Organic Semiconductors with High Conductivity II. Structural Aspect of Violanthrene-Iodine Complex

By Hideo AKAMATU, Yoshio MATSUNAGA and Haruo KURODA

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Introduction

In the preceding paper[1], we have presented that polycyclic aromatic hydrocarbons form solid molecular complexes with bromine or iodine, and these complexes behave as typical semiconductors with high conductivity of 10^{0}—10^{-3} ohm^{-1}. cm^{-1} at room temperature and low activation energy for conduction, the energy gap of 0.1–0.2 eV. It has been suggested that the high conductivity is due to an appropriate electronic structure which arises from the formation of the molecular additive compounds. To throw light upon the mechanism of the electrical conduction in these organic materials, it should be most interesting to make clear the structure of these molecular complexes. In the present paper, the structural aspect of the violanthrene-iodine system is presented.

Violanthrene-iodine complex is the most stable among the complexes between polycyclic aromatic hydrocarbons and halogens so far as is known. The electrical resistivity varies as the composition varies, and has the minimum value at the composition in which the mole ratio of iodine to violanthrene (V) is 2, where the resistivity at room temperature is about 40 ohm. cm with the thermal energy gap of 0.15 eV.

The magnetic susceptibility-composition curve[2] shows a great discrepancy from the additive law, and has also the minimum value (depression of diamagnetism) at the same composition, where the discrepancy exceeds 35 per cent. Both these facts suggest the existence of molecular complex consisting of one molecule of violanthrene and two of iodine. On the other hand, a preliminary examination by X-ray revealed an amorphous pattern, while most of the other complexes showed sharp crystalline patterns.

In this paper, the thermodynamical study on the equilibrium of violanthrene-iodine system as well as the full examinations by X-ray are presented.

Preparation of the Complex and Isotherm of Violanthrene-Iodine System

The preparation of the complexes has been described in the previous papers. In the present case, however, with the purpose of studying the isothermal equilibrium between violanthrene and iodine, the following method was applied to the preparation of complexes having varied compositions. The crystalline powder of violanthrene of known quantity was treated with carbon tetrachloride solution of iodine for more than three days. After the equilibrium has been reached, the precipitated complex was filtered through glass wool and the concentration of iodine in the filtrate was determined by titration with 0.025 N aqueous solution of sodium thiosulfate. The composition of the complex obtained was estimated from the difference in concentration of iodine between the initial and the final solution.

Two isotherms have been obtained; one is at the room temperature 27 ± 1°C, and the other is at the temperature of refrigerated chamber -3 ± 2°C. The relation between the equilibrium

1) H. Akamatu, H. Inokuchi and Y. Matsunaga, This Bulletin, **29**, 213 (1956).
2) Y. Matsunaga, ibid, **28**, 475 (1955).

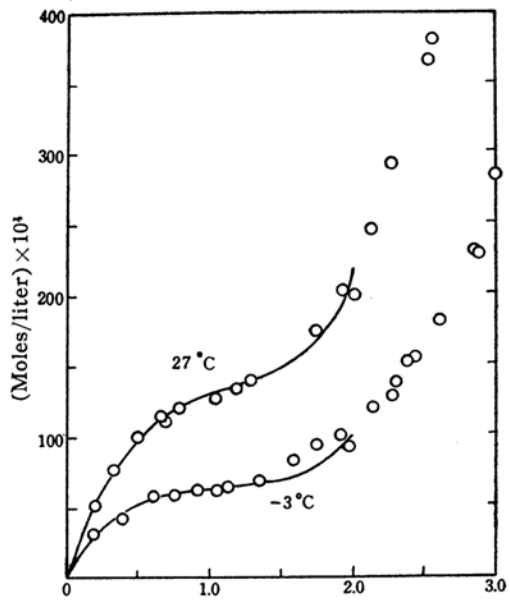

Fig. 1. Equilibrium concentration of iodine in carbon tetrachloride solution plotted against composition of the complex.

concentration of iodine in the carbon tetrachloride solution and in the complex is shown in Fig. 1.

