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Kyoto University

OPTICAL STUDIES OF PRESSURE EFFECTS I.

THE MEASUREMENT OF THE O-H STRETCHING VIBRATION BAND OF ETHANOL

BY JIRO OSUGI AND YOICHI KITAMURA

The infrared spectra near 3 micron of ethanol in solution were measured up to 8000kg/cm². The main pressure effects observed were the shifts of the absorption maxima and the increase of intensities. The effect of pressure on the mean potential energy of the hydroxyl group due to environments is discussed from the shifts. The effect of pressure on the equilibrium between monomeric and associated alcohol is estimated from the intensity changes.

Introduction

It is well known that the infrared spectrum near 3 micron of ethanol consists of two bands. One is a narrow band near 3600 kayser and is attributed to free O–H (monomeric). The other is a broad band near 3300 kayser and is attributed to hydrogen bonded O–H (polymeric). These were confirmed experimentally by W. C. Coburn[1] and others.

In the present experiment we measured the pressure effects on these bands. The main pressure effects observed were the shifts of the bands to lower frequencies and the increase of the absorption intensities with increase of pressure.

The shift of absorption maximum with pressure is concerned with the mean potential energy of the hydroxyl group due to surrounding solvent molecules.

It is experimentally confirmed that the absorption maximum of a band varies more or less with variations of solvent at the normal pressure. Many attempts have been done to find the relation between these frequency shifts and some bulk properties of the solvent. But, at present, there is no formula to fit these relationships for a variety of bands and solvents.

Buckingham[2] explained theoretically this frequency shift by means of the mean potential energy of the chromophore due to surrounding solvent molecules. The following equation for the frequency shifts was derived assuming the harmonic Hamiltonian with small anhamonicity and small perturbations due to environments:

$$\nu_S - \nu_0 = (4\pi c \sqrt{\mu k_B})^{-1}[-3(k_A/k_B)(\partial U/\partial r)_e + (\partial^2 U/\partial r^2)_e] \tag{1}$$

where,

ν_S: absorption maximum in solvent

ν_0: absorption maximum in gas phase

1) W. C. Coburn and E. Grunwalt, *J. Am. Chem. Soc.*, **80**. 1318 (1958)

2) A. D. Buckingham, *Proc. Roy. Soc.*, *A*, **248**. 169 (1958)

c: light velocity

μ: reduced mass of the hydroxyl group

k_B: force constant

k_A: anharmonic coefficient

U: mean potential energy of the hydroxyl group.

r: intermolecular distance of the O–H bond.

suffix e: indicates the values at the equilibrium distance of the O–H bond.

From eq. (1) it is evident that the shift of the absorption maximum with variation of the solvent is due to the term $[-3(k_A/k_B)(\partial U/\partial r)_e+(\partial^2 U/\partial r^2)_r]$. mainly to $(\partial^2 U/\partial r^2)_e$. Hence, the change of ν_S with pressure indicates the change of the term $[-3(k_A/k_B)(\partial U/\partial r)_e+(\partial^2 U/\partial r^2)_e]$ with pressure, in other words, with the change of intermolecular distance of solvent molecules.

The other pressure effect examined is the increase of the absorption intensities with increase of pressure.

It was experimentally confirmed that the absorption intensities of bands change with variation of the solvent. However, neither formula to relate this change with the bulk properties of the solvent nor theoretical formula to relate it with any microscopic properties of the solvent was found. The intensity change with pressure will give us some informations on the properties concerned with the intensity change and of the pressure effect on the equilibrium between the monomeric and the associated alcohols.

Experimentals

An optical vessel with sapphire windows developed by H. G. Drickamer was used, as shown in Fig. 1. The infrared spectrometer used was Hitachi EPI S2.

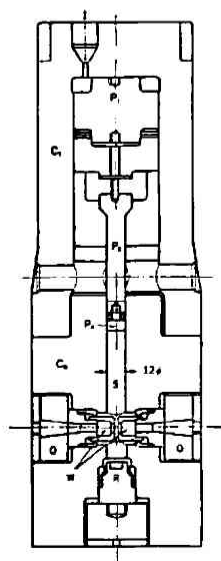The measurement was performed at pressures of 1, 2000, 4000, 6000, and 8000 kg/cm². The pres-

Fig. 1   Optical vessel

P_1 : low pressure piston
P_2 : high pressure piston
P_3 : piston rod
C_1 : low pressure cylinder
C_2 : high pressure vessel
S : sample
W : sapphire windows
O : window plugs
R : closure

sure was measured by a gauge at lower pressure side and was calculated from the piston ratio (20 : 1).

