Interaction Polarization of the Hydrogen Bonded Complexes

By Ko KIMURA and Ryoichi FUJISHIRO

(Received October 20, 1958)

A strong intermolecular interaction such as hydrogen bonding will be expected to give rise to some variation in the charge distribution of the interacting molecules[1]. Hence the dielectric measurement for the system containing hydrogen bonds will give some useful information about the intermolecular association through hydrogen bonding. Hammic, Norris and Sutton[2] investigated the polarization of molecular complexes from this point of view and pointed out[3] that it was not generally practicable to derive both the association constant and the dipole moment of a complex from polarization data alone. Few and Smith[4] also studied this problem, and proposed a method by which both values for a complex were obtained from the dielectric measurement alone. The association constant of a complex derived by them, however, was much lower than the value obtained by other methods such as infrared absorption spectroscopy. Although their analysis is correct, in principle, such a discrepancy may probably result from the difficulty in estimating polarization owing to the solvent effect within the accuracy of 0.1 cc. If an accurate correction for the solvent effect is possible, the method proposed by them will be applied extensively.

This report describes a somewhat different approach from those above mentioned to the interaction polarization of hydrogen bonded complexes such as benzyl alcohol-dioxane and phenol-dioxane in benzene.

Experimental

All materials used in this work were purified by the standard method[5], and dried carefully. The solvent used throughout this work was benzene which was a very "*good solvent*" compared with other non-polar solvents such as cyclohexane or carbon tetrachloride.

Molecular polarizations were determined by measuring dielectric constants ε, refractive indexes n and specific volumes v of the binary or the ternary solutions. The apparatus for the dielectric measurement is almost the same as that generally used; that is to say, the heterodyne beat method. A very stable oscillator is necessary in order to obtain high accuracy, so the circuits devised by Gouriet[6] are employed without any improvement. The beat frequency of both tank circuits was again coupled with a standard tuning fork by making use of the cathode-ray oscilloscope. The dielectric cell was made of nickel and has three coaxial cylindrical electrodes[7], the outer side of which are connected to the ground. The capacity of the cell is about 100 pF. The cell constant was determined by carefully purified and dried benzene. An oil bath was used as a thermostat to minimize the error due to stray capacity. The temperature was kept at 25±0.05°C throughout this work. The refractive index of the solution was measured by a Pulfrich refractometer, and a sodium lamp was used as the light source. The density of the solution was determined by a Lipkin pycnometer.

The calculation of molecular polarization was performed according to Halvelstadt and Kumler's method. For the ternary systems, the amount of the proton acceptor, that is dioxane, was kept constant and the polarization was extrapolated to zero concentration with regard to the proton donor.

Results

The results of the measurements of ε, n^2 and v for the two ternary systems, i.e., benzyl alcohol-dioxane-benzene and phenol-dioxane-benzene, are summarized in Table I together with those for the corresponding binary systems, i.e., benzyl alcohol-benzene and phenol-benzene. Experimentally determined formulae relating ε, n^2 and v to w, respectively, are also included in Table I for each system, where w represents the weight fraction of the proton donor.

---

[1] See the following reviews. C. A. Coulson, *Research*, **10**, 147 (1957); L. Keller, *Repts. Progr. in Phys.*, **15**, 1 (1952).

[2] J. W. Smith, "Electric Dipole Moments", Butterworths Scientific Publications, London (1955).

[3] J. R. Hulett, J. A. Pegg and L. E. Sutton, *J. Chem. Soc.*, **1955**, 3901.

[4] A. V. Few and J. W. Smith, ibid., **1949**, 2781.

[5] A. Weissberger, et al., "Organic Solvents", Interscience Publishers, New York (1955).

[6] G. G. Gouriet, *Wireless Engineer.*, **72**, 105 (1950).

[7] A. W. Weissberger, et al., "Physical Methods of Organic Chemistry III", Interscience Publishers, New York (1954), p. 2293.