Equilibrium in Violanthrene-Iodine System

Fig. 1 suggests that the observed isotherms are the ones near a boundary of the univariant and bivariant phases and just above the critical temperature, below which two solid phases should be separated, one has the ideal composition of $V \cdot 2I_2$ and the other is V.

Such an isotherm has been discussed by a few authors. Anderson[3] discussed the conditions of equilibrium of non-stoichiometric chemical compounds. Rees[4] derived the pressure-temperature-composition relations for two-component interstitial solid solutions. His theory is applicable to any non-stoichiometric system in which one component is volatile. Both theories are applicable to the present case. However, referring the results of density measurements described in the later section, Rees' model is more conveniently applicable to our case.

The problem is to derive the pressure-temperature-composition relation in a system composed of molecules A(violanthrene) and B (iodine) up to composition A_mB_n where m and n are small integers, and so delineate a boundary of the univariant and the bivariant phase. The fundamental assumptions are as follows.

The solvent lattice of A molecules is referred to as the parent lattice, and the solute component B is in equilibrium with molecules of B in the vapor phase. B molecules occupy interstitial sites in the parent structure*. Several kinds of site are assumed; they are distinguished from each other by the difference in the amount of energy which is gained by a B molecule against free molecular state when it occupies one kind of site. These energies are denoted as E^a, E^b *etc.* for the *a*th, *b*th *etc.* kind of site, respectively.

The interaction energies per pairs of B molecules in each kind of site are considered, and denoted as E^{aa}, E^{bb} *etc.* Furthermore, it is assumed that the number of the sites of the *i*th kind accessible for occupation by B molecule depends on the number of sites of the $(i-1)$th kind already occupied by B molecules. Let N stand for the total number of sites of the *a*th kind, N^a, N^b, N^c *etc.* for the numbers of sites of the *a*th, *b*th, *c*th *etc.* kinds occupied at equilibrium, and α, β *etc.* for the number of sites of the *b*th, *c*th *etc.* kind created for one of the *a*th, *b*th *etc.* kind occupied by a B molecule respectively. The contribution of the parent lattice of A molecules to the total partition function of the crystal is assumed to be independent of the contents of B molecules, so that it is concerned only with the factor representing the contribution of the added B molecules; then the extra configurational grand partition function is expressed as,

$$\begin{aligned}\Theta(T,\ \lambda^a,\ \lambda^b\cdots\cdots N^a,\ N^b\cdots\cdots) &= \sum_a\sum_b\cdots\cdots[\lambda^a\kappa^a(T)]^{N^a}[\lambda^b\kappa^b(T)]^{N^b}\cdots\cdots \\ &\times \frac{N!}{N^a!\ (N-N^a)!}\ \frac{(\alpha N^a)!}{N^b!\ (\alpha N^a-N^b)!}\cdots\cdots \\ &\times\exp\left[\left\{N^aE^a+N^bE^b\cdots\cdots+\frac{(N^a)^2}{N}E^{aa}\right.\right. \\ &\left.\left.+\frac{(N^b)^2}{\alpha N^a}E^{bb}\cdots\cdots\right\}\Big/kT\right] \qquad (1)\end{aligned}$$

where λ^a, $\lambda^b\cdots\cdots$ are the absolute activities of B molecules in sites of the *a*th, *b*th *etc.*, and $\kappa^a(T)$, $\kappa^b(T)$ *etc.* are the additional factors in the partition function per molecules for the contribution of B molecules

3) J. S. Anderson, *Proc. Roy. Soc.*, **A185**, 69 (1946).
4) A. L. G. Rees, *Trans. Faraday Soc.*, **50**, 335 (1954).