The sapphire windows are almost transparent to the wave length near 3 micron except very small absorption at 3275 kayser. Carbon disulfide has no absorption in this range. But, toluene does not uniformly transmit the light of these wave lengths, so we used a reference cell which contains toluene only and the equation below was used to calibrate the deviation induced by pressure:

$$\frac{\{\log(I'/I)_{3700} - \log(I'/I)_\nu\}}{\{\log(I'_p/I_p)_{3700} - \log(I'_p/I_p)_\nu\}} = \frac{l_r - l_s}{l_r - (C_p/C)l_s} \tag{2}$$

where

I', I : light intensities transmitted through specimen and reference cells respectively at normal pressure

I'_p, I_p : I' and I at higher pressures

l_s, l_r : path length of specimen and reference cells respectively

C_p/C : ratio of concentration at higher pressures to that at normal pressure

ν : wave number in kayser

Results and Considerations

Figs. 2, 3, show some results of the measurement of the absorption spectra of ethanol in carbondisulfide and in toluene respectively. The full curve indicates the spectrum at 1kg/cm² and the broken one that at 4000kg/cm² in Fig. 2 and that at 6000 kg/cm² in Fig. 3.

It is clear that the absorption maxima shift to lower frequencies and the intensities increase with the increase of pressure. The frequencies of the absorption maximum of the broad bands are not precise, so only the absorption maximum of the sharp bands will be discussed.

Assuming eq. (1) also holds under pressure, we have the following equation:

$$\varDelta\nu = \nu_{so} - \nu_{sp} = (4\pi c\sqrt{\mu k_B})^{-1}[-3(k_A/k_B)(\partial U/\partial r)_{e \cdot o} + (\partial^2 U/\partial r^2)_{e \cdot o} + 3(k_A/k_B)(\partial U/\partial r)_{e \cdot p} - (\partial^2 U/\partial r^2)_{e \cdot p}] \tag{3}$$

where, suffixes o and p indicate the values at normal and higher pressures, respectively. The plot $\varDelta\nu$ vs. pressure indicates how the term in parenthesis of eq. (3) changes with pressure. In this case $\log \varDelta\nu$ vs.
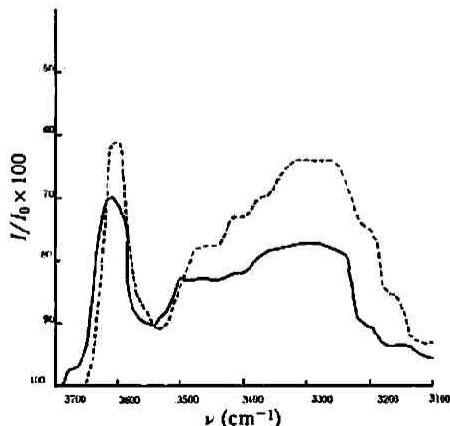

Fig. 2 Spectra of ethanol in carbondisulfide (3 vol%)

Full line : at normal pressure
Broken line : at 4000 kg/cm²

$\log(\rho/\rho_0)$ is plotted, where ρ and ρ_0 indicate the density of the solvent at higher pressures and at normal pressure.

The volume of liquids is considered reasonably to be proportional to the 3rd power of the mean intermolecular distance R; hence the density to -3rd power. So, if $\Delta\nu$ is proportional to R^a, $\log\Delta\nu$ becomes proportional to $a\log R$ or $-\frac{1}{3}a\log(\rho/\rho_0)$. The values of a, thus, can be determined from the slopes in Fig. 4.