TABLE I. DIELECTRIC CONSTANTS, REFRACTIVE INDEXES AND DENSITIES OF THE TERNARY AND THE BINARY SYSTEMS

$w\times10^2$	ε	n^2	v	
Benzyl alcohol-Dioxane-Benzene				
(The weight percentage of dioxane is 31.26)				
0	2.2593	2.1791	1.0895	
0.26	2.2689	2.1795	1.0893	$\varepsilon=2.2593+3.14w$
0.50	2.2766	2.1800	1.0887	$n^2=2.1791+0.167w$
1.49	2.3106	2.1816	1.0873	$v=1.0895-0.146w$
2.18	2.3353	2.1827	1.0863	
Benzyl alcohol-Benzene				
0	2.2725	2.2427	1.1446	
0.51	2.2878	2.2433	1.1434	$\varepsilon=2.2725+3.10w$
0.94	2.3011	2.2439	1.1429	$n^2=2.2427+0.109w$
2.28	2.3431	2.2453	1.1402	$v=1.1446-0.190w$
2.98	2.3666	2.2460	1.1390	
Phenol-Dioxane-Benzene				
(The weight percentage of dioxane is 41.05)				
0	2.2556	2.1578	1.0729	
0.50	2.2781	2.1591	1.0717	$\varepsilon=2.2556+4.26w$
0.99	2.2986	2.1603	1.0710	$n^2=2.1578+0.251w$
2.33	2.3554	2.1640	1.0688	$v=1.0729-0.160w$
3.69	2.4117	2.1671	1.0667	
Phenol-Benzene				
0	2.2725	2.2427	1.1446	
0.29	2.2813	2.2433	1.1439	$\varepsilon=2.2725+2.82w$
0.52	2.2866	2.2437	1.1434	$n^2=2.2427+0.15w$
0.77	2.2944	2.2441	1.1427	$v=1.1446-0.242w$
1.44	2.3131	2.2450	1.1411	

Polarization values calculated from these experimental data are shown in Table II, where p or P is the specific or the molecular polarization, and r or R the corresponding refraction. The values of dipole moment were evaluated on the assumption that $P_{E+A}=[R_D]$ or $P_{E+A}=1.05$ $[R_D]$ and shown in the same table as μ or μ'.

TABLE II. POLARIZATIONS AND DIPOLE MOMENTS OF THE HYDROGEN BONDED COMPLEXES AND THE FREE PROTON DONORS

	Benzyl alcohol -Dioxane	Benzyl alcohol	Phenol-Dioxane	Phenol
p	0.9039 cc.	0.8674	1.0264	0.8993
r	0.2074 cc.	0.3005	0.3009	0.2931
P	97.7 cc.	93.8	96.6	84.9
R_D	32.1 cc.	32.5	28.3	27.6
μ	1.79 D	1.73	1.84	1.67
μ'	1.76 D	1.70	1.82	1.65

Attention was called especially to the association among the proton donors. For example, when the dipole moment of benzyl alcohol was measured in cyclohexane, the value obtained was 1.55 D or so which was a little smaller than 1.70 D[8] of methanol measured in the vapor phase. This fact seems attributable probably to the association of benzyl alcohol in this solvent. On the other hand, we used benzene as a solvent for benzyl alcohol and could obtain almost the same dipole moment as that of methanol in the vapor phase. Infrared absorption spectroscopy showed that the bridged bands were not perceived at concentrations less than ca. 0.01 mol./l. in carbon tetrachloride. Although the dielectric measurements in such a dilute solution are desirable, the change in the dielectric constants within the range of concentrations where the bridged bands are not observed, is not detected by the present apparatus and technique. But it seems probable that the fraction of solutes capable of existing as free molecules without association is more or less altered from one solvent to another. Although we have not ascertained it, it seems appropriate to use benzene as the dispersing solvent to minimize the effect of association of solutes.

