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The Effect of the Hydrostatic Pressure on the Hydrogen-bond Formation between Phenol and Dioxane in Hexane*

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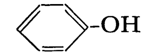
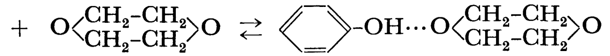
The near-UV absorption spectra of phenol-dioxane in *n*-hexane were observed under hydrostatic pressures up to 1480 atm and at 30 °C. With an increase in the pressure, the spectra shift toward the longer wavelength side and the amount of the hydrogen-bonded phenol increases. The equilibrium constant for 



$+ \mathrm{O}\genfrac{}{}{0pt}{}{\mathrm{CH_2{-}CH_2}}{\mathrm{CH_2{-}CH_2}}\mathrm{O} \rightleftarrows -\mathrm{OH}\cdots\mathrm{O}\genfrac{}{}{0pt}{}{\mathrm{CH_2{-}CH_2}}{\mathrm{CH_2{-}CH_2}}\mathrm{O}$

was obtained, and the volume change accompanying the hydrogen-bond formation was estimated to be -3.0—$-3.4\ \mathrm{cm^3/mol}$.

The effect of the hydrostatic pressure on the hydrogen-bond formation has been investigated by Shishkin and Novak,[1] Fishman and Drickamer,[2] and Osugi and Kitamura[3] on the basis of IR-absorption measurements. Shishkin and Novak[1] studied the system of phenol and some alcohols in carbon tetrachloride under pressures up to 3200 kg/cm². A pressure rise of 90—130 kg/cm² is found to have the same effect as a temperature drop of 1 °C. Using this result, Hamann[4] estimated the volume change accompanying the hydrogen-bond formation, ΔV, to be -4.5—$-6\ \mathrm{cm^3/mol}$. Fishman and Drickamer[2] investigated the association of *n*-butyl alcohol in carbon disulfide up to 11300 atm. The ΔV values estimated were $-4.64\ \mathrm{cm^3/mol}$ in the range from 1 to 5820 atm, and $-2.47\ \mathrm{cm^3/mol}$ in the range from 5820 to 11300 atm. The system of *n*-butyl alcohol in carbon disulfide was studied up to 8000 atm by Osugi and Kitamura.[3] Assuming the association numbers to be 2, 3, and 4, the ΔV was estimated to be -2.20, -4.31, and $-5.74\ \mathrm{cm^3/mol}$ respectively. The high concentration of solute used in these experiments seems to permit a higher degree of association due to hydrogen bonding. The number of solute molecules participating in the association is not necessarily certain, so that it seems difficult to estimate the ΔV value per mol H-bond exclusively from these data.[3]

Using the molecular model of hydrogen bonding, the ΔV has been calculated theoretically by Hamann.[4,5] Assuming that the distance between the α and β oxygen atoms in the hydrogen bonding ($\overset{\alpha}{\mathrm{O}}\mathrm{-H}\cdots\overset{\beta}{\mathrm{O}}$) is contracted by about 0.9 Å, and that this contraction occurs along the axis of a cylinder having a radius equal to the van der Waals radius of the oxygen atoms, he estimated the ΔV to be about $-3.8\ \mathrm{cm^3/mol}$.

The purposes of the present paper are to observe the near-UV absorption spectrum of phenol–dioxane in *n*-hexane, where the concentration of phenol is very dilute and where the only hydrogen-bonded complex is 

$-\mathrm{OH}\cdots\mathrm{O}\genfrac{}{}{0pt}{}{\mathrm{CH_2{-}CH_2}}{\mathrm{CH_2{-}CH_2}}\mathrm{O}$,

under hydrostatic pressures up to 1480 atm, and to estimate the ΔV value accompanying the hydrogen-bond formation. A series of excellent studies of the same system has been performed at atmospheric pressure by Baba and Nagakura,[6,7] Nagakura and Baba,[8] and Nagakura.[9] The pressure effect on the hydrogen-bond formation, however, has never been studied on the basis of UV-absorption measurements.