To calculate the values (ρ/ρ_0), the compressibility data of P. W. Bridgman was used for carbondisulfide and those measured in our laboratory for toluene, which is shown in Table 1.
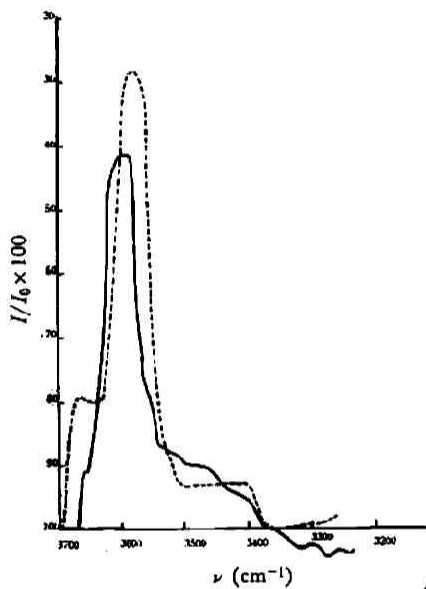

Fig. 3   Spectra of ethanol in toluene. (3 vol%)

Full line : at normal pressure
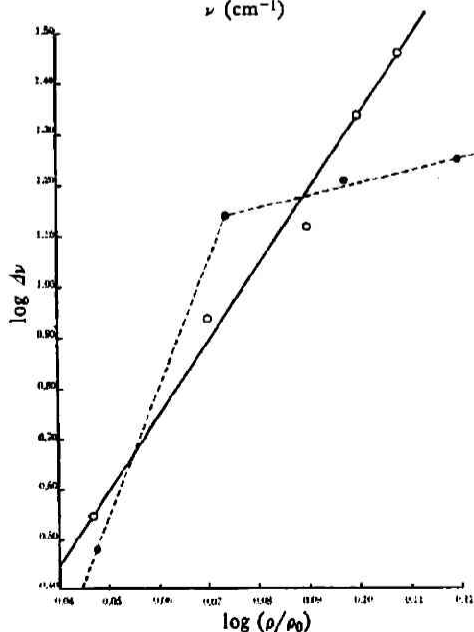Broken line : at 6000 kg/cm²

Fig. 4   Log $\Delta\nu$ vs. log (ρ/ρ_0).

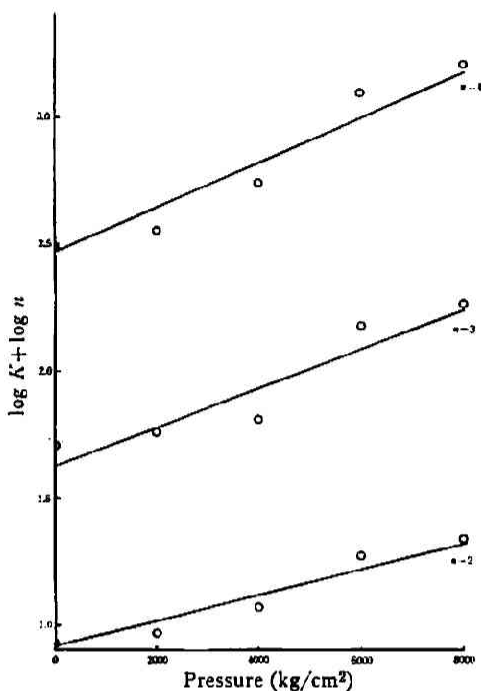Full line : carbondisulfide as a solvent
Broken line : toluene as a solvent

Fig. 5   (log K+log n) vs. pressure.

Table 1   Relative volumes of toluene (tempreature 20°C)

Press.(kg/cm²)	1	1000	2000	3000	4000	5000	6000	7000
(V_p/V_1)	1.000	0.934	0.896	0.868	0.844	0.821	0.800	0.782

In Fig. 4 the full line shows the result in case of carbon disulfide as a solvent and the broken line in case of toluene. From the slope of the full line, the term in parenthesis in eq. (3) is proportional to $R^{-4.5}$ for carbon disulfide. From the broken line, the term is proportional to $R^{-7.8}$ up to 4000 kg/cm² and to $R^{-0.78}$ above 4000 kg/cm² for toluene.

Assuming the interaction between the hydroxyl group and solvent molecules to be of the type of dipole-dipole interaction and R is independent on r, the potential U becomes proportional to R^{-6} and so $(\partial^2 U/\partial r^2)_e$ is also to R^{-6}.

