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EFFECT OF PRESSURE ON IODINE COMPLEX WITH DIETHYL ETHER IN n-HEPTANE

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The equilibrium constant K and the volume change ΔV accompanying the formation of diethyl ether-iodine complex in n-heptane was estimated by measuring the visible absorption spectra up to 3300 bar at 25°C. The ΔV value of -6.7 ± 1.0 cm^3/mol accompanying the complex formation is comparable with that of -2.8 or -6.4 cm^3/mol estimated by the X-ray data.

There are many investigations about iodine complexes as examples for charge transfer complex on both experimental and theoretical point of view. Pressure effects on the iodine complexes with π-donor such as benzene, toluene, and mesitylene have been studied by Ham,[1] and Kwun and Lentz.[2] They concluded that the complex formation constant increased with increasing pressure. But there has been no investigation for the iodine complex with n-donor such as ether or amine under high pressure. In the present work we studied the effect of pressure on the iodine complex with diethyl ether as n-donor in n-heptane by measuring the visible absorption spectra.

Iodine was purified by sublimation under nitrogen atmosphere. Diethyl ether was shaken with sodium carbonate solution, and dried with calcium chloride and sodium metal successively prior to fractional distillation. n-Heptane was purified in the usual way.[3] Since iodine solution is highly corrosive for the high pressure vessel, an inner cell similar to that designed by le Noble and Schlott[4] was utilized. It was set inside the clamp type vessel for high-pressure optical measurement.[5] The path length of the cell at 1 bar was determined by comparing with the absorbance of the same solution in a 1-cm cell.

A set of spectra of the iodine solution containing diethyl ether in n-heptane at 25°C and various pressures up to 3300 bar is shown in Fig. 1. The path length of the cell under high pressure is corrected from the compressibility data of n-heptane.[6] It has been established that there is an equilibrium between the free iodine ($\lambda_{max}\approx520$ nm) and the iodine complex with diethyl ether ($\lambda_{max}\approx460$ nm) shown by the following equation.[7]

$$(C_2H_5)_2O + I_2 \overset{K}{\rightleftarrows} (C_2H_5)_2O\text{-}I_2 \qquad (1)$$

The equilibrium constant K in Eq. 1 is estimated by using the modified Benesi-Hildebrand equation.[7]

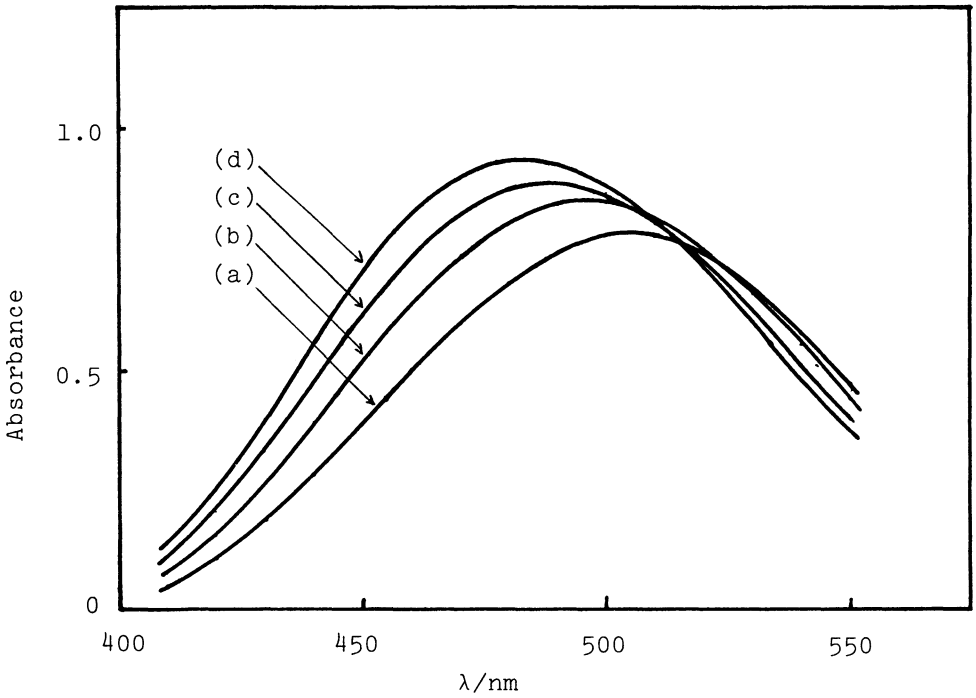

Fig. 1 Spectra of diethyl ether-iodine in n-heptane at 25°C and various pressures.
diethyl ether: 0.107, iodine: 1.52×10^{-4} (in mole fraction);
(a) 1 bar, (b) 1100 bar, (c) 2200 bar, (d) 3300 bar.

