Interaction Polarization of the Hydrogen Bonded Complexes. II

By Ko Kimura and Ryoichi Fujishiro

An increase of the molecular polarization due to hydrogen bonding reported by Sutton et al.[1], by Tsubomura[2] and also by the present authors[3] is one of variations of dielectric properties arising from the molecular interaction. Many obstacles are present in the precise determination of the molecular polarizations for the hydrogen bonded complexes from the measurements of dielectric constants, specific volumes and refractive indexes of ternary solutions (proton donors, proton acceptors and inert solvents). The most important point is

1) J. R. Hulett, J. A. Pegg and L. E. Sutton, *J. Chem. Soc.*, 1955, 3901.
2) H. Tsubomura, This Bulletin, 31, 435 (1958).
3) K. Kimura and R. Fujishiro, ibid., 32, 433 (1959).

whether or not Debye's equation holds even approximately in ternary solutions, because the measurements are carried out in such solutions that the interaction between proton donors and proton acceptors can take place. This problem will be discussd elsewhere. In so far as polarization values for the complexes are calculated by the use of Debye's equation, we must devise a way to make the difference as small as possible between the dielectric constant of a pure solvent and that of a ternary solution containing large quantities of a proton acceptor. Otherwise the polarization values obtained from observed dielectric constants and specific volumes are not reliable because of the solvent effect. In order to make the dielectric constants of ternary solutions with high concentrations of proton acceptors as low as possible, it is necessary to use nonpolar proton acceptors such as p-dioxane and bipyridyl. For example, it follows that when we want to investigate the polarization value of the phenol + pyridine complex, examination of the phenol + bipyridyl complex instead of the phenol + pyridine complex itself is more reasonable from consideration of the solvent effect.

In the previous paper, the dielectric measurements were carried out for some of the OH···O hydrogen bonded systems by using benzene as an inert solvent, and the analysis was performed based on a model with the covalent character of the hydrogen bonds[4]. This report describes first the results of dielectric measurements for the OH···N hydrogen bonded systems such as benzyl alcohol + bipyridyl, benzyl alcohol + triethylamine, phenol + bipyridyl and phenol + triethylamine by exactly the same procedure as in the previous report, and secondly the correlation between the dielectric data and the infrared spectra.

Experimental

Materials used in this work were purified by the method described in Weissberger's text-book[5]. Benzene was used as a solvent throughout this work. It was frozen three times after being shaken with concentrated sulfuric acid and with dilute sodium hydroxide, dried over phosphorous pentoxide, and then fractionally distilled through a "Heli-Pack" column. Benzyl alcohol was purified by shaking with aqueous potassium hydroxide solution and extracting with ether, which had been freed from peroxides. The extract was treated with saturated sodium hydrogen sulfite solution and dried over potassium carbonate. After the removal of ether, benzyl alcohol was dried over lime and distilled under reduced pressure. α, α'-Bipyridyl (the

4) C. A. Coulson and U. Danielsson, *Arkiv Fysik*, **8**, 239, 245 (1954): H. Tsubomura, This Bulletin, **27**, 445 (1954).
5) A. Weissberger et al., "Organic Solvents", Interscience Publishers, New York (1955).

special grade made by Wako Pure Chemicals Co., Ltd.) was dried in a desiccator and used without further purification. Its melting point was 70. 5°C. The measurements of dielectric constants ε, refractive indexes n and specific volumes v were carried out at 25°C with the apparatus already reported[3].

Results

The results of the measurements of ε, n^2 and v for the four ternary systems i. e., benzyl alcohol + α, α'-bipyridyl + benzene, benzyl

TABLE I. POLARIZATION DATA AND FORMATION CONSTANTS OF THE HYDROGEN BONDED COMPLEXES

Benzyl alcohol + α, α'-Bipyridyl		Benzyl alcohol	
(The weight per cent of α, α'-bipyridyl is 4.011.)			
$\varepsilon = 2.2988 + 3.36\,w$			
$n^2 = 2.2555 + 0.07\,w$			
$v = 1.13442 - 0.163\,w$			
P'	98.7 cc.		
K	5.5 l./mol.		
P_1	102.6 cc.	P	93.8 cc.
R_D	32.4 cc.	R_D	32.5 cc.
μ_1	1.85 D	μ	1.73 D

Benzyl alcohol + Triethylamine			
(The weight per cent of triethylamine is 9.300, or 29.95.)			
$\varepsilon = 2.3025 + 5.70\,w$		$\varepsilon = 2.3512 + 6.18\,w$	
$n^2 = 2.2104 + 0.156\,w$		$n^2 = 2.1411 + 0.240\,w$	
$v = 1.16696 - 0.282\,w$		$v = 1.21583 - 0.347\,w$	
P'	145.6 cc.	P'	157.9 cc.
K	2.9 l./mol.	K	2.9 l./mol.
P_1	168.2 cc.	P_1	167.0 cc.
R_D	30.8 cc.	R_D	31.4 cc.
μ_1	2.57 D	μ_1	2.57 D

