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Fluorophotometric Determination of an Equilibrium Constant for the Formation of a Molecular Complex between Fluoranthene and Benzene in Solution

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A fluorophotometric method was used to obtain equilibrium constants for the formation of a van der Waals molecular complex between fluoranthene and benzene in the ground state. The equilibrium constant for the above-mentioned complex formation is estimated to be 0.13 dm^3 mol^{-1}, which compares well with that (K = 0.15 dm^3 mol^{-1}) obtained from a traditional electronic absorption method.

Many investigations have been performed on van der Waals complexes between nonpolar aromatic hydrocarbons by using a supersonic cool jet and ab initio MO methods.[1] For instance, benzene forms a van der Waals dimer with a parallel-displaced configuration in a supersonic jet-cooled condition.[2] In a previous paper, we reported on thermodynamic quantities obtained from the electronic absorption method for molecular complex formation between fluoranthene (FA) and benzene in cyclohexane; the equilibrium constant K (at 298 K) and enthalpy change $\Delta H°$ for complex formation are 0.147 ± 0.03 dm^3 mol^{-1} and -1.41 ± 0.3 kcal mol^{-1}, respectively.[3] In the present investigation, we used a fluorophotometric method to obtain equilibrium constants for the weak molecular complex formation mentioned above.[4]

Commercially available FA (Aldrich) was recrystallized twice from cyclohexane. Cyclohexane (Wako, guaranteed) was purified by an already described method.[3] Fluorescence spectra were recorded on a Hitachi F3010 fluorescence spectrophotometer.

Figure 1 exhibits the fluorescence (a) and excitation (b) spectra of FA in cyclohexane, ethanol, acetonitrile and benzene. The fluorescence spectrum of FA, excited at 370 nm, shows peaks or shoulders at 408, 416, 435, 444, 462.5, and 492 nm in cyclohexane. The excitation spectrum monitored at each fluorescence peak position well reproduces the absorption spectrum, indicating that all of the fluorescence bands are of FA, itself. The fluorescence band maximum is, as in the case of the absorption spectra,[3] red-shifted by ca. 2 nm in benzene compared with that in cyclohexane, whereas the fluorescence band maxima observed in ethanol and acetonitrile remain unshifted. This fluorescence behavior shows that the molecular complex between FA and benzene formed in the ground state still remains undissociated even in the excited state.

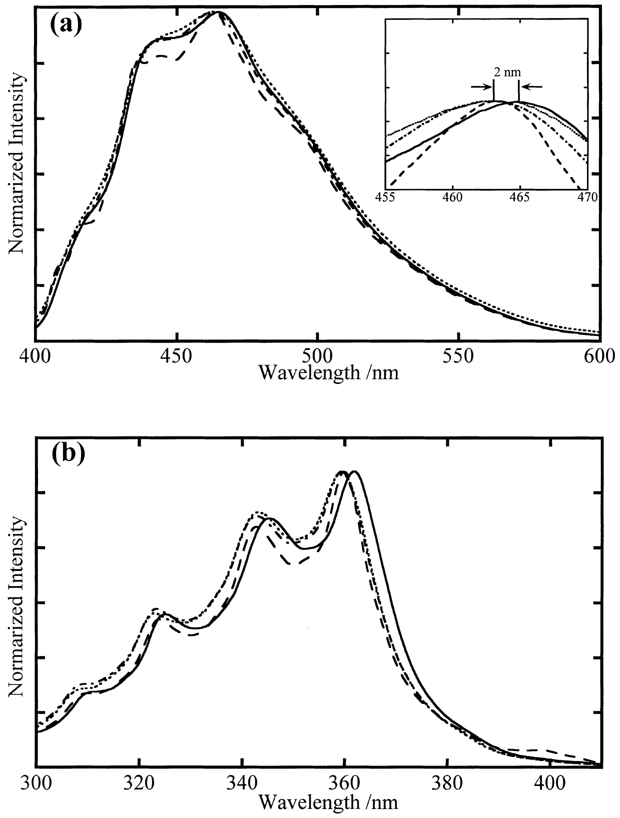

Fig. 1. Fluorescence (a) and excitaion (b) spectra of FA in cyclohexane (– – – –), ethanol (– · – · –), acetonitrile (············), and benzene (————).

To know the stoichiometry for the FA-benzene complex, fluorescence spectra of FA were measured in mixed solvents of cyclohexane and benzene (Fig. 2). In all fluorescence measurements, excitations were performed at 360 nm, corresponding to the isosbestic point in the absorption spectra.[3] The fluorescence band of FA in neat cyclohexane is red-shifted with an increase in the benzene concentrations, accompanying isoemissive points at 408.8, 428.1, and 436.1 nm. This implies that FA forms a 1 : 1 molecular complex with benzene in the excited state. This FA–benzene complex is not considered to be an exciplex, since the fluorescence of the present complex accompanies a vibrational structure. That is, the molecular complex formed in the ground state survives even in the excited state, meaning that the fluorescence intensity of the complex is proportional to the concentration of the complex formed in the ground state for dilute solutions. In our previous work, the equilibrium constant for the formation of the complex was obtained by using the variation of the optical densities with the benzene concentrations.[3] In this investigation, we tried to estimate the same equilibrium constant by using the changes in the