According to the result mentioned above, the dependencies are rather close to R^{-6}. Hence, it may be concluded that the interaction has a nature of dipole-dipole interaction and R is not so much influenced by r. In the case of toluene as a solvent above 4000 kg/cm², the dependency is far from R^{-6}. It is difficult to give proper explanations of this result. However, it will be very interesting to consider this result from the phenomenon called hyperconjugation.

The intensity change is examined only in the case with carbon disulfide as a solvent. In the present examination. we assumed the following facts:

A)   At normal pressure. the Lambert-Beer law holds for both bands.

B)   The absorption coefficients ε and ε' for the monomeric and associated bands respectively and the path length l do not change with variations of pressure:

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$$S=\int(-\log T)d\nu=\int \varepsilon\cdot C\cdot l d\nu \qquad (4)$$

$$S'=\int(-\log T)'d\nu=\int \varepsilon'\cdot C'\cdot l d\nu \qquad (5)$$

where,

$-\log T$: optical density

ν: wave number in kayser

C: concentration

l: path length

prime: indicates those of the associated O–H band.

C) At higher pressures a coefficient γ (>1) which varies with pressure is introduced on the right side of eqs. (4) and (5):

$$S_p=\int(-\log T)_p d\nu=\gamma\int \varepsilon\cdot C_p\cdot l d\nu \qquad (6)$$

$$S'p=\int(-\log T)'_p d\nu=\gamma\int \varepsilon'\cdot C'_p\cdot l d\nu \qquad (7)$$

The values of S and S' are obtained by plotting $-\log T$ against ν.

According to Coburn and Grunwalt[1], the fraction of monomeric alcohol is 0.41 in carbontetrachloride at normal pressure and this may be approximately the case in carbondisulfide as these two solvents are both non-polar. The values of C and C' at the normal pressure is obtained from this fraction and the total concentration of 0.514 mole/l. Then, from eqs. (4) and (5), the values $\int \varepsilon\cdot l d\nu$ and $\int \varepsilon'\cdot l d\nu$ are obtained. From eqs. (6) and (7):

$$S_p/S'_p=C_p\cdot\int \varepsilon\cdot l d\nu/C'_p\cdot\int \varepsilon'\cdot l d\nu$$

Thus, C_p/C'_p is calculated from the values of $S_p S'_p$, $\int \varepsilon\cdot l d\nu$ and $\int \varepsilon'\cdot l d\nu$. The values C and C' obtained are illustrated in Table 2.

The equilibrium between monomeric and associated alcohol can be written as follows:

$$n(C_2H_5OH)=(C_2H_5OH)_n \qquad K=\frac{C'/n}{C^n} \qquad (8)$$
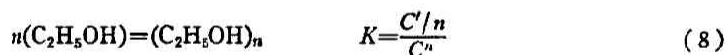
$$RT\left(\frac{\partial \ln K}{\partial p}\right)_T=-\Delta V \qquad (9)$$

Here as n is unknown, assuming several values, the equillibrium consant K is calculated at each pressure from the values in Table 2. Plotting $\log K$ vs. pressure (Fig. 5), we obtained the values of ΔV as follows:

n	2	3	4
ΔV cc/mole	-2.20	-4.31	-5.74

Table 2 The concentration of monomeric and associated alcohol

Press.(kg/cm²)	C (mole/l)	C' (mole/l)
1	0.211	0.303
2000	0.206	0.308
4000	0.187	0.327
6000	0.156	0.358
8000	0.147	0.367

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Table 3   The values of γ at each pressure

Press. (kg/cm²)	γ
1	1.00
2000	1.10
4000	1.33
6000	1.78
8000	1.90

S. D. Hamann[3] estimated the volume change associating a formation of a hydrogen bond to be about -3.4 cc/mole. Comparing our result with this value, the value of n may be deduced to distribute mainly between 2 and 3.

Having calculated the values of S_p, C_p and $\int \varepsilon \cdot l d\nu$ or S'_p, C'_p, $\int \varepsilon' \cdot l d\nu$, the values of γ are given at each pressure. In Table 3, γ is shown at each pressure. These values will give some criteria to determine what properties of the solvent have to do with the intensity change.

Acknowledgement

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3)   S. D. Hamann, "Physico-Chemical Effects of Pressure" p. 147 (Butterworths Scientific Publications, London)