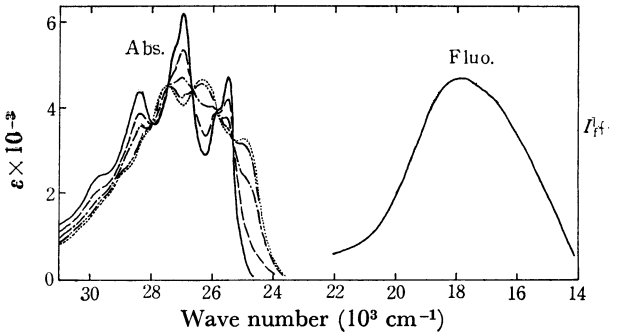

Fig. 6. Absorption and fluorescence spectra of hydrogen bonded 1-A with triethylamine.
Absorption spectra: [1-A]=1.33×10^{-4}M
——: [triethylamine]=0.0 M, — —: [triethylamine]=3.56×10^{-3}M, — · —: [triethylamine]=1.43×10^{-2}M, —·· —: [triethylamine]=3.56×10^{-2}M, ------: [triethylamine]=7.17×10^{-1}M.

changes drastically, being almost structureless and shifting to a smaller wavenumber to a great extent. Fluorescence maxima lie at 17900 and 17500 cm^{-1} for triethylamine and *N,N*-dimethylbenzylamine, respectively, which are smaller by 3600 and 4000 cm^{-1} than those in the glycerol–water mixture. The fluorescence spectrum resembles that of aqueous alkaline solution of 1-A in which maximum lies at 15000 cm^{-1}. We thus concluded that in the 1-A–amine–liquid paraffin system the usual hydrogen bond is formed between 1-A and amine in the ground state, while proton transfer occurs through the hydrogen bond in the excited state. On account of a low dielectric constant of liquid paraffin, 1-A–amine complex can exist as a hydrogen bonded ion pair. The difference in fluorescence maxima of liquid paraffin and aqueous alkaline solutions might be due to the solvent effects resulting from a very large difference in the dielectric nature.

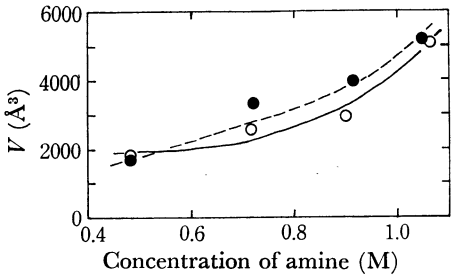

Fig. 7. Change of the molecular volume for various concentrations of amine.
—○—: triethylamine, --●--: *N,N*-dimethylbenzylamine.

Molecuar volumes obtained for the system containing amines depend also on the amine concentration (Fig. 7). The same empirical formula as that for ether fits the results. The V_0 values for triethylamine and benzylamine are given in Table 1. The molecular volume for benzylamine is considerably larger than that for triethylamine reflecting the larger size of benzylamine. However, the molecular volume for triethylamine is considerably large as compared with that for ethers such as butyl , hexyl-, and benzyl ether which

have larger molecular size than that of triethylamine. The most significant difference between amines and ethers is that the fluorescent molecule exists as a hydrogen bonded ion pair. The highly dipolar species may further interact with excess amine molecules which have a large dipole moment. Thus, there is a possibility that even at an amine concentration lower than 0.4 M more than one molecule of amine take part in the rotating fluorescent unit by forming an amine-shared ion pair or some other kind of aggregate. This may be the reason why V_0 for the amine system is appreciably large compared with that for the ether one.

Due to the short lifetime of the amine complex, the degree of polarization is relatively large. Consequently, viscosity can be varied in a wide range by adding less viscous *n*-hexane instead of varying the temperature. The molecular volume of the amine complex was proportional to the concentration of *n*-hexane added. At a given temperature, viscosity was inversely proportional to *n*-hexane concentration up to at least 4×10^{-2} M. The molecular volume, therefore, was proportional to the reciprocal of viscosity. The reason for such a relation is not clear. The difference between 'macro' and 'micro' viscosity is a possible explanation.

Rotational Relaxation Time. Rotational relaxation times in various solutions were evaluated. For anthracene in liquid paraffin, ρ is 5.2 ns at 22 °C. The rotational relaxation time of benzophenone in benzene at room temperature determined by the dielectric relaxation method is 18.7 ps. Viscosity of benzene at 20 °C is 0.65 cp, which is $\sim$1/100 of liquid paraffin. Hence, the relaxation time in liquid paraffin should be several ns. The ρ value obtained by fluorescence depolarization method gave the same order of magnitude as that obtained by other methods.

Temperature dependence of ρ is given by

$$\rho = \rho_0 \exp(E_{rot}/kT)$$

where E_{rot} is the activation energy of rotational relaxation. The values of E_{rot} for various solutions were 11—14 kcal/mol. These values correspond to the activation energy of viscous flow of each solution as expected.

The rotational relaxation time of hydrogen bonded 1-A is given in Fig. 8 as a function of acceptor concentration. In the case of ethers, a minimum value of ρ appears at certain ether concentration. At low acceptor concentration, the molecular volume is small but viscosity is large enough to give a greater ρ value.

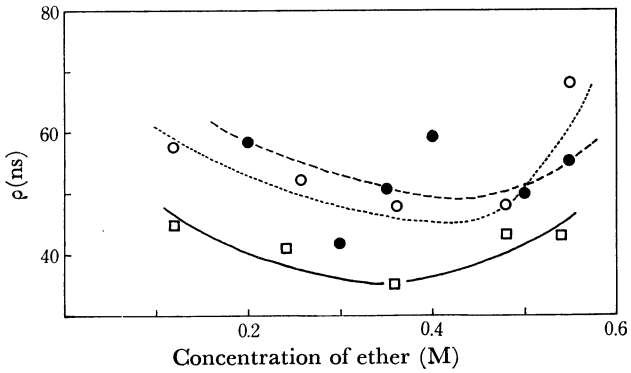

Fig. 8. Relationship of the rotational relaxation time to the concentration of ether at 12 °C.
—□—: *n*-butyl ether, ---○---: *n*-hexyl ether, --●--: benzyl ether.

With increasing acceptor concentration, viscosity decreases to give shorter ρ value. Further increase of acceptor concentration gives rise to a prominent increase in molecular volume reducing the viscosity. However, the trend for volume expansion to lengthen ρ overcomes that to shorten ρ by viscosity change, giving longer ρ as a whole. In the case of amines, the presence of minimum is not clear because of scattering of data.

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