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SOLUTE-SOLVENT INTERACTION IN PERFLUOROHEXANE

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The absorption spectra of benzene and naphthalene revealed the very weak solute-solvent interaction in perfluorohexane (PFH) while the fluorescence lifetime and the fluorescence quantum yield of naphthalene indicated the ordinary relaxation process of the Franck-Condon state in this solvent. These findings suggest that the poor polarizability of the PFH molecules causes the weak solute-solvent interaction in PFH.

Solvation plays an essential role to dominate physical properties and chemical reactivities of solutes. Although dielectric constant (ε) shows the polarity of the solvent, this parameter is not preferable to discuss solute-solvent interaction. One of the measures to evaluate the solute-solvent interaction is Kamlet-Taft π^* value of the solvent dipolarity/polarizability.1) Brady and Carr have reported the π^* values of the following four perfluorocarbons: perfluorooctane ($\pi^* = -0.41$, $\varepsilon = 1.85$), perfluoroheptane (-0.39, 1.765), perfluorodimethyldecalin (-0.33, 1.94), and perfluorotributylamine (-0.36, 1.90).2,3) Comparison of the π^* and ε values of heptane ($\pi^* = -0.081$, $\varepsilon = 1.90$) with those of the perfluorocarbons suggests that the solute-solvent interaction in perfluorocarbons is much weaker than that in the corresponding hydrocarbon solvents. A very weak solute-solvent interaction in perfluoromethylcyclohexane has also been suggested in the absorption spectroscopic study on metal pentacarbonyls formed intermediately by laser-flash photolysis of metal hexacarbonyls.4) In spite of these studies, the effects of perfluorocarbons as solvents have not been understood satisfactorily. In order to accumulate the fundamental knowledge on the solute-solvent interaction in perfluorocarbons, we studied the absorption and fluorescence spectra of the simple aromatic molecules in perfluorohexane (PFH).

Figure 1 shows the absorption spectra (${}^1A_{1g} \rightarrow {}^1B_{2u}$) of benzene in PFH, hexane, and 1,1,2-trichlorotrifluoroethane (TCTFE) at 25 °C. The slit of the spectrophotometer (Shimadzu MPS 5000) was 0.1 mm. The spectrum of the benzene vapor is also shown in Fig. 1 for comparison. As Fig. 1 shows, lots of the vibronic bands of benzene in the vapor phase were diffused in the solutions of hexane, cyclohexane, and TCTFE due to the collision of the benzene molecules with the solvent molecules. In PFH, however, very sharp absorption spectrum with the vibronic structures were observed. Although the vibronic structures became somewhat obscure, most of the bands observed in the vapor phase were also detected in PFH.