For the ternary systems a few remarks must be added. The dielectric constant of the mixed solvent composed of ca. 0.7 benzene and 0.3 dioxane in weight fraction is about 2.26 compared with 2.27 of bezene. Even such a small change in the dielectric constant of the medium may cause the change in polarization due to the solvent effect. Generally speaking, the following factors are considered to contribute to the solvent effect: (1) dielectric constant of the medium, (2) anisotropy of solvent molecules, (3) polarizability of solute molecule and (4) geometrical shape of the solute molecule. The change in polarization by the first factor was estimated as the order of magnitude of 0.1 cc.[9] Contributions of the other factors are difficult to estimate, but will probably lie within the limit of experimental errors. The experiemntal data for the ternary systems were, therefore, employed without any correction for the solvent effect. Molecular polarization obtained by the usual method of extrapolating to zero concentration contains, however, the contributions of both the free molecules and the molecular complexes. In order to divide the observed value into polarization of the free

---

8) A. A. Maryott and F. Bucklay, *N. B. S. Circular*, **537**, 13 (1953).

9) K. Shogenji, *J. Phys. Soc. Japan*, **12**, 166 (1958).

molecules and that of the molecular complexes, the following procedure was adopted.

Let us consider the equilibrium for the complex formation between molecules A and B. We assume the interaction between A and B to be one to one. The equilibrium constant of this system is

$$K=\frac{x}{(a-x)(b-x)}=\frac{1}{(a-x)(b/x-1)} \qquad (1)$$

where a and b are concentrations of molecular species A and B, respectively, in the initial state and x is that of the molecular complex. A is dioxane and B is benzyl alcohol or phenol in the present work. When b is reduced smaller, x also diminishes, and the ratio $f_x=x/b$, i.e., the fraction of the complex in the system approaches to a definite value,

$$\lim_{b\to 0} f_x=\lim_{b\to 0} x/b=aK/(aK+1) \qquad (2)$$

since x becomes negligible against a in the denominator of Eq. 1. The formation constants are reported to be about 5,000[10] and 9,400[11] for benzyl alcohol-dioxane and phenol-dioxane complexes, respectively, using mol./cc. as the unit of concentration. Hence f_x is calculated to be 0.942 for the former, and 0.976 for the latter. The contribution of the free proton donor to the observed polarization is, therefore, estimated as $93.8\times 0.058=5.4$ in the former, and $84.6\times 0.024=2.0$ in the latter. If the difference between the observed polarization and the above one is divided by the fraction of the complex, then the value for the true polarization of the complex is obtained as 97.9 cc. for benzyl alcohol-dioxane, and 96.9 cc. for phenol-dioxane. These values are almost the same as those without any correction. It can therefore be concluded that there is no need for this correction when the equilibrium constant is comparatively large and, moreover, the nonpolar proton acceptors exist in large quantities.

Discussion

Perturbation of the proton donor by the proton acceptor and vice versa will be relatively small since the energy of hydrogen bonding is generally about 5 kcal./mol. or so. Hence, the deformation of σ-orbitals or even that of lone pair orbitals not participating in the hydrogen bond but existing in its neighborhood, is completely out of the question in the present treatment as generally believed, whereas in the case of the polarizable π-orbitals their deformation is comparatively large even by a small perturbation. It seems probable therefore that the change in the distribution of π-electrons may be induced by the access of lone pair electrons of a proton acceptor within the range of van der Waals radius. Coulson and Sutton[12] already discussed the hyperpolarizability of benzene and pointed out the importance of this effect in the vicinity of an ion or a dipole. The system of benzyl alcohol-dioxane will not need consideration of the hyperpolarizability as already stated. Contrary to this, the system of phenol-dioxane is supposed to receive a comparatively large effect. It will, therefore, be necessary first to consider the polarizability of the π-electrons of phenol due to the lone pair field of the proton acceptor. To estimate this effect, we try at first to determine the simple molecular orbitals of phenol and those of dimethyl ether, the molecular size of which is presumed to be half as great as a dioxane molecule, and then to evaluate the induced polarization of the π-orbitals of phenol. Then a brief discussion on the delocalization due to hydrogen bonding will be given.