Experimental

Materials. All the reagents, of an extra pure grade, were used after the following purification. The *n*-hexane was purified as has been described previously[10,11] (bp 68.9 °C) and was optically transparent to 230 nm. The phenol was purified twice by vacuum distillation (mp 40.5±0.5 °C). The dioxane was refluxed with sodium metal for two days and then fractionally distilled (bp 101.3 °C).

Apparatus. A Shimadzu model MPS-501 double-beam spectrophotometer was used to measure the absorption spectra. Figure 1 shows schematically the clamp-type optical cell used to measure the absorption spectra under high pressures. The optical cell, which was constructed from cobalt alloy (HAYNES alloy No.25, manufactured by the Mitsubishi Metal Mining Co., Ltd.), was designed so as to be set in the sample space of the spectrophotometer after the pressure had been raised. The windows of sapphire permitted measurement to wavelengths of about 230 nm. The pressure generated in the cell was calibrated against the readings of the Bourdon-tube gauge of the oil press by

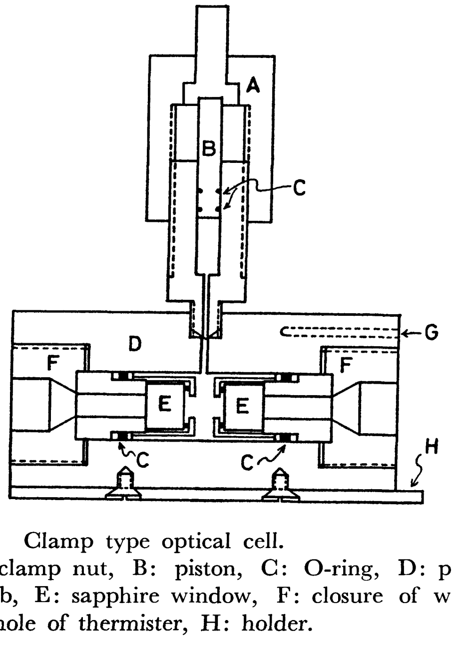


Fig. 1. Clamp type optical cell.
A: clamp nut, B: piston, C: O-ring, D: pressure bomb, E: sapphire window, F: closure of window, G: hole of thermister, H: holder.

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means of a manganine gauge, which was inserted in the cell instead of the window. The accuracy of the pressure was ±2.7% at 1400 atm.

Procedures. The measurement of the absorption spectra under pressure was carried out at 30 °C by the following procedures. The sample solution was admitted into the cell directly using a glass pipet before a piston was inserted into the cylinder. The piston was pushed into the cylinder by an oil press until the desired pressure was generated. Then the piston was fixed by a clamp nut to keep the pressure constant after the press load had been released. The absorption spectra were measured, with air as the reference, and the base line, which was not affected by the pressure, was subtracted. No optical contamination was observed throughout the experiment. The concentration of the solution under pressure was corrected from the compressibility data of *n*-hexane.[12]

Results and Discussion

Figure 2-1 shows the pressure effect on the absorption spectrum of phenol and dioxane (0.15 mol/l) in *n*-hexane. The a and c arrows and the b and d arrows in the figure represent the absorption bands of free phenol and hydrogen-bonded phenol respectively at atmospheric pressure.[6–9] Figures 2-2 and 2-3 show the absorption spectra corrected by the compressibility of *n*-hexane.[12] Figures 3-1 and 3-2 also show the pressure effect on the absorption spectra of the solution with a different concentration of dioxane (0.10 mol/l). Two characteristic points are noticeable from these figures: (1) the spectrum shifts toward a longer wavelength. As is shown in Fig. 4, the results of the red shift, $\Delta\lambda$, for the a-band and c-band of phenol as a function of the pressure are in good agreement with those obtained by Robertson *et al.*[13] A similar shift is found for the b-band and d-band of hydrogen-bonded phenol, though the bands are so broad that it is hard to determine $\Delta\lambda$ precisely. Many authors

