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Spectroscopic Studies on Molecular Interactions. II.[1] Complexation between Polyvinylpyrrolidone and Iodine

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The nature and strength of the complexation of polyvinylpyrrolidone (PVP) with iodine were investigated by spectroscopic method. The complex included combined triiodide anion in the structure, and was considered to be an "inner complex" reported by Mulliken. This was supported from the fact that triethylamine, a strong electron–donor, exhibited spectroscopically same behavior as PVP and 2-pyrrolidone toward tetracyanoethylene as well as iodine in a polar medium.

The apparent complexation constant was evaluated by utilizing the Langmuir isotherm equation at 30° in ethanol. The complexation constant appeared generally dependent on the size of PVP and 2-pyrrolidone molecules, and therefore the complexation between PVP and iodine may be attributed to van der Waals–type forces or the like as well as charge–transfer forces.

Polyvinylpyrrolidone (PVP) is known to interact with iodine to form a complex which retains the germicidal nature of iodine but is less toxic.[3] The retaining of the activity of iodine may be due to weakness of the interaction between the species, but the mechanism of the complexation has not yet been revealed. In the present work the nature of the complexation was investigated by spectroscopic method.

Experimental

Materials——PVP K90, K30, and PL (grade for plasma expander) used in the experiments were manufactured by General Aniline Co., and the mean molecular weight was evaluated to be 6.9×10^5 for K90, 4.0×10^4 for K30, and 3.8×10^4 for PL by viscometry. Iodine and potassium iodide were of JIS special grade. Aqueous iodic acid solution was prepared from iodine pentoxide of JIS special grade. Tetracyanoethylene was purchased from Tokyo Kasei Kogyo Co. and purified by sublimation. Triethylamine, 2-pyrrolidone, pyridine, and all the solvents used were of JIS special grade or the like, and purified by redistillation.

Measurements of Absorption Spectra——The spectra were measured in 1 cm cells at room temperature (22—25°) with a Hitachi model EPS-2 recording spectrophotometer, or at 30° with a Hitachi-Perkin Elmer model 139 spectrophotometer, about 24 hours after preparing the test solutions.

Results and Discussion

The absorption spectra of PVP–iodine aqueous solutions are recorded in Fig. 1, together with spectrum of KI–iodine solution.

The two peaks at 287 and 351 mμ for KI–iodine solution were obviously originated from free triiodide anion.[4] PVP–iodine solutions gave the same shape of spectra though the peaks were slightly red–shifted, and the characteristic absorptions were disappeared by the addition

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[1] Part I: I. Moriguchi, M. Nayuki, and N. Kaneniwa, *Chem. Pharm. Bull.* (Tokyo), **17**, 1339 (1969).

[2] Location: *Hatanodai, Shinagawa-ku, Tokyo.*

[3] *a*) G. Oster and E.H. Immergut, *J. Am. Chem. Soc.*, **76**, 1393 (1954); *b*) S. Siggia, *J. Am. Pharm. Assoc.*, **46**, 201 (1957).

[4] J.A. Thoma and D. French, *J. Am. Chem. Soc.*, **82**, 4144 (1960).

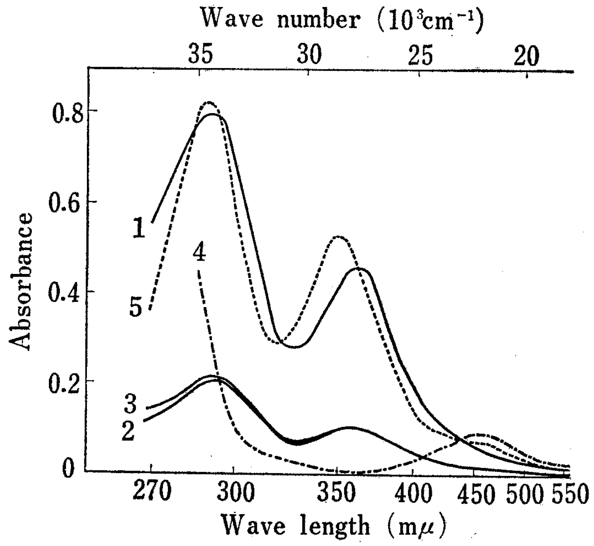

Fig. 1. Absorption Spectra of Iodine Complexes in Water

1—3: 1.5×10^{-4}M I_2 with 0.45% PVP (1:K90, 2:K30, 3:PL)
4 : 1.5×10^{-4}M I_2 with 0.45% PVP and 0.2M iodic acid
5 : 5×10^{-5}M I_2 with 10^{-4}M KI