* In the present case, interstitial sites are assumed to arise from violanthrene lattice being made expansion. See the later section.

in the ath, bth *etc.* sites to the vibrational modes of the crystal. For the equilibrium state where $\partial\Theta/\partial N^a=0$, $\partial\Theta/\partial N^b=0$,

$$\lambda^a=\frac{1}{\kappa^a(T)}\frac{N^a}{(N-N^a)}\left\{1-\left(\frac{N^b}{\alpha N^a}\right)\right\}^{\alpha}\times\exp\left[\left\{-E^a-\frac{2N^a}{N}E^{aa}+\frac{1}{\alpha}\left(\frac{N^b}{N^a}\right)^2E^{bb}\right\}\Big/kT\right] \quad (2)$$

$$\lambda^b=\frac{1}{\kappa^b(T)}\frac{N^b}{(\alpha N^a-N^b)}\left\{1-\left(\frac{N^c}{\beta N^b}\right)\right\}^{\beta}\times\exp\left[\left\{-E^b-\frac{2N^b}{\alpha N^a}E^{bb}+\frac{1}{\beta}\left(\frac{N^c}{N^b}\right)^2E^{cc}\right\}\Big/kT\right] \quad (3)$$

etc.

In applying the theory to our results, we assume that the composition of $\overline{V\cdot 2I_2}$ (idealized formula) corresponds to that of the interstitial solid solution where the ath kind site is saturated and the other sites are completely empty. This means that the violanthrene lattice made of N_0 molecules has $2N_0$ sites of the ath kind for iodine molecules. In reality, however, n molecules of iodine occupy a part of $2N_0$ sites of the ath kind and some numbers of molecules occupy the sites of the bth, cth *etc.* kind. We have no foundation to assume the numbers of sites of the bth, cth *etc.* kind. However, in the range of composition where the total mole ratio of iodine to V is not greater than 2, it may not be far from the truth if we presume that the number of iodine molecules occupying the other sites is far less than the number of molecules occupying the ath kind sites. This leads to the assumption of $N^b/\alpha N^a\ll 1$ in eq. (2).

Introducing $\theta=n/2N_0$ instead of N^a/N in eq. (2), we obtain

$$\lambda(\theta)=\frac{1}{\kappa^a(T)}\frac{\theta}{1-\theta}\times\exp[-\{E^a+2\theta E^{aa}\}/kT] \quad (4)$$

for the activity of the iodine molecule in the ath site.

In the isotherm of Fig. 1, at the composition of mole ratio being 2, θ is not equal to unity, but less than unity for the reason mentioned above. Let θ be $\delta<1$ at the composition where total mole ratio is 2, then the relative activity at any composition can be expressed as

$$\frac{\lambda(\theta)}{\lambda(\delta)}=\frac{\theta}{1-\theta}\frac{1-\delta}{\delta}\times\exp[4(\delta-\theta)T_c^a/T] \quad (5)$$

where $T_c^a=-E^{aa}/2k$, which is the critical temperature above which two phase region should disappear.

Eq. (5) can be applied to the experimental data to delineate the isotherm. For this purpose, we assume $\lambda(\theta)/\lambda(\delta)\simeq c(\theta)/c(\delta)$, where c is the concentration of iodine in carbon tetrachloride at the equilibrium. We further assumed that $\delta=0.87$, $c(\delta)=0.0105$ at -3°C; $\delta=0.84$, $c(\delta)=0.0220$ at 27°C and $T_c^a=260$°K. These values have been estimated to be as good as possible to be fitted to the observed values. The theoretical isotherms are shown by the curves in Fig. 1.

The agreement between the experimetal results and the theoretical calculations is satisfactory when we realize that the theory contains many approximations. This leads to the conclusion that " violanthrene-iodine complex " at room temperature is a solid solution between violanthrene and a non-stoichiometric molecular compound, which has the composition of $\overline{V\cdot 2I_2}$ as the idealized formula and should be separated as a solid phase below the critical temperature of 260°K.