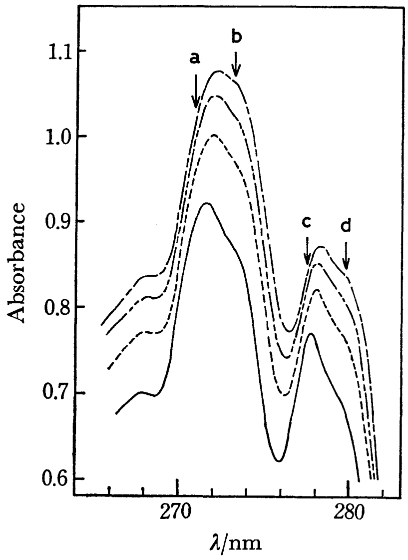


Fig. 2-1. Pressure effect on the absorption spectrum of phenol-dioxane in *n*-hexane at 30 °C.
phenol: 5.000× 10^{-4} mol/l, dioxane: 0.150 mol/l
——: 1 atm, —·—: 600 atm, -----: 1160 atm, ----: 1480 atm

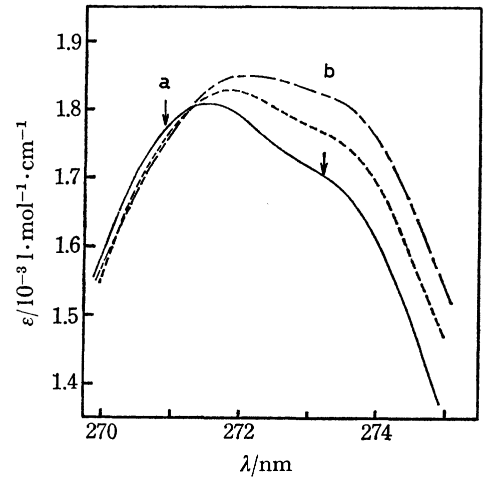


Fig. 2-2. Pressure effect on the absorption spectrum corrected by compressibility data of *n*-hexane at 30 °C.
phenol: 5.000× 10^{-4} mol/l, dioxane: 0.150 mol/l
——: 1 atm, -----: 600 atm, ----: 1480 atm

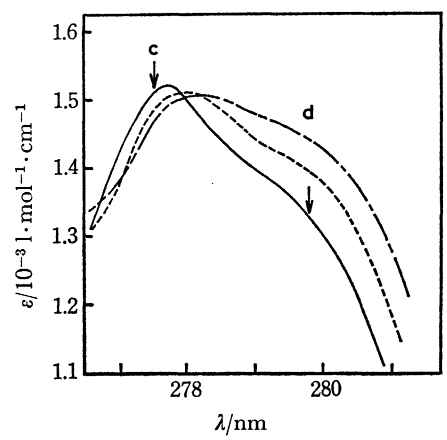


Fig. 2-3. Pressure effect on the absorption spectrum corrected by compressibility data of *n*-hexane at 30 °C.
phenol: 5.000× 10^{-4} mol/l, dioxane: 0.150 mol/l
——: 1 atm, —·—: 600 atm, ----: 1480 atm

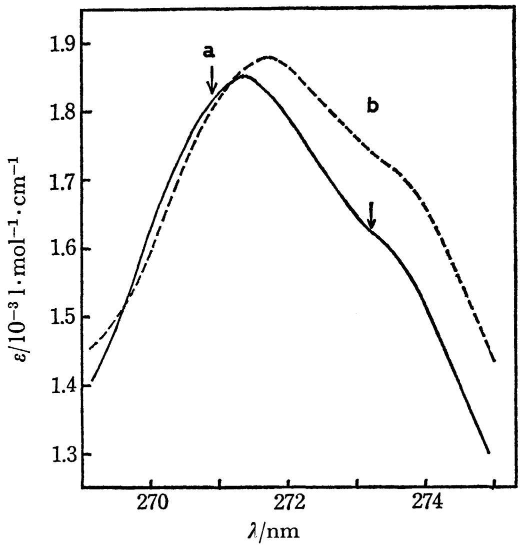


Fig. 3-1. Pressure effect on the absorption spectrum corrected by the compressibility data of *n*-hexane at 30 °C.
phenol: 5.000× 10^{-4} mol/l, dioxane: 0.100 mol/l
——: 1 atm, -----: 1160 atm