Molecular Orbitals of the π-Electrons of Phenol.—Molecular orbitals of π-electrons of phenol were determined by the use of Matsen's parameter[13]. All the notations used in this section are the same as those of Matsen's paper. According to the molecular symmetry the secular determinant of the seventh order was factored into one of the second and one of the fifth order. All the orbitals obtained by solving these secular determinats are shown in Table III. Orbitals belonging to the symmetry group B_1 are the same as those of benzene, whereas those of A_1 receive a modification as shown in this table. An energy and a moment of each molecular orbital are also tabulated. The calculated π-moment is 1.46 D and its direction is directed toward the benzene ring from the

---

[10] N. D. Coggeshall and E. L. Saier, *J. Am. Chem. Soc.*, **73**, 5414 (1951). Measurements were made at room temperature.

[11] H. Tsubomura, *J. Chem. Phys.*, **23**, 2130 (1955). As the values reported were in the range between 9.4 and 9.8 in the unit of mol./l., the lower value of 9.4 was adopted here.

[12] C. A. Coulson and L. E. Sutton, *Trans. Faraday Soc.*, **48**, 106 (1952).

[13] F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).

TABLE III. COEFFICIENTS, ENERGIES AND MOMENTS OF THE π-ORBITALS OF PHENOL

B_1:

M.O.	energy	moment
$\chi_2=\psi_2$	$\alpha+\beta$	10.632 a.u.
$\chi_4=\psi_4$	$\alpha-\beta$	—

A_1: $\chi_i=c_{i1}\varphi_1+c_{i3}\psi_3+c_{i5}\psi_5+c_{i6}\psi_6+c_{i7}\psi_7$

c_{11}	0.601	c_{13}	0.283	c_{15}	0.107
		c_{16}	0.066	c_{17}	0.736
c_{71}	0.786	c_{73}	−0.370	c_{75}	−0.101
		c_{76}	−0.052	c_{77}	−0.481
c_{31}	0.136	c_{33}	0.880	c_{35}	−0.143
		c_{36}	−0.143	c_{37}	−0.427
c_{51}	0.026	c_{53}	0.055	c_{55}	0.973
		c_{56}	−0.093	c_{57}	−0.202
c_{61}	0.012	c_{63}	0.022	c_{65}	0.066
		c_{66}	0.989	c_{67}	−0.121

M.O.	energy	moment
χ_1	$\alpha+2.494\beta$	3.379
χ_7	$\alpha+1.749\beta$	10.090
χ_3	$\alpha+0.722\beta$	8.369
χ_5	$\alpha-1.116\beta$	—
χ_6	$\alpha-2.050\beta$	—

The total π-moment

$$\mu=\mu_1+\mu_7+\mu_2+\mu_3-\mu_c{}^*=0.575\ \text{a.u.}=1.46\ \text{D}$$

* μ_c represents the σ-core moment.

position of the oxygen atom, the positive pole lying at the oxygen nucleus.

Equivalent Orbitals of Dimethyl Ether.—The LCAO SCF MO method developed by Roothaan[14] will give the most reliable results for the electronic structure of a molecule. However, the low symmetry of the molecule of dimethyl ether prevents us from following this procedure. On the other hand, the unique treatment by Pople[15] of some simple molecules with lone pair electrons, such as water or ammonia, seems to express the electronic structures of these molecules quite well, though the results obtained by his method show that the lone pair moment may be overestimated. For example, in the case of water the lone pair moment obtained by Pople's method is about twice as large as that obtained by the LCAO SCF MO method[16]. This defect will be overcome by considering properly the apparent nuclear charge of oxygen as seen later.