From the isotherms of 27°C and -3°C, the heat of dissociation of the complex can be calculated by Clapeyron's relation. This value is 3.8 kcal. per one mole of iodine for the complex having composition of mole ratio being 1 (where assumed $\theta=0.5$). The heat of dissociation depends on the composition in such a manner as expressed as $E^a+2\theta E^{aa}$. Therefore, this value corresponds to the mean heat of dissociation in the composition range from $\theta=0$ to $\theta=1$, where the interstitial sites of the ath kind have been completely occupied by iodine molecules. Alternatively one may say that the integral heat of dissociation of the complex having the composition of $\overline{V\cdot 2I_2}$ is 3.8 kcal. per mole of iodine. Then,

$$2I_2(\text{in } CCl_4)+C_{34}H_{18}(\text{solid})=C_{34}H_{18}\cdot 2I_2(\text{solid})+7.6\,\text{kcal.} \quad (6),$$

and, since the heat of dissolution of iodine in carbon tetrachloride is 5.8 kcal. per mole of iodine[5],

$$2I_2(\text{solid})+C_{34}H_{18}(\text{solid})=C_{34}H_{18}\cdot 2I_2(\text{solid})-4.0\,\text{kcal.} \quad (7).$$

X-Ray Studies on Violanthrene-Iodine Complex

X-Ray studies were made by Norelco

5) K. Hartley and H. A. Skinner, ibid, **46**, 621 (1950).

diffractometer with Ni-filtered Cu-K_α radiation. Typical diffractometer records of complexes having varied compositions are shown in Fig. 2.

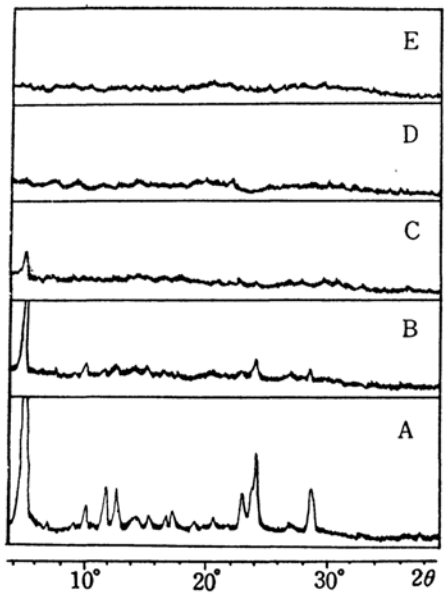

Fig. 2. Diffractometer record of violanthrene-iodine complex.
Mole ratio of iodine to violanthrene: A 0.12, B 0.40, C 1.48, D 2.27, E 4.69.

Sharp crystalline peaks are seen in the diffraction patterns of complexes which have a low content of iodine. These peaks coincide with the diffraction peaks of violanthrene crystal itself, and decrease their intensities as the mole ratio of iodine to V is increased. In this process, no change is found in either positions or the relative intensities of peaks, and no appearence of any other crystalline peaks can be found. These facts show the presence of non-reacted violanthrene crystallites in the specimen, and they also show that the main part which has combined with iodine becomes amorphous. As for the specimens, in which the mole ratio is greater than 2, crystalline peaks disappear completely.

The preliminary examination of violanthrene-bromine complex has also shown an amorphous pattern. However, both these cases seem to belong to the special cases. The complexes between polycyclic aromatic hydrocarbons and halogens are not necessarily amorphous. The complex of perylene or pyranthrene shows a clearly crystalline pattern. For instance, in the case of perylene-iodine complex two kinds of crystalline pattern are found in the same specimen; one is probably due to molecular compound between one molecule of perylene and one of iodine, and the other to one molecule of perylene and two of iodine. This fact makes the analysis of the diffraction pattern of this complex complicated. On the other hand, the violanthrene-iodine system gives a completely amorphous pattern and is suited for the application of the radial-distribution analysis. For this purpose, it is desired that the specimen will have enough iodine content to give a completely amorphous structure, but not such an excess in amount as to separate iodine crystals. An intensity distribution curve of scattered X-rays by the complex is shown in Fig. 3.