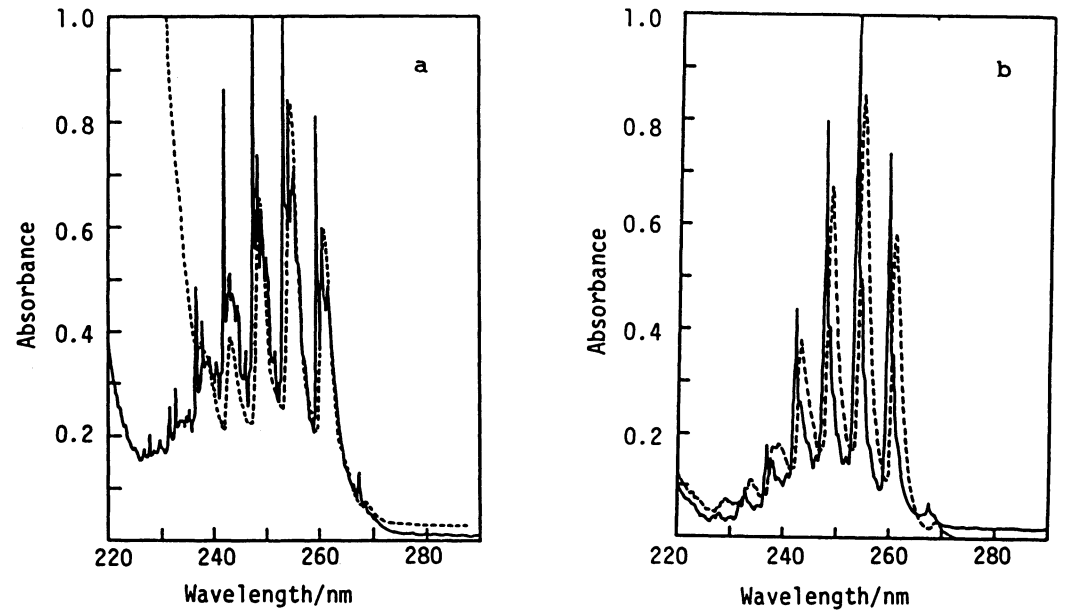

Fig. 1. Absorption spectra of benzene in vapor phase (a, ——) and in PFH (b, ——), hexane (b, – – –), and TCTFE (a, – – –) at 25 °C. The concentration of benzene in liquid phase was 3.75 x 10^{-3} mol dm^{-3}.

For example, a series of the vibronic bands appeared at 250.0 (G^0_1), 249.0 (A^2_2 and B^0_3), 248.3 (A^1_2), and 247.3 nm (A^0_2) in the vapor phase was observed at 250.2, 249.0, 248.3, and 247.5 nm, respectively, in PFH. These vibronic bands were coalesced resulting in a broad absorption band in hexane (248.6 nm), cyclohexane (249.2 nm), TCTFE (248.5 nm), or ethanol (249.2 nm). These results indicate clearly that the solute-solvent interaction in PFH is much weaker than those in the nonpolar hydrocarbon solvents such as hexane and cyclohexane. It seems that PFH provides "vapor-like phase" for benzene.

Figure 2 shows the absorption spectra of naphthalene (^1L_a and ^1L_b) in PFH and hexane. Each absorption band of naphthalene shifted to shorter wavelength and sharpened in PFH compared with that in hexane. The solvatochromism was remarkable for the ^1L_a absorption bands. For example, the absorption maxima at 281.5, 278.5, 271.0, and 268.5 nm in PFH shifted to 285.0, 282.8, 274.7, and 272.5 (sh) nm, respectively, in hexane. The corresponding bands appear at 280, 277, 270, and 266 nm, respectively, for the collision-free naphthalene vapor.[5)] The fact that the absorption spectrum of naphthalene in PFH is much closer to that in the vapor phase rather than that in the hydrocarbon solution phase also indicates the weak solute-solvent interaction in PFH.

The results of the absorption spectroscopic measurements of benzene and naphthalene indicate the very weak solute-solvent interaction in PFH. It seems that the solute molecules in PFH exist in the vapor-like phase. It is well known that fluorescence behavior in liquid phase is markedly different from that in vapor phase because of rapid relaxation of Franck-Condon state due to collision with surrounding solvent molecules. If the solute molecules in PFH are relatively free from the collision with the solvent molecules, it should be reflected in the fluorescence behavior. In this study, we compared the fluorescence spectrum, the fluorescence lifetime (τ_f), and the fluorescence quantum yield (ϕ_f) of naphthalene in PFH with those in hexane, cyclohexane, and TCTFE. The fluorescence spectral measurements were carried out by exciting naphthalene to its second excited state (excitation wavelength = 255 nm, excitation bandwidth = 3 nm, and emission bandwidth = 5 nm). Under these conditions, the diffused fluorescence spectrum was observed for each system and no significant difference was observed between PFH and the hydrocarbon solvents except the blue shifts of the emission maxima of naphthalene in PFH (λ^F_{max} in PFH = ca. 385 (sh), 363.5, 346.0, 333.5, 321.7, and ca. 310 (sh) nm; λ^F_{max} in hexane = ca. 385 (sh), ca. 366 (sh), ca. 347 (sh), 335.2, 323.0, and ca. 312 (sh) nm). The τ_f and ϕ_f values and the rate constants for the radiative decay ($k_f = \phi_f/\tau_f$) of naphthalene in degassed solvents are listed in Table 1. The fluorescence decay was followed by exciting naphthalene at ca. 270 nm and was single exponential for each system. The fluorescence lifetime in PFH appreciably smaller than those in hexane and cyclohexane while ϕ_f in PFH was in agreement with those in hexane and cyclohexane within the experimental error. These results suggest that the excess vibronic energy of the Franck-Condon excited state of naphthalene in PFH is consumed by the collision with the solvent molecules leading to the lowest excited singlet state, which is the ordinary process in the liquid phase. The k_f value of naphthalene in PFH (2.0×10^6 s^{-1}) is much larger than that in the lowest excited singlet state of the collision-free naphthalene vapor ($k_f = 7.42 \times 10^5$ s^{-1}),6) suggesting that the solute-solvent interaction in PFH accelerate the radiative process. The fluorescence behavior of naphthalene in TCTFE is novel; i.e., both τ_f and ϕ_f are markedly smaller than those in the other solvents. The fluorescent state of naphthalene was quenched by TCTFE. The rate constant for the fluorescence quenching of naphthalene by TCTFE in cyclohexane was determined to be 6.3×10^7 mol^{-1} dm^3 s^{-1}. Choi and Lipsky have reported the fluorescence quenching of saturated