Our treatment is similar to that by Pople and the values of the dipole moment used in our calculation are 1.30 D[8] and 0.30 D[2] for an ether molecule and a C–H bond, respectively. For the latter, its direction is assumed to be along the direction of the C–H bond with the negative center at the hydrogen atom. Outer electrons of $2s$ and $2p$ alone were considered explicitly and $1s$ inner electrons of the oxygen atom and the two carbon atoms were treated together with the nucleus as the rigid cores. Thus the nuclear charge of oxygen becomes 6 and that of carbon 1.059 upon the following approximations. For the orbitals of each carbon atom the sp^3 hybridization was a priori assumed. Moreover, to avoid complexity arising from the existence of methyl groups, each methyl group was replaced by a single C–H bond and its charge distribution was assumed to be expressed by point charges located at each nucleus with the distance of 1.09 Å. On these assumptions, the hybridization parameters at the oxygen atom and the coefficients in each bonding orbital were adjusted so as to be reconciled with the observed resultant moment. Such a simplification does not seem to be accompanied by any serious error within the limit of the approximation used here in the determination of wave functions.

TABLE IV. MOLECULAR CONSTANTS AND ATOMIC ORBITALS USED IN THE CALCULATION OF EQUIVALENT ORBITALS OF DIMETHYL ETHER, AND THEIR CALCULATED RESULTS

Molecular constants: Bond distance O-C 1.43Å; Bond angle 111°

Atomic orbitals:

$$\phi(2s)=(Z^5/3\pi)^{1/2}\ r\exp(-Zr)$$
$$\phi(2p)=(Z^5/\pi)^{1/2}\ r\cos\theta\ \exp(-Zr)$$

where $Z=2.275$ for the oxygen atom
$Z=1.625$ for the carbon atom

Equivalent orbitals

$$\chi(l_1)=\cos\varepsilon_l\phi(O_{2s})+\sin\varepsilon_l\phi(O_{2p_1})$$
$$\chi(l_2)=\cos\varepsilon_l\phi(O_{2s})+\sin\varepsilon_l\phi(O_{2p_2})$$
$$\chi(b_1)=\lambda\{\cos\varepsilon_b\phi(O_{2s})+\sin\varepsilon_b\phi(O_{2p_1})\}+\mu\psi(c_1)$$
$$\chi(b_2)=\lambda\{\cos\varepsilon_b\phi(O_{2s})+\sin\varepsilon_b\phi(O_{2p_2})\}+\mu\psi(c_2)$$

where

$$\psi(c_i)=1/2\{\phi(c_{i2s})+\sqrt{3}\,\phi(c_{i2p})\}$$

Acceptable values for the parameters:

$\lambda=0.665$ $\cos\varepsilon_b=0.367$ $\cos\varepsilon_l=0.508$
$\mu=0.475$ $\sin\varepsilon_b=0.929$ $\sin\varepsilon_l=0.860$
$\beta=110°$ $\gamma=108°$

The calculated total moment:

$$M=M_b+M_l+M_m{}^*=-8.89+2.80+7.43=1.34\text{D}$$

* M_m represents the moment of methyl group.

---

[14] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[15] A. B. F. Duncan and J. A. Pople, *Trans. Faraday Soc.*, **49**, 218 (1953). See also, *Proc. Roy. Soc.*, **A202**, 323 (1950).

[16] F. O. Ellison and H. Shull, *J. Chem. Phys.*, **23**, 2348 (1955); L. Burnelle and C. A. Coulson, *Trans. Faraday Soc.*, **53**, 403 (1957).; W. C. Hamilton, *J. Chem. Phys.*, **26**, 345 (1957).

The molecular constants and the atomic orbitals used in evaluating the necessary integrals are tabulated in Table IV together with the final results thus obtained, where the symbols used are the same as those employed by Pople, et al.$^{15)}$ Necessary overlap integrals and dipole moment integrals are all found in the tables or the formulae given by Mulliken, et al.$^{17)}$

The distinction between the present results shown in Table IV and those by Duncan and Pople lies in the hybridization parameters at the oxygen atom. As pointed out by Pople, this discrepancy originates from the small overlap integral between $\psi(c_1)$ and $\psi(c_2)$ because of the comparatively long distance between the two carbon atoms of an ether molecule, and the larger Z-value of Slater's atomic orbital of carbon.