Phenol + α, α'-Bipyridyl		Phenol	
(The weight per cent of α, α'-bipyridyl is 2.527.)			
$\varepsilon = 2.2900 + 4.80\,w$			
$n^2 = 2.2512 + 0.168\,w$			
$v = 1.13811 - 0.259\,w$			
P_1	108.7 cc.		
K	55 l./mol.		
P_1	111.7 cc.	P	84.6 cc.
R_D	27.2 cc.	R_D	27.6 cc.
μ_1	2.03 D	μ	1.67 D

Phenol + Triethylamine			
(The weight per cent of triethylamine is 28.35.)			
$\varepsilon = 2.3430 + 10.54\,w$			
$n^2 = 2.1459 + 0.380\,w$			
$v = 1.21204 - 0.424\,w$			
P'	214.2 cc.		
K	83.8 l./mol.		
P_1	214.8 cc.		
R_D	28.0 cc.		
μ_1	3.02 D		

TABLE II

	$\Delta\mu_T$	$\Delta\mu_D$	[III]	$\Delta\nu$	
Benzyl alcohol+bipyridyl	0.19D	0.19D	1.6%	240 cm^{-1}	a)
Benzyl alcohol+triethylamine	1.17	1.17	10	400	b)
Phenol+bipyridyl	0.48	0.39	3.4	480	c)
Phenol+triethylamine	1.54 (1.00)*	1.45	13	600	d)
Benzyl alcohol+dioxane	0.10	0.10	0.7	110	e)
Phenol+dioxane	0.29	0.21	1.5	250	f)

* This value reported by Sutton et al.[1] was calculated by the use of the formula $P=\sum f_i p_i$.
a) Measurements for the ethanol+pyridine system were carried out by the present authors with a Perkin-Elmer model 21 spectrophotometer.
b) C. H. Huggins and G. C. Pimental, *J. Phys. Chem.*, **60**, 1615 (1956).
c) N. Fuson, P. Pineau and M-L. Josien, *J. Chem. Phys.*, **55**, 454 (1958).
d) Measurements were carried out by the present authors with a Perkin-Elmer model 21 spectrophotometer.
e) N. D. Coggeshall and E. L. Saier, *J. Am. Chem. Soc.*, **73**, 5414 (1951).
f) H. Tsubomura, *J. Chem. Phys.*, **24**, 927 (1956).

alcohol + triethylamine + benzene, phenol + α, α'-bipyridyl + benzene and phenol + triethylamine + benzene, are expressed in Table I by formulae relating ε, n^2 and v to w, respectively, where w represents the weight fraction of the proton donors. The calculation of the molecular polarizations from these experimental data was performed according to the method described in the previous paper[3]. Polarization values P' thus obtained are also shown in Table I, together with those for the corresponding binary systems already reported i. e., benzyl alcohol + benzene and phenol + benzene. P' will contain the polarization for the free proton donor as well as that for the complex. If the fraction of the proton donor existing in the form of the complex in the limit $w \to 0$ is estimated by the use of the formation constant K of the complex, the true polarization value P_1 for the complex is determined by both the polarization value P for the free proton donor and P'. The formation constants of the complexes tabulated in Table I are either taken from literatures or measured by the present authors. As K for the benzyl alcohol + α, α'-bipyridyl complex is expected to be of the same order as that for the ethanol + pyridine complex, we measured the ultraviolet spectra[6] of the latter system by using n-heptane as a solvent, and determined K from the variation of the intensity of the $n \to \pi$ electronic transition of pyridine[7] due to the addition of ethanol. K for the benzyl alcohol + triethylamine complex is reported to be about 2.9 l./mol.[8] by the measurement of

infrared absorptions. When the content of triethylamine is 9.30 or 29.95 weight per cent, P_1 is calculated to be 168.2 cc. or 167.0 cc. The difference 1.2 cc. between these two values is attributable to the solvent effect. On the other hand, one can deduce both K and P_1 from P's in two concentrations of triethylamine. The calculated values of K and P_1 are 3.2 l./mol. and 166.2 cc., respectively. This result indicates the fact that the reliable association constant can be obtained in the case of the complexes of the small K and large $\Delta P = P_1 - P$. As K for the phenol + α, α'-bipyridyl complex, we used the formation constant for the phenol + pyridine[9] determined by the measurement of infrared absorptions. The value of K for the phenol + triethylamine complex is reported to be about 83.8 l./mol.[10] by the measurement of ultraviolet absorptions.

If we assume that the distortion polarization does not vary with complex formation and is equal to the molecular refraction R_D at the sodium D line, then we can calculate the permanent dipole moment μ_1 for the proton donor forming the complex. This assumption is not always reasonable, because it is conceivable to ascribe ΔP to an increase of the atomic polarization. However, we shall carry out tentatively the analysis of experimental data under the assumption that ΔP arises from the intermolecular charge transfer. The vector subtraction of the dipole moment μ of the free proton donor from μ_1 gives the increment of the dipole moment due to complex formation. The results of the vector calculations are summarized in Table II.

6) Ultraviolet absorption spectra were measured with a Beckman model DU spectrophotometer.
7) G. J. Brealey and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955).
8) G. M. Barrow and E. A. Yerger, ibid., **76**, 5247 (1954).