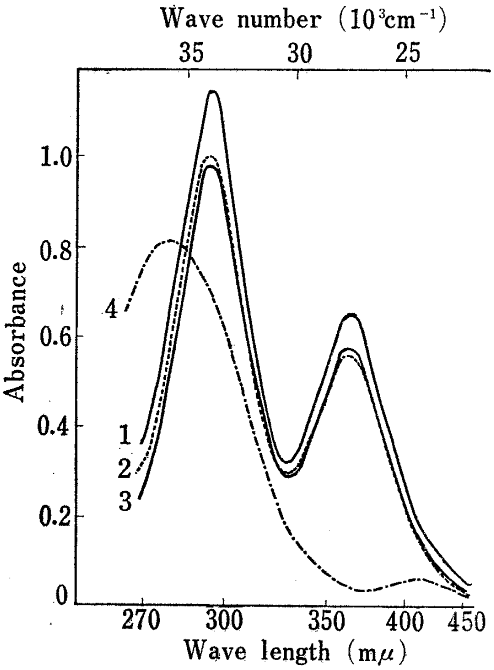

Fig. 2. Absorption Spectra of Iodine Complexes in Organic Solvents

1: 10^{-4}M I_2 with 0.5% PVP (PL) in CH_2Cl_2
2: 10^{-4}M I_2 with 10^{-3}M triethylamine in CH_2Cl_2
3: 10^{-4}M I_2 with 0.4M 2-pyrrolidone in CH_2Cl_2
4: 5×10^{-5}M I_2 with 10^{-3}M triethylamine in hexane

of iodic acid. This may suggest that the spectra of PVP–iodine solutions are due to triiodide anion combined with PVP molecules.

The spectra similar to that of triiodide anion were also observed in dichloromethane solutions of iodine with PVP, 2-pyrrolidone, and triethylamine as shown in Fig. 2. Triethylamine has been known as a good electron–donor, and was reported to form a charge–transfer complex with iodine in non–polar solvents.5) A charge–transfer band for the complex was observed at 278 mμ in hexane (Fig. 2). According to Mulliken,6) an "outer complex" (usual charge–transfer complex) can dissociate to an "inner complex" having an ionic structure in a polar medium. It is, therefore, expected from the spectra in Fig. 2 that a charge–transfer structure of triethylamine–iodine complex as recognized in hexane is converted into an ionic structure including triiodide anion in dichloromethane. Iodine complexes with PVP and 2-pyrrolidone are also considered to be inner complexes like the iodine–triethylamine complex in polar solvents because a number of amides were reported to behave as electron–donors.7)

PVP was insoluble to non–polar solvents, and a charge–transfer band between PVP and iodine was not recognized. Accordingly an attempt was made to obtain another support to the formation of an inner complex of iodine with PVP, though it was also indirect, by using tetracyanoethylene8) instead of iodine as the electron–acceptor. The spectra of tetracyanoethylene with PVP, 2-pyrrolidone, triethylamine, and pyridine in dichloromethane are shown in Fig. 3. All the solutions gave the same characteristic spectrum which seemed due to the anion radical of tetracyanoethylene.9) This may indicate the occurrence of inner complexes,

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5) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).

6) C. Reid and R.S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3869 (1954).

7) C.D. Schmulbach and R.S. Drago, *J. Am. Chem. Soc.*, **82**, 4484 (1960); R.L. Carlson and R.S. Drago, *ibid.*, **84**, 2320 (1962); R.S. Drago and D. Bafus, *J. Phys. Chem.*, **65**, 1066 (1961).

8) Tetracyanoethylene is also known as a strong electron–acceptor (L.J. Andrews and R.M. Keefer, "Molecular Complexes in Organic Chemistry," Chapter IV Holden-Day, Inc., San Francisco, 1964).

9) W. Liptay, G. Briegleb, and K. Schindler, *Z. Elektrochem.*, **66**, 331 (1962).