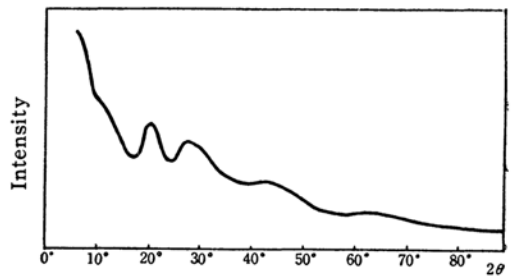

Fig. 3. Intensity distribution curve of violanthrene-iodine complex (1 : 4.9)

Radial-Distribution Analysis

The intensity, I, of scattering in the direction of 2θ (scattering angle) is given by the theory[6] as

$$I=\sum_i f_i^2+\sum_i\sum_j f_i f_j \frac{\sin sr_{ij}}{sr_{ij}}, \qquad s=\frac{4\pi \sin\theta}{\lambda} \tag{8}$$

where r_{ij} is the distance between the i-th and j-th atoms, f is the atomic scattering factor, and λ the wave length of the X-ray. In the case where the specimen contains more than one kind of atom, the general formula for the intensity of scattering can be written[7] as,

$$I=N\sum_p f_p^2+\sum_m^{m\neq n}\sum_n f_m f_n \cdot \frac{\sin sr_{mn}}{sr_{mn}} \tag{9}$$

where m, n,…… denote the kinds of atom constituting an appropriate unit of structure of which the entire specimen is

6) P. Debye, *Ann. Physik*, **46**, 809 (1915).
7) B. E. Warren, H. Krutter and O. Morningstar, *J. Am. Ceram. Soc.*, **19**, 202 (1936); H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures" John Wiley and Sons, Inc , 1954, p. 590.

regarded as being composed, and N is the number of such units.

Let the average numbers of atoms lying at $r \sim r+dr$ from the reference atom be a_m, a_n, *etc.*, and let the atomic density function $\rho_m(r)$ which is defined by eq. (10) be used; then eq. (9) can be expressed as eq. (11),

$$4\pi r^2 \rho_m(r)dr = \sum_m a_m f_m \tag{10}$$

$$I = N\left[\sum_m f_m^2 + \sum_m f_m \int 4\pi r^2 \rho_m(r) \frac{\sin sr}{sr} dr\right] \tag{11}$$

The following approximations are introduced,

$$f_m = K_m f_e \tag{12}$$

$$\rho_m(r) = f_e g_m(r) \tag{13},$$

where f_e is the scattering factor of a single electron, K_m is the effective number of electrons per atom of type m, and $g_m(r)$ is the electron-density function. Using those approximations, eq. (11) is expressed as

$$I = N\left[\sum_m f_m^2 + 4\pi f_e^2 \int \sum_m K_m g_m(r) r^2 \frac{\sin sr}{sr} dr\right] \tag{14}$$

Finally, introducing g_0, the average density of electrons in the specimen, eq. (14) can be transformed to eq. (15) by means of the Fourier integral theorem.

$$4\pi r^2 \sum_m K_m \cdot g_m(r) = 4\pi r^2 \cdot g_0 \cdot \sum_m K_m + \frac{2r}{\pi} \int_0^\infty s \cdot i(s) \cdot \sin sr \cdot ds \tag{15}$$

in which

$$i(s) = \left(\frac{I}{N} - \sum_m f_m^2\right) / f_e^2 \tag{16}$$

From the observed intensity curve of scattering, the radial-distribution function, $4\pi r^2 \sum_m K_m g_m(r)$, can be obtained by eq, (15).