$$\frac{X_A}{Ab-Ab'} = \frac{V}{K(\varepsilon_C-\varepsilon_A)\cdot\iota}\cdot\frac{1}{X_D} + \frac{V}{(\varepsilon_C-\varepsilon_A)\cdot\iota} \qquad (2)$$

where X_A and X_D represent the initial mole fraction of iodine and diethyl ether, respectively, Ab is the absorbance of the mixture solution of diethyl ether and iodine, Ab$'$ is that of the iodine solution whose concentration is X_A, ε_A and ε_C are the molar extinction coefficient of free iodine and complexed iodine, ι is the path length, and the molar volume V of the solution is assumed to be equal to that of the solvent.[6] According to Eq. 2 it is possible to evaluate K from the intercept and the slope of $X_A/(Ab-Ab')$ vs. $1/X_D$ plot. Table 1 shows the complex formation constant K at various pressures. The K value of 6.0 at 1 bar coincides well with 5.9 (in mole fraction) obtained by Brandon et al.[7] Pressure dependence of log K is shown in Fig. 2. The volume change ΔV accompanying the formation of the complex can be calculated from the following equation.

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V}{RT} \qquad (3)$$

Table 1 Equilibrium constants K of diethyl ether-iodine complex in n-heptane at 25°C and various pressures

P/bar	1	1100	2200	3300
K[a]	6.0 ±1.0	8.4 ±1.2	11.0 ±1.2	12.1 ±1.6

a) mean value of the K at 430, 440, and 450 nm in mole fraction.

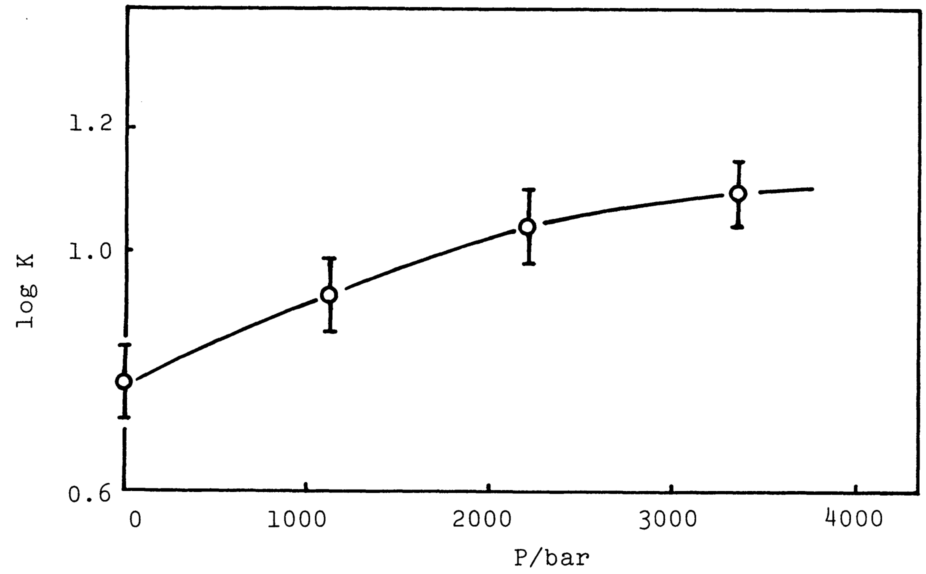

Fig. 2 Log K vs. P for diethyl ether-iodine complex in n-heptane at 25°C.

The ΔV value obtained from the initial slope in Fig. 2 is -6.7 ± 1.0 cm^3/mol at 1 bar. The negative sign of ΔV in n-σ complex(8) is the same as in π-π complex by Ewald(9) and π-σ complex by Ham,(1) and Kwun and Lentz.(2)

From the X-ray diffraction work of Hassel(10) the structure of the iodine complex with 1,4-dioxane is known in the solid state. The O-I (oxygen atom-iodine atom) bond distance of this complex is 0.281 nm(10) and the sum of the van der Waals radii of oxygen atom (0.140 nm) and iodine atom (0.215 nm) is 0.355 nm.(11) Assuming that the O-I bond distance in the 1,4-dioxane-iodine complex is equal to that in the diethyl ether-iodine complex, we can estimate the volume change ΔV associated with the formation of the diethyl ether-iodine complex by the following equation

$$\Delta V = \pi r^2 \Delta d \cdot N \qquad (4)$$

where it is assumed that the contraction Δd of the distance between O and I with the complex formation occurs along the axis of a cylinder having the radius r equal to the van der Waals radius of the oxygen atom or iodine atom, and N is Avogadro's number. Taking the values of (0.281-0.355) nm for Δd and 0.140 or 0.215 nm for r, the value of ΔV was -2.8 or -6.4 cm^3/mol, respectively. This value is comparable with -6.7 ± 1.0 cm^3/mol estimated by the observed pressure dependence of equilibrium constant.

References and note

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