The Induced Polarization of the π-Electrons of Phenol.—The induced polarization due to the lone pair field was easily calculated by means of the first order perturbation theory based on the equivalent and the molecular orbitals already given. The geometrical configuration of the complex between a proton donating molecule and an accepting one is not clear enough for the present case. However, it is well known that in ice a tetrahedral arrangement prevails and its arrangement has the large electrostatic energy$^{18)}$ and the large overlap integral which is concerned largely with the delocalization energy$^{19)}$. It seems, therefore, probable to assume that the three atoms, O–H···O lie on a straight line, though the thermal motion will, in fact, induce some deviation. Moreover the distance between the oxygen atom of phenol and that of ether is not measured in solution. But according to the relationship proposed by Nakamoto, Margoshes and Rundle$^{20)}$ between the atomic distance and the shift of the infrared absorption, the distance between the two oxygen atoms was estimated as being about 2.9 Å which is larger than that of ice. For the purpose of comparison, the perturbed wave functions of phenol were calculated in the case of three O···O internuclear distances of 2.7, 2.8 and 2.9 Å, respectively. The following two approximations were employed for this calculation. Firstly, only the interaction between the lone pair electrons of ether and the π-electrons of the oxygen atom of phenol was considered, and the interaction of the lone pair electrons with other π-electrons in the benzene ring of phenol was neglected. Molecular integrals required in this computation were obtained by making use of the formulae described in Roothaan's paper$^{21)}$. Secondly, an apparent nuclear charge of the oxygen atom of ether was determined by the point charge approximation. The apparent nuclear charges obtained at the three interatomic distances are as follows:

O···O distance, R	2.7	2.8	2.9
Z'	2.200	2.196	2.192

These large values of the apparent charges look curious, and may probably be due, as already stated, to the effect of overestimation of lone pair moments. It is believed that such a defect will be excluded if the same treatment as that of water by Ellison and Shull$^{16)}$ is carried out. The extent of the interaction between the apparent nuclear charge of the oxygen atom of ether and the π-electrons of the oxygen atom of phenol was also estimated by Roothaan's formulae as before.

Finally we formulate the calculating procedure for the perturbed wave functions of phenol. The perturbation H' is given by

$$H'=2\int\frac{\chi(l_i)\chi(l_i)}{r}\mathrm{d}\tau-\frac{Z'}{r'}$$

The first term represents a coulombic potential due to the lone pair electrons of ether in the orbital, χ (l_i) which participates in the hydrogen bond, and the second is that due to the apparent nuclear charge Z' of the oxygen atom of ether. The first-order perturbed wave functions of phenol will then be expressed as

$$\chi_i^{(1)}=\chi_i+\sum_{j\neq i}\frac{H'_{ij}}{E_i-E_j}\chi_j,\quad\begin{pmatrix}i=1,7,3\\ j=1,7,3,5,6\end{pmatrix}$$

Values of the π-moments calculated from these orbitals are tabulated in Table V at each internuclear separation.

This table shows that the polarization of the π-orbitals arising from the lone pair field is the order of a magnitude of 0.1 D compared with the value of about 0.2 D given by Hampson and Weissberger$^{22)}$, who

---

17) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, ibid., **17**, 1248 (1949).

18) W. G. Schneider, ibid., **23**, 26 (1955); W. S. Fyfe, ibid., **21**, 2 (1953).

19) H. Tsubomura, This Bulletin, **27**, 445 (1954).

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

21) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

22) G. C. Hampson and A. Weissberger, *J. Chem. Soc.*, **1936**, 393.