9) N. Fuson, P. Pineau and M-L. Josien, *J. chim. phys.*, **55**, 454 (1958).
10) S. Nagakura and M. Gouterman, *J. Chem. Phys.*, **26**, 881 (1957).

Discussion

It is generally believed that the hydrogen bond is not only of the electrostatic, but also of the covalent character. If the hydrogen bond is somewhat of the covalent character, structure III among the following three

(I)   O —H$\cdots$Y

(II)   O$^-$ H$^+\cdots$Y

(III)   O$^-\cdots$H—Y$^+$

will play a relatively important role. Then the observed increment of the dipole moment $\overrightarrow{\Delta\mu_T}=\overrightarrow{\mu_1}-\overrightarrow{\mu}$ is considered to be due to the contribution of structure III in the case of benzyl alcohol + triethylamine, whereas in the phenol + triethylamine system, polarization of π-electrons of phenol will, to a certain extent, arise owing to the lone pair field of triethylamine. This induced moment will be of the magnitude of 0.16 D, as estimated from the detailed description for the phenol + dioxane system. In systems such as phenol + triethylamine, therefore, the vector subtraction of 0.16 D from $\Delta\mu_T$ gives the average increment of the dipole moment due to the contribution of the structure III. Furthermore, in the case of phenol + bipyridyl, it must be considered that polarization of π-electrons will be induced in pyridine owing to the proton field of phenol. This calculation is very difficult, and we could not estimate this value. The increase of the dipole moment $\Delta\mu_D$ arising from delocalization in this system, therefore, may be smaller than the tabulated $\Delta\mu_D$ which gives the upper limit.

If we estimate the O$\cdots$Y distance from the shift of the wave number of the OH stretching vibration[11], the electric moment for structure III is evaluated. Moreover, when we suppose that the ratio of the weight of structure I to that of structure II is the same as in a free state, then we can estimate the contribution of structure III from the increment of the dipole moment. The results thus obtained are shown for all systems in Table II. The large contribution of structure III means the weakening of the OH bond, which is reflected on the decrease of the force constant of the OH bond, and hence leads to a decrease in the wave number of the OH stretching vibration. The wave number shift $\Delta\nu$ of the OH stretching vibration has often been correlated with the strengths of the hydrogen bonds. Therefore, we may expect the correlation of $\Delta\nu$ with the weight of structure III. The observed $\Delta\nu$'s for the OH stretching vibration are given in the
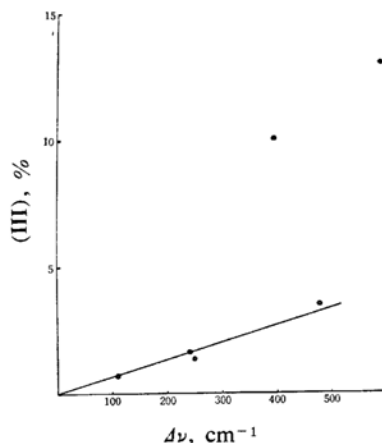

Fig. 1. The correlation of the weight of the structure III with $\Delta\nu$.

last column in Table II. The weight of structure III is plotted against $\Delta\nu$ in Fig 1. The four complexes lie on a straight line except benzyl alcohol + triethylamine and phenol + triethylamine, but the latter two complexes show extraordinarily great values for the weight of structure III in spite of the small $\Delta\nu$. If the spectroscopic results are correct, it seems that there are some questions about the above-mentioned treatment of the dielectric data. This is because it is natural to expect that the weight of structure III varies continuously with $\Delta\nu$. However, it has already been found by Barrow[12] that when pyridine and triethylamine are used as proton acceptors, the latter shows a character considerably different from that of the former. He distinguished acetic acid + pyridine from acetic acid + triethylamine, and called the former and the latter the hydrogen bonded complex and the hydrogen bonded ion pair, respectively. If we accept the idea suggested by Barrow, the hydrogen bonded complex belongs to a different category from the hydrogen bonded ion pair, that is to say, there is a distinct boundary between the former and the latter. The dielectric data suggest this idea, but it seems difficult to understand even qualitatively that benzyl alcohol + triethylamine is of the ion pair character without showing an intermediate character. This point will be discussed elsewhere in near future.

Summary

The dielectric measurements were carried out for benzyl alcohol + α, α'-bipyridyl, benzyl alcohol + triethylamine, phenol + α, α'-bipyridyl and phenol + triethylamine by using

---

11) K. Nakamoto, M. Margoshes and R. E. Rundle, *J. Am. Chem. Soc.*, **77**, 6480 (1955).

12) G. M. Barrow, ibid., **78**, 5802 (1956).

benzene as a solvent, and the polarization value for each system was calculated. The additional moments due to complex formation were evaluated, as in the previous paper, from both the polarization data and the spectroscopically determined formation constants. Then the weight of structure III was estimated and correlated with the wave number shift $\Delta\nu$ of the OH stretching vibration.

Department of Chemistry
Faculty of Science
Osaka City University
Kita-Ku, Osaka