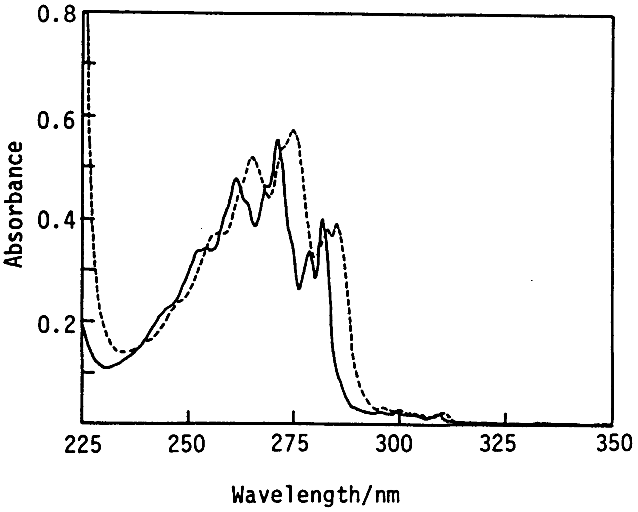

Fig. 2. Absorption spectra of naphthalene (1×10^{-4} mol dm^{-3}) in PFH (——) and hexane (- - -) at 25 °C.

Table 1. Fluorescence Parameters of Naphthalene in PFH, Hexane, Cyclohexane, and TCTFE at 25 °C

	τ_f/ns	ϕ_f	$10^{-6}k_f/s^{-1}$
PFH	99	0.20	2.0
Hexane	120	0.21	1.8
Cyclohexane	117	0.21	1.8
TCTFE	10.3	0.019	1.8

hydrocarbons by perfluorodecalin and assumed that the fluorescence quenching occurs via electron transfer from photoexcited species to perfluorodecalin.7) The similar quenching may occur for the naphthalene-TCTFE system. The weak electron affinity of PFH7) may cause the slight reduction in τ_f of naphthalene.

The present study revealed that the solute-solvent interaction in PFH is extremely weak for the nonpolar solutes such as benzene and naphthalene in the ground states while PFH acts as a solvent which perturbs the excited states of the solutes more strongly than the corresponding hydrocarbon solvent, hexane. The dispersion force (London force) provides the interaction between nonpolar solute and nonpolar solvent. The appearance of this short range interaction needs the collision of the solute molecule with the solvent molecule. The dispersion force affects the absorption spectra of benzene and naphthalene in hexane, cyclohexane, and TCTFE as shown in Figs. 1 and 2. The origin of the dispersion force is the polarizabilities of the solute and solvent molecules. The polarizability of the PFH molecule is so small because of the strong electronegative property of the fluorine atoms that the solute molecules may interact very weakly with PFH molecules. Meanwhile, it seems that a chlorofluorocarbon, TCTFE, has a large polarizability and shows relatively strong solute-solvent interaction compared with PFH.

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