TABLE V. MOMENTS OF THE PERTURBED π-ORBITALS OF PHENOL

At 2.7 Å $\mu=\mu_1+\mu_7+\mu_2+\mu_3+\mu_c$

$=3.704+9.946+10.632+8.250-31.896$

$=0.637$ a.u. $=1.62$ D

At 2.8 Å $\mu=3.647+9.970+10.632+8.277-31.896$

$=0.630$ a.u. $=1.60$ D

At 2.9 Å $\mu=3.615+9.980+10.632+8.92-31.896$

$=0.624$ a.u. $=1.58$ D

The increment of π-moment, $\Delta\mu_\pi$

R in Å	2.7	2.8	2.9
μ in D	0.16	0.14	0.12

estimated the induced moment of the π-electrons due to a polar substituent group by making use of the average polarizability of the molecule. The induced moment decreases almost linearly with the increase of the interatomic distance from 2.7 to 2.9 Å. When we extrapolate it to the distance of 3.5 Å which corresponds to the sum of the van der Waals radii of both the oxygen atom of ether and the O–H of phenol, then the value obtained will be zero. These results show quite well that the theoretical treatment already described is reasonable. But it must be noted that the numerical values thus obtained are those of the interacting molecules which are placed mutually in the fixed configuration.

The Increment of the Dipole Moment Arising from Delocalization.—As is well known, the structures largely contributing to hydrogen bonding are considered as the following three:

[I] O–H O
[II] O^-H^+O
[III] $O^-H–O^+$

If we suppose that the ratio of the weights of structures I and II is of the same as that in a free state, then the increase of the dipole moment due to hydrogen bonding will be attributable only to the participation of the structure III. Strictly speaking, the transitional structures also must be taken into account. But it is difficult to treat them without making more precise quantum mechanical calculations. Neglecting these transitional structures, we can easily estimate the weight of the structure III from the additional moment observed.

One obstacle remains as yet. That is the direction of the resultant moment of the molecule in the free state. However, in view of the result[16] that the O–H bond moment in a water molecule is not so large as hitherto believed, it is assumed that only the lone pair dipoles make a contribution to the molecular dipole moment of benzyl alcohol. In the case of phenol, the direction of the resultant moment, as usually done, is determined by vectorial combination of dipole moments of both phenol itself and some of *p*-substituted phenols. The result[3] obtained shows that the direction of the resultant vector of phenol makes an obtuse angle of 91° with the O–C bond.

Once the direction of the resultant moment in the free state for benzyl alcohol and phenol, respectively, and the value of the induced moment of phenol in the bonded state are determined, then it is possible to calculate the increment of dipole moment, $\Delta\mu_D$ only due to delocalization.

Firstly, let us discuss the system of benzyl alcohol-dioxane. The bond angle about the oxygen atom of benzyl alcohol was taken to be 110°. Then, the value of $\Delta\mu_D$ obtained from the method mentioned above amounts to 0.10 D. When the interatomic distance between the two oxygen atoms is taken to be 3.0 Å from the shift of the infrared absorption[10], we obtain 14.41 D as the moment referring to the structure III, and its weight is estimated as about 0.7%.

Next, let us consider the system of phenol-dioxane. As the sp^2 hybridization was assumed for the orbitals of the oxygen atom, the bond angle about it was taken to be 120°. The interatomic distance between the two oxygen atoms was estimated as 2.9 Å as already stated. If the value of 0.12 D is used for the induced polarization of the π-electrons as already tabulated, $\Delta\mu_D$ is calculated as 0.21 D. This value corresponds to 1.5% as the weight of the structure III. Although it is qualitatively understood from the viewpoint of acidity that the contribution of the structure III in the latter system is about twice as large as that in the former, further discussion on this point will be given in the forthcoming report together with other data.

Summary

The dielectric measurements for the system of benzyl alcohol-dioxane and that of phenol-dioxane, respectively, were carried out by using benzene as the solvent.

The induced polarization of the π-electrons in the latter system was evaluated based on some assumptions. From these,

the additional moments due to delocalization were estimated and the weights of the structure III were evaluated for both systems.

The authors wish to express their thanks to Professor S. Kawaguchi for his kind inspection and revision of this manuscript, and also Messrs. N. Mataga and K. Nishimoto for their helpful discussions. The cost of this work has been partly defrayed by a Grant from the Ministry of Education.

Institute of Polytechnics
Osaka City University
Kita-ku, Osaka