The approximation of eq. (12) is possible only in the case where the specimen is made of atoms whose atomic numbers are near to each other. In the cases of iodine and carbon, their atomic numbers are far from each other. However, since the atomic number of iodine is much larger than that of carbon, in such a composition as that of one molecule of violanthrene and five of iodine, it has been revealed that the intensity of coherent scattering is determined mainly from the contribution of iodine atoms. In such a case, the above approximation is again allowed.

We assume the structure unit as $I \cdot (C_{34}H_{18})_{0.1}$ for the complex made of one molecule of violanthrene and five molecules of iodine, and the effective numbers of electrons being one for hydrogen, 6 for carbon and 53 for iodine atom. From the observed density, $d=3.03$, $g_0 = 0.602d \times \sum_m K_m / \sum_m M_m$, where M_m is the atomic weight, is given as 0.809 electrons per Å^3.

The integral in eq. (15) is replaced by the equivalent summation,

$$\int_0^\infty s \cdot i(s) \cdot \sin sr \cdot ds = \sum_{s=0}^{s=s\max} s \cdot i(s) \cdot \sin sr \cdot \Delta s \tag{17}$$

and the computation has been made, giving $\Delta S = 0.04\pi$, for every interval of 0.2 Å for r. The radial-distribution function obtained is shown in Fig. 4.

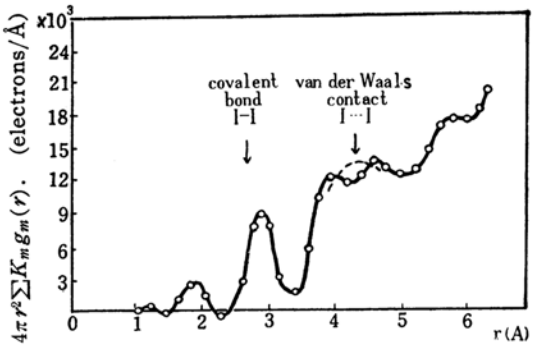

Fig. 4. Radial distribution curve of violanthrene-iodine complex (mole ratio 1 : 4.9).

The radial-distribution curve has a remarkable maximum at $r=2.85$ Å. This peak is clearly resolved and encloses an area of 3500 electrons. If this peak is due to the coherent scattering between carbon atoms in a violanthrene molecule, the area will be $(34/10) \times 3 \times 6^2 = 368$ electrons, since the statistical average number of carbon atoms surrounding a reference carbon atom at the distance of 2~3 Å is 3. This can not explain the above large area of the peak. On the other hand, I-I distance in an iodine molecule is 2.667 Å from optical data, and 2.70 Å from the analysis of crystal structure. If we assume that the peak is due to the interaction between iodine atoms in an iodine molecule, the area will be $1 \times 53^2 = 2800$ electrons. The summation of the effects due to iodine molecule and violanthrene molecule can almost explain the area under the peak. However, it is clear that the

most part of the effect arises from the contribution of the iodine molecule. From this, it is revealed that most iodine molecules do not dissociate into ions, but I-I distance is extended to 2.85 Å.

In the region of $r=4\sim5$ Å, two maxima are seen. They are rather poorly resolved. In eq. (17), the upper limit, ∞, of the integral is replaced by a finite value, s. This procedure leads to the result of the so-called termination error[8]. In our case, the termination effect due to the major peak at $r=2.85$ Å will result in the appearance of subsidiary maxima at $r=1$, 1.8, 3.7 and 4.5 Å, and minima at $r=1.5$ and 4.2 Å. In Fig. 4, two small maxima at 1~2 Å may be due to this termination error. Therefore, the similar effect is also presumed in the region of 4~5 Å. The true distribution curve seems to be shown by a dotted line in Fig. 4. The maximum, ranging from 3.5 to 5.5 Å, encloses an area of about 16500 electrons.