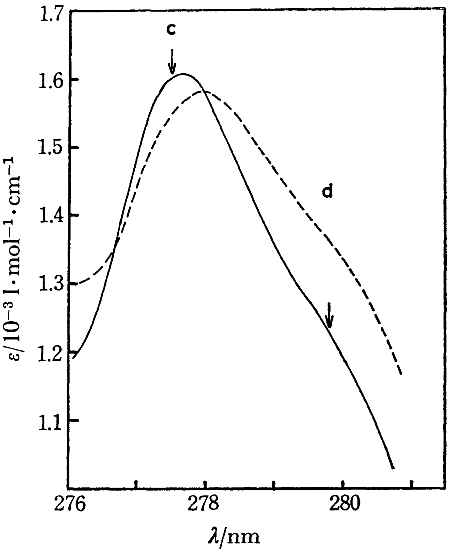


Fig. 3-2. Pressure effect on the absorption spectrum corrected by the compressibility data of *n*-hexane at 30 °C.
phenol: 5.000×10^{-4} mol/l, dioxane: 0.100 mol/l
——: 1 atm, – – –: 1160 atm

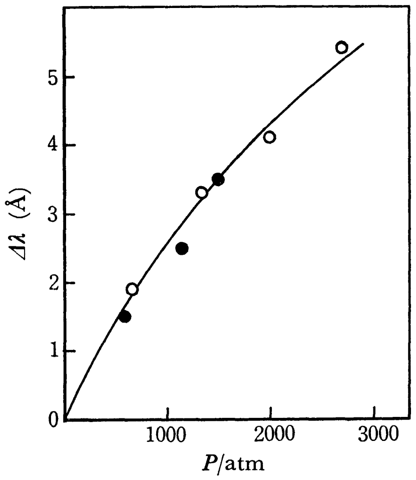
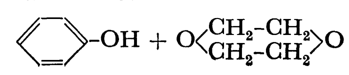
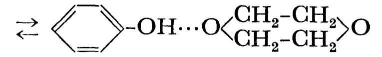


Fig. 4. Pressure effect on the amount of red shift for the a- and c-bands of phenol in *n*-hexane.
●: this work, ○: Robertson *et al.*[13]

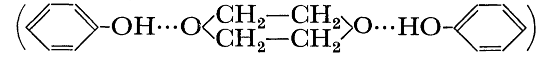
have indicated that such a red shift is attributable to an increase in the intermolecular interaction of the London–van der Waals type between the solvent and solute molecules upon an increase in the pressure, and that the energy level of the excited state is lowered.[13,14]
(2) The ratio of the absorbance of the hydrogen-bonded-phenol band to that of the free-phenol band increases with an increase in the pressure. This shows that the hydrogen-bonded phenol increases with an increase in the pressure. From these spectral data, the equilibrium constant at each pressure and the volume change accompanying the hydrogen-bond formation can be obtained.

The following equilibrium is assumed to be established in *n*-hexane:




(1)

Here, the concentration of phenol is so dilute that the self-association of phenol[15,16] and the formation of 2-mol hydrogen bonds for a dioxane molecule[7]



are eliminated. The equilibrium constant, K, is represented as follows:

$$K=\frac{C_H}{C_P C_D} \tag{2}$$

where C_P, C_H, and C_D are the concentrations of free phenol, hydrogen-bonded phenol, and dioxane respectively. According to Lambert–Beer's law, C_P and C_H are given as follows:

$$C_P=\frac{\beta(\alpha\varepsilon_b'-\varepsilon_a')}{(\alpha\varepsilon_b'-\varepsilon_a')+(\varepsilon_a-\alpha\varepsilon_b)} \tag{3}$$

$$C_H=\frac{\beta(\alpha\varepsilon_b-\varepsilon_a)}{(\alpha\varepsilon_b-\varepsilon_a)+(\varepsilon_a'-\alpha\varepsilon_b')} \tag{4}$$

Here, β is the total concentration of phenol, which is a sum of C_P and C_H, α is the ratio of the absorbances of the a-band and the b-band, ε and ε' are the molar absorption coefficients of free phenol and hydrogen-bonded phenol, and the subscript denotes each absorption band. When we insert Eqs. (3) and (4) in Eq. (2), K is represented as:

$$K=\frac{\varepsilon_a-\alpha\varepsilon_b}{C_D(\alpha\varepsilon_b'-\varepsilon_a')} \tag{5}$$