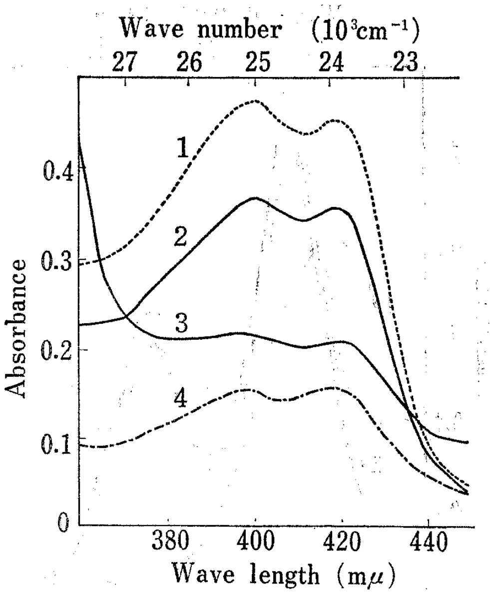

Fig. 3. Absorption Spectra of Tetracyanoethylene Complexes in Dichloromethane

1: 2×10^{-3}M tetracyanoethylene with 2×10^{-2}M pyridine
2: 2×10^{-3}M tetracyanoethylene with 0.4% PVP (PL)
3: 5×10^{-3}M tetracyanoethylene with 0.5M 2-pyrrolidone
4: 5×10^{-4}M tetracyanoethylene with 7×10^{-3}M triethylamine

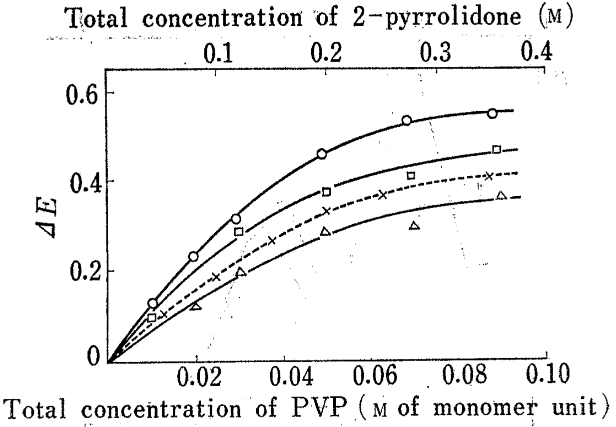

Fig. 4. Absorption Developments of Iodine (6×10^{-5}M) with PVP at 363 mμ and 2-Pyrrolidone at 360 mμ in Ethanol at 30°

—○—: K90
—□—: PL
—△—: K30
---×---: 2-pyrrolidone

and may support the explanation that PVP behaves as an electron–donor to form inner complexes with strong electron–acceptors as iodine in polar media.

Fig. 4 shows the development of the optical absorption of iodine ethanol solutions at the wave length of one of the peaks of triiodide anion by the addition of PVP or 2-pyrrolidone. Because the curves for PVP in Fig. 4 were appeared to be of Langmuir–type, we have attempted to estimate the constant K which indicates the strength of the complexation by utilizing the Langmuir isotherm equation.

The multiple equilibria in which a single molecule of PVP may combine with many molecules of iodine are expressed as the following general form

$$\mathrm{PVP}\cdot(i\text{-}1)\mathrm{I}_2+\mathrm{I}_2 \rightleftharpoons \mathrm{PVP}\cdot i\mathrm{I}_2, \qquad i=1,2,\cdots,n$$

where $\mathrm{PVP}\cdot i\mathrm{I}_2$ denotes an inner complex including triiodide anion. In such multiple equilibria the Langmuir equation is shown as

$$b/x=1/n+1/nK(a-x) \tag{1}$$

where a and b are the total concentrations of iodine and PVP, respectively, x is the concentration of iodine combined with PVP, and n the maximum number of iodine possible to combine with a unit of PVP.

The development of the optical absorption, ΔE, induced by complexation may be expressed by

$$\Delta E=l\cdot\Delta\varepsilon\cdot x \tag{2}$$

where $\Delta\varepsilon$ is the difference between the molar extinction coefficients of combined and free iodine, and l the length of the optical path. Substitution of x from Eq. (2) into Eq. (1) gives

$$a/\Delta E=(1/K+a-\Delta E/l\Delta\varepsilon)/l\Delta\varepsilon nb+1/l\Delta\varepsilon \tag{3}$$

Therefore, $\Delta\varepsilon$ can be obtained graphically by utilizing the relation

$$1/l\Delta\varepsilon = \lim_{1/b \to 0} a/\Delta E \tag{4}$$

Thus the apparent values of $\Delta\varepsilon$ were estimated from the plot of $a/\Delta E$ *vs.* $1/b$ shown as Fig. 5, and the values of x were calculated by using Eq. (2).