In a violanthrene molecule, the average number of carbon atoms surrounding a reference atom at the distance of 3.5~5.5 Å is not more than 5. It is clear that the observed area can not be explained by the interaction between these carbon atoms. The distance of 3.5~5.5 Å corresponds to the distance between iodine atoms which make van der Waals contact with each other. In iodine crystal, from a reference atom there are 2 atoms at 3.6 Å, 8 at 4.4 Å, 2 at 4.8 Å, and 1 at 5.1 Å, i.e., 13 atoms at the distance of this range. If the maximum arises due to the interaction between these iodine atoms, the area should be $13\times53^2=36400$ electrons, which is much larger than the observed area. Therefore, the observed area is not explained by the arrangement of iodine molecules as that in iodine crystal. It appears that an atom should be surrounded by $5\sim6(=16500/53^2)$ atoms. This suggests the presence of small groups of iodine molecules presumably in two dimensional arrangement.

Density of Violanthrene-Iodine Complex

The density measurement was made with a pycnometer. Carbon tetrachloride solution of iodine which is in equilibrium with complex was used as the liquid medium. The results are shown in Fig. 5, where specific volumes of complexes are plotted against compositions. It has been found that the specific volume of a complex is larger than the sum of the specific volumes of its constituents, in the region up to the mole ratio of 2.5. Beyond this mole ratio, the volume becomes additive. This result suggests that, at an early stage of the complex formation, in the range of low iodine content, violanthrene molecular lattice is expanded and the structure with vacant space is produced. As iodine content increases, the vacancies are gradually occupied by iodine molecules and filled up at the concentration where the total mole ratio becomes 2.5. This is clearly seen in the change of partial molal volume of iodine in this system.

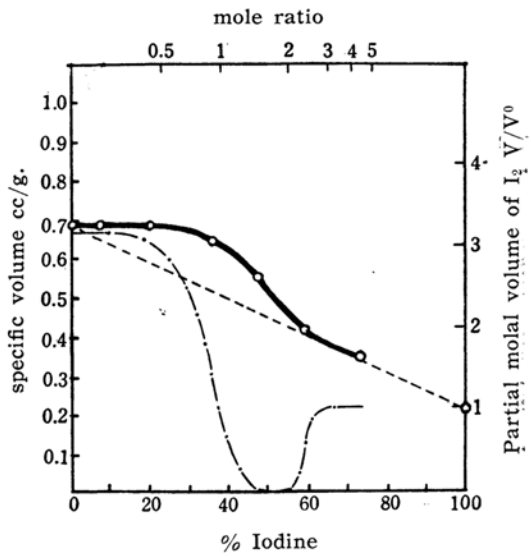

Fig. 5. Specific volume of voilanthrene-iodine system ——, and partial molal volume of iodine in the same system —·—.

The analysis of crystal structure has not yet been made for violanthrene. However, the crystal structures of many kinds of polycyclic aromatic hydrocarbon have been studied by Robertson[9]. The analogy suggests that (001) plane will be the cleavage plane in violanthrene lattice as in other crystals of polycyclic hydrocarbons. If it is so, it will be most facile for iodine molecules to penetrate into interstices between (001) planes. This will lead to the expansion of the crystal in the c-axis direction. However, as mentioned in the preceding section, there is no sign of any preferential change of crystal structure in the complex formation, but the whole structure becomes amorphous. Therefore,

8) W. L. Bragg and J. West, *Phil. Mag.*, **10**, 823 (1930).

9) J. M. Robertson, "Organic Crystals and Molecules", Cornell Univ. Press., Ithaca, N. Y., 1953, p. 183.

it may be concluded that iodine molecules do not penetrate into interstices between the preferential crystal plane, but wedge themselves directly between the molecules of violanthrene.

