# Intensity Enhancement Caused by Complex Formation between Pyrene and Alcohols

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**Synopsis.** The enhancement of the weak 0-0 band in the absorption spectrum of pyrene has been observed using various mixtures of cyclohexane and alcohols. The relations of the absorption coefficients with the alcohol concentrations have been studied on the assumption of 1:1 complex formation between pyrene and alcohols. The association constants for the hydrogen-bonded complexes have been estimated to be of a reasonable order of magnitude (0.1—0.4 mol$^{-1}$ dm$^3$).

Growing interest has been shown in the investigations of the microenvironments in micellar and membraneous systems. For spectroscopic studies of the structures and mechanisms in these systems a variety of molecular probes[1)] have been employed with appreciable success. It has been demonstrated[2—4)] that pyrene (and other related aromatic hydrocarbons) can also be used as such a probe. It may be said however that pyrene has a unique character in that one can utilize not only the overall intensities of its emission and absorption spectra but also the variations of their vibronic structures in various media.

The enhancement of weakly allowed vibronic bands in the absorption and fluorescence spectra of pyrene in polar solvents was first studied by this author[5)] and a number of investigations[3,6—9)] have so far been undertaken for the purpose of elucidation and application of this phenomenon.

Recently Lianos and Georghiou[10)] have studied the systems of pyrene and alcohols in nonpolar solutions by infrared spectroscopy and fluorescence decay analysis and shown that the intensity enhancement arises from the formation of stoichiometric complexes. As reported previously, the present author[11,12)] has observed that the weak 0-0 band of pyrene in a nonpolar solvent can gain considerable intensity on addition of a polar solvent and indicated that the large initial increase can be explained by the complex formation between pyrene and polar molecules.

In this work, the enhancement of the 0-0 band has been studied employing various mixtures of nonpolar and polar solvents; cyclohexane was used as a nonpolar component, while 2-methyl-2-propanol, ethanol, and phenol were adopted as polar components. An attempt has been made to interpret the enhancement in terms of 1:1 complex formation between pyrene and the alcohols or phenol and to estimate the association constants.

## Experimental

GR grade pyrene obtained from Wako Pure Chemical Industries was recrystallized repeatedly from ethanol. Checking by the absorption spectra indicated no impurity absorption present in the spectral range studied. Spectrograde cyclohexane from Kanto Chemical Co. was used without further purification. Ethanol and 2-methyl-2-propanol were purified by fractional distillations after drying. Phenol was recrystallized many times from the melt.

The solutions were carefully prepared by the volumetric method from various mixtures of cyclohexane and alcohols or phenol with a constant concentration of pyrene ($2.99\times 10^{-3}$ mol dm$^{-3}$).

The absorption spectra were recorded at room temperature on a Shimadzu 210A double-beam spectrophotometer, with a slit width for 0.5 nm resolution and at a scan speed of 50 nm/min. In the lowest electronic transition of pyrene the absorption coefficient for the 0-0 band (around 371 nm), which has been found to be most sensitive to the solvent polarity, has been measured by varying the alcohol concentrations. The variation of the band width in different solvents has been observed to be relatively small (less than 3%), of which no account has been taken.

The preparations of the solutions and the measurements were repeated several times, especially at lower alcohol concentrations, followed by averaging the measured values to compensate volumetric and instrumental errors.

## Results and Discussion

The observed relations between the absorption coefficients for the 0-0 band ($\varepsilon$) and the concentrations of alcohols or phenol ($C_A$) are shown in Fig. 1. From the figure it should be noticed that relatively large increases in $\varepsilon$ can be observed at lower $C_A$ and changes in the higher $C_A$ region are appreciable. In pure cyclohexane $\varepsilon$ is small with a value of 135.0 (mol$^{-1}$ dm$^3$ cm$^{-1}$), while its value increases to 226.0 in 2-methyl-2-propanol and 276.3 in ethanol. The general tendency of the increase seems to be explained in terms of the solvent polarity and has been considered on the basis of the bulk properties of solvents.[5)] However, recent studies[10—12)] have indicated that the formation of complexes occurs considerably. In particular, Lianos and Georghiou[9)] have concluded that the enhancement is the result of the reduction of the molecular symmetry caused by the 1:1 complex formation between pyrene and alcohols.

Accordingly, it may be assumed also in this study that the intensity enhancement is primarily induced by the formation of weak 1:1 complexes between pyrene and alcohols or phenol. Thus, an equilibrium is postulated among a pyrene molecule P, an alcohol or phenol molecule A, and a complex PA as follows

$$\mathrm{P} + \mathrm{A} \overset{K}{\rightleftharpoons} \mathrm{PA}.$$

Here the association constant $K$ is given by

$$K = \frac{[\mathrm{PA}]}{[\mathrm{P}][\mathrm{A}]}$$

with the additional conditions:

$$[\mathrm{P}] + [\mathrm{PA}] = C_\mathrm{P}$$
$$[\mathrm{A}] + [\mathrm{PA}] = C_\mathrm{A}$$