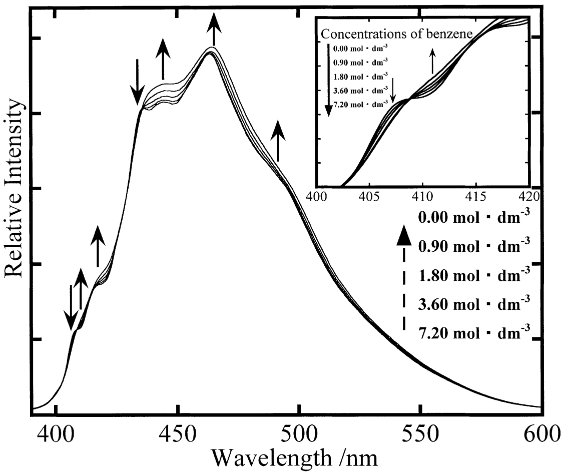

Fig. 2. Fluorescence spectra of FA in mixed solvents of cyclohexane and benzene at various benzene concentrations. Concentration of fluoranthene = 1.7 × 10^{-4} mol dm^{-3}.

fluorescence intensities against the benzene concentrations.

$$\text{FA} + \text{Benzene} \overset{K}{\rightleftarrows} \text{FA–benzene} \tag{1}$$

$$K = \frac{C_C}{(C^0_{FA} - C_C)\cdot(C^0_{Be} - C_C)} \tag{2}$$

Here, $C^0{}_{Be}$ and $C^0{}_{FA}$ are the initial concentrations of benzene and FA, respectively. C_C is the concentration of the FA–benzene complex formed in the ground state. Since $C_C \ll C^0{}_{Be}$ in this experiment, K is expressed as

$$K = \frac{C_C}{(C^0_{FA} - C_C)\cdot C^0_{Be}}. \tag{3}$$

When the monochromatic (wavelength λ) excitation light intensity is maintained constant during the measurements, the fluorescence intensity ($I_C(\lambda)$) of a complex is proportional to the concentration ($C_C{}^*$) of the excited complex, and $C_C{}^*$ is proportional to C_C; thus, $I_C(\lambda)$ is proportional to C_C, which is expressed as

$$I_C(\lambda) = F_C(\lambda)\cdot C_C, \tag{4}$$

where $F_C(\lambda)$ is a proportionality constant. Similarly, the fluorescence intensity $I_{FA}(\lambda)$ of FA is expressed as

$$I_{FA}(\lambda) = F_{FA}(\lambda)\cdot C_{FA}, \tag{5}$$

where $F_{FA}(\lambda)$ is a proportionality constant. The fluorescence intensity ($I(\lambda)$) of an equilibrium mixture of FA and FA–benzene complex is given as

$$I(\lambda) = F_C(\lambda)\cdot C_C + F_{FA}(\lambda)\cdot(C^0{}_{FA} - C_C). \tag{6}$$

The fluorescence intensity ($I^0(\lambda)$) of FA in neat cyclohexane is also proportional to $C^0{}_{FA}$, i.e.,

$$I^0(\lambda) = F_{FA}(\lambda)\cdot C^0{}_{FA}. \tag{7}$$

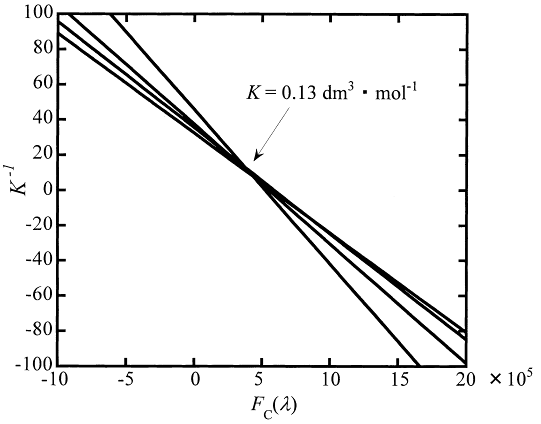

Fig. 3. Plots of K^{-1} vs $F_C(\lambda)$. λ = 470.6 nm.

From Eqs. 3, 6 and 7, the following equation is obtained:

$$K^{-1} = \frac{C^0_{FA}\cdot C^0_{Be}}{I(\lambda) - I^0(\lambda)}F_C(\lambda) + \frac{I(\lambda)\cdot C^0_{Be}}{I^0(\lambda) - I(\lambda)}. \tag{8}$$

This equation has two unknown parameters, K^{-1} and $F_C(\lambda)$, the values of which we can obtain by solving two-dimensional simultaneous equations. That is, by drawing straight lines of K^{-1} against $F_C(\lambda)$ for various benzene concentrations, we can estimate the equilibrium constant K from the crossing point (Fig. 3). The equilibrium constant obtained by the present method was 0.13 dm^3 mol^{-1}, which compare well with that (K = 0.147) obtained from the electronic absorption spectra.[3]

In conclusion, it is found that the present fluorophotometric method allows us to estimate accurate equilibrium constants for the formation of weak molecular complexes in the ground state, and is promising for studying weak intermolecular interactions in solutions.

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