The molecular volume of violanthrene is about five times as large as that of iodine, and the surface of a violanthrene molecule can be occupied by 5~6 iodine molecules. Therefore, as the result of penetration of an iodine molecule between two neighboring violanthrene molecules, a large vacant space is produced. It is noteworthy that the vacancies are filled up by iodine molecules at the composition where the total mole ratio is 2.5, which is a larger value than the composition corresponding to $\overline{V \cdot 2I_2}$. From this it is most plausible to assume that the complex, having the composition of $\overline{V \cdot 2I_2}$, has the structure in which 4 iodine molecules are sandwiched between two neighboring molecules of violanthrene.

Such a model is consistent with the result of the radial-distribution analysis which indicates that an iodine atom is surrounded by statistically 5~6 iodine atoms in van der Waals contact. It is also not inconsistent with the assumption which has been made in the thermodynamical treatment. What we called the *a*th site before can be made to correspond to the site which can be occupied by 4 molecules of iodine between two neighboring violanthrene molecules.

Summary and Discussion

From the thermodynamical consideration on the isotherm of the violanthrene-iodine system, it was revealed that the system can be seen an interstitial solid solution. Up to the point where the mole ratio is 2, the solid solution is the one between violanthrene and a molecular compound. The latter has no stoichiometric composition, but consists of approximately one violanthrene molecule and two iodine molecules, and can be written as $\overline{V \cdot 2I_2}$ in the idealized formula. Beyond the above mole ratio, the solid solution is the one presumably between $V \cdot 2I_2$ and iodine. The radial distribution analysis of X-ray diffraction also supports the entity of the molecular complex $\overline{V \cdot 2I_2}$.

The heat of formation in eq. (6) or eq. (7) is a roughly estimated value. There is a great deal of information on the heat of formation of the molecular compounds of iodine. For instance, the heat of formation of molecular compound between pyridine and iodine dissolved in pyridine was presumed to be 7.95 kcal[5]. In eq. (6), if we consider the heat of dissolution of violanthrene which is presumably a larger one, the heat of complex formation between iodine and violanthrene molecules should have a much larger value than 7.6 kcal.

The heat of formation, in eq. (7), among the solid phases is endothermic. However, a large amount in entropy change will be expected and it will cover the heat of formation to gain the free energy for complex formation. In reality, when violanthrene crystalline powder is brought into contact with iodine the solid complex is formed spontaneously.

From the radial-distribution analysis, it was revealed that, after the complex formation, the interatomic distance of an iodine molecule is extended to 2.85 Å from 2.67 Å of normal iodine molecule. G. Dallinga[10] reported that in pyridine solution of iodine the I-I distance is increased to 2.90 Å. This value is comparable to our case. If we assume the intermolecular charge-transfer force for the complex formation, an electron will be transferred from violanthrene to iodine molecule, getting into the anti-bonding orbital. This will lead to an increase in the I-I distance according to the degree of contribution of the dative structure $\phi(V^+ - I_2^-)$. However, we can not get any single solution for the ionic character of iodine molecule from its interatomic distance alone.

It was concluded from the density measurement, that the molecular complex of $\overline{V \cdot 2I_2}$ has the structure in which iodine molecules are sandwiched between two neighboring violanthrene molecules. If this is true, such a structure is one of the characteristics of this system, with the facts that the molecular compound is not stoichiometric in its nature and that the system as a whole is amorphous, and is very similar to the molecular compounds of graphite. It is not known in detail how iodine molecules are arranged in relation to hydrocarbon molecules. However, the above structure suggests strongly that each iodine molecule is not localized preferentially to a fixed position of violanthrene molecule, but occupies the sites rather freely with a diffuse interaction force.

10) G. Dallinga, Abstract of paper at the 3rd. Congress of International Union of Crystallography, cf. *Acta Cryst.*, **7**, 665 (1954).

Such a structure like this is frequently seen amongst the intermediate phases of metallic system and among the quasi-metallic compounds. It is most interesting to see such a structure in an organic substance which has a high electrical conductivity.

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Department of Chemistry, Faculty of Science, The University of Tokyo
Hongo, Tokyo