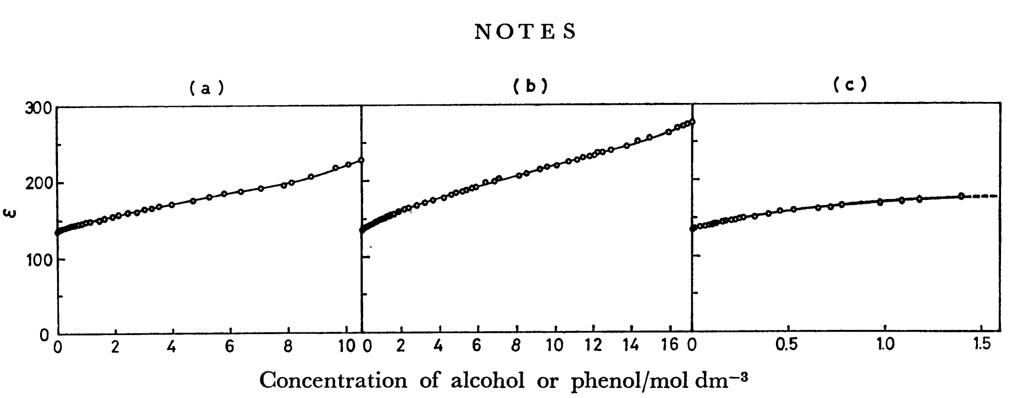

Fig. 1. Relations between the absorption coefficient for the 0-0 band of pyrene and the concentrations of (a) 2-methyl-2-propanol, (b) ethanol, and (c) phenol.

Table 1. The association constants and absorption coefficients for the systems of pyrene in alcohol– or phenol–cyclohexane mixtures, with some relevant properties of alcohols and phenol

| Compound | $D^{a,c)}$ | $\mu^{b,c)}$ | $pK_a{}^{c)}$ | $K$/mol$^{-1}$ dm$^3$ | $\varepsilon_C$/mol$^{-1}$ dm$^3$ cm$^{-1}$ |
|---|---|---|---|---|---|
| 2-Methyl-2-propanol | 12.47 | 1.66 | 19 | 0.22±0.06 | 208.5±18 |
| Ethanol | 24.55 | 1.66 | 15.9 | 0.14±0.07 | 261.6±23 |
| Phenol | 9.78 | 1.45 | 10.02 | 0.43±0.04 | 275.8±12 |

a) Dielectric constant. b) Dipole moment in Debye units. c) J. A. Riddick and W. B. Bunger, "Technique of Chemistry, Vol. 3, Organic Solvent," 3rd ed, Wiley-Interscience, New York (1970).

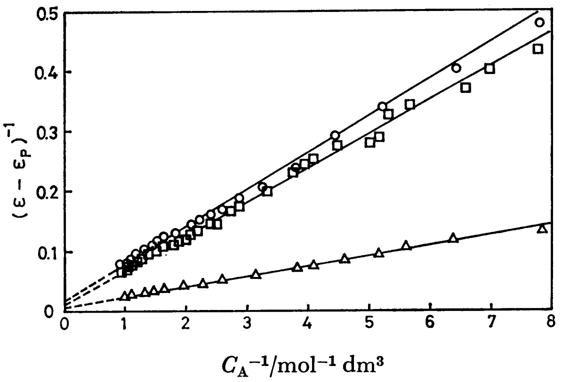

Fig. 2. Plots of $(\varepsilon - \varepsilon_P)^{-1}$ *vs.* $C_A{}^{-1}$ for 2-methyl-2-propanol–cyclohexane (○), ethanol–cyclohexane (□), and phenol–cyclohexane (△) solutions. $\varepsilon_P$ is taken as the absorption coefficient in pure cyclohexane.

where $C_P$ and $C_A$ are the total concentrations of pyrene and alcohol or phenol, respectively.

The absorbance measured at the wavelength for the 0-0 band can be expressed as

$$A = \varepsilon_P\, l\, [\mathrm{P}] + \varepsilon_C\, l\, [\mathrm{PA}],$$

where $\varepsilon_P$ and $\varepsilon_C$ denote the absorption coefficients for free pyrene and the complex, respectively, and $l$ is the optical path length (1 cm).

Provided that $C_A$ is much larger than $C_P$ $(=2.99\times 10^{-3}\ \mathrm{mol\ dm^{-3}})$, [A] is approximated to $C_A$, and the following relation[12] can be derived between $C_A$ and the apparent absorption coefficient $\varepsilon = A/C_P l$:

$$\frac{1}{\varepsilon-\varepsilon_P} = \frac{1}{\varepsilon_C-\varepsilon_P} + \frac{1}{(\varepsilon_C-\varepsilon_P)KC_A}.$$

Thus, a plot of $1/(\varepsilon-\varepsilon_P)$ *vs.* $1/C_A$ should give a straight line, from the intercept and slope of which the values of $\varepsilon_C$ and $K$ can be determined.

Figure 2 shows such plots for the systems of pyrene in various alcohol– or phenol–cyclohexane mixtures. Because of the condition $C_A \gg C_P$ and much complicated interactions at higher $C_A$, the concentration range effective for plots should be considerably narrowed (roughly $0.1 < C_A < 1$). As shown in Fig. 2, fairly good linear relationships have been obtained, a fact which indicates that the stoichiometry corresponds to 1:1 complexation in the lower concentration region. From the values of the slopes and intercepts, the association constants $K$ and the absorption coefficients $\varepsilon_C$ have been estimated, as listed in Table 1. The values of $K$ obtained are in good order-of-magnitude agreement with those ($\lesssim 1\ \mathrm{mol^{-1}\ dm^3}$) estimated by Lianos and Georghiou,[10] though more accurate determinations are difficult because of unavoidable experimental errors. Similar values have been obtained using aprotic polar solvents.[12]

It can be seen from Table 1 that the $K$ and $\varepsilon_C$ values bear no direct relation to the dielectric constants or dipole moments; they seem to be rather correlated with the acidities, which may imply that hydrogen-bonded complexes are formed between pyrene and phenol or alcohols.[10]

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