Similar expressions can be deduced for the c-band and the d-band. The following values were obtained in this experiment for each molar absorption coefficient ($\times10^{-3}$ l/mol): $\varepsilon_a=2.102$ and $\varepsilon_a'=1.670$ at 270.9 nm, $\varepsilon_b=1.134$ and $\varepsilon_b'=1.922$ at 273.2 nm, $\varepsilon_c=2.030$ and $\varepsilon_c'=1.318$ at 277.5 nm, $\varepsilon_d=0.650$ and $\varepsilon_d'=1.604$ at 279.8 nm. The ε' values were decided at 0.80 mol/l of dioxane, where the spectral change became to level. On the right-hand side of Eqs. (3)—(5), all the values except α are known. Therefore, C_P, C_H, and K can be calculated by using the experimental value of α. The results at atmospheric pressure are shown in Table 1, in which the K value is held approximately constant, at least in the lower concentrations cited here.[17]

TABLE 1. EQUILIBRIUM AT ATMOSPHERIC PRESSURE (30 °C)

C_D (mol/l)	α	$C_P\times10^4$ (mol/l)	K (l/mol)
From a-band/b-band			
0.020	1.511	3.802	15.8
0.060	1.233	2.493	16.3
0.080	1.176	2.172	16.3
0.100	1.117	1.818	17.5
From c-band/d-band			
0.020	2.109	3.790	15.9
0.060	1.521	2.594	15.5
0.080	1.409	2.291	14.8
0.100	1.278	1.895	16.4

The total concentration of phenol: 5.000×10^{-4} mol/l.

Assuming that the absorbance observed under high pressures follows Lambert–Beer's law, and that the molar absorption coefficient and the optical path length do not change with the pressure, Eqs. (3)—(5) hold also under high pressure. The concentration of a solution is, of course, corrected from the compressibility data of *n*-hexane.[12] The free-energy change, ΔG°, and the volume change, ΔV, accompanying the hydrogen-bond formation are given by:

$$\Delta G^\circ = -RT\ln K \qquad (6)$$

$$\Delta V = -RT\left(\frac{\partial \ln K}{\partial P}\right)_T \qquad (7)$$

TABLE 2. EFFECT OF PRESSURE ON THE EQUILIBRIUM OF HYDROGEN-BOND FORMATION (30 °C)

Pressure (atm)	α	$C_P \times 10^4$ (mol/l)	K (l/mol)	$-\Delta G^\circ$ (kcal/mol)
a-band/b-band, dioxane: 0.15 mol/l				
1	1.036	1.286	19.3	1.78
600	1.019	1.169	20.4	1.82
1480	0.995	0.995	23.6	1.90
c-band/d-band, dioxane: 0.15 mol/l				
1	1.131	1.385	17.4	1.72
600	1.099	1.263	18.4	1.75
1480	1.053	1.080	21.3	1.84
a-band/b-band, dioxane: 0.10 mol/l				
1	1.117	1.818	17.5	1.72
1160	1.073	1.535	20.2	1.81
c-band/d-band, dioxane: 0.10 mol/l				
1	1.278	1.895	16.4	1.68
1160	1.188	1.593	19.1	1.78

Pressure (atm)	$-\Delta V$ (cm^3/mol)	
	a-band/b-band	c-band/d-band
dioxane: 0.15 mol/l		
1—1480	3.4	3.4
dioxane: 0.10 mol/l		
1—1160	3.0	3.3

Where R is the gas constant, and T, the absolute temperature. The $-\Delta G^\circ$ value (1.66—1.78 kcal/mol) coincides well with the calorimetric result (1.79 kcal/mol).[18] The ΔV value obtained in this experiment is -3.0—-3.4 cm^3/mol. This value is comparable with those in alcohol (-4.6—-6 cm^3/mol)[2,3] and calculated theoretically (-3.8 cm^3/mol).[4,5]

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