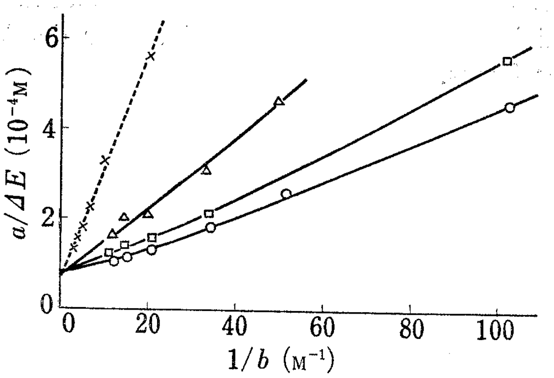

Fig. 5. Plot of $a/\Delta E$ *versus* $1/b$ at 30° in Ethanol

—○—: K90 —△—: K30
—□—: PL ---×---: 2-pyrrolidone

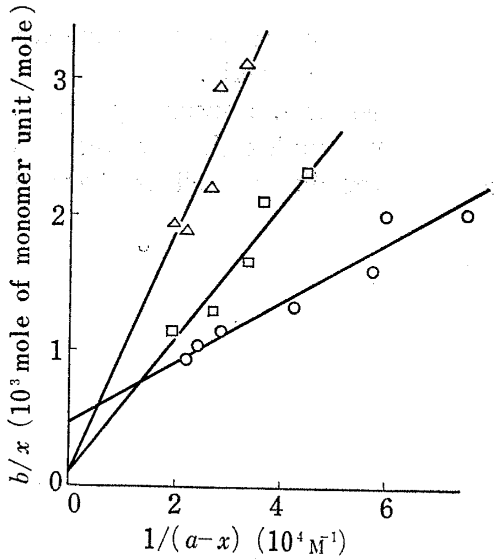

Fig. 6. Langmuir Plot for PVP–Iodine Complexation at 30° in Ethanol

—○—: K90 —□—: PL
—△—: K30

Fig. 6 shows the Langmuir plot for the data of PVP–iodine complexation in Fig. 4, and the values of n and K were obtained. In the case of 2-pyrrolidone, the plot in Fig. 5 was identical with the Benesi–Hildebrand plot,[10] and therefore both values of $\Delta\varepsilon$ and K could be estimated from the graph. The influence of an interaction between iodine and ethanol on the above-estimated values of K seemed negligible because the interaction was very weak.[11]

Table I lists apparent values of $\Delta\varepsilon$, n, and K for PVP, together with some of those for 2-pyrrolidone. The values of $\Delta\varepsilon$ for PVP and 2-pyrrolidone complexes were about a half of that for triiodide anion of which the extinction coefficient was 2.53×10^4 in ethylene chloride,[12]

Table I. Apparent Values of $\Delta\varepsilon$, K, and n for Complexations of Iodine with PVP and 2-Pyrrolidone at 30° in Ethanol

		$\Delta\varepsilon$	Per polymer		Per monomer	
			n	K (M^{-1})	n	K (M^{-1})
PVP	K90	1.25×10^4	13.5	20.63×10^3	1/460	44.8
	K30	1.25×10^4	4.5	0.90×10^3	1/80	11.3
	PL	1.25×10^4	4.3	1.61×10^3	1/80	20.2
2-Pyrrolidone		1.33×10^4	—	—	*a*)	3.1

a) 2-Pyrrolidone apparently formed a 1:1 complex with iodine under the experimental conditions.

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[10] H.A. Benesi and J.H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).
[11] I.D. Kuntz, Jr., F.P. Gasparro, M.D. Johnston, Jr., and R.P. Taylor, *J. Am. Chem. Soc.*, **90**, 4778 (1968).
[12] R.E. Buckles, J.P. Yuk, and A.I. Popov, *J. Am. Chem. Soc.*, **74**, 4379 (1952).

and accordingly the following formulas, for example, may be possible for the complexations of iodine with PVP and 2-pyrrolidone (Py) under the conditions employed.

$$\mathrm{PVP}\cdot(i-1)\mathrm{I_2}+\mathrm{I_2} \rightleftharpoons \underset{\text{(outer complex)}}{\mathrm{PVP}\cdot i\mathrm{I_2}} \rightleftharpoons \underset{\text{(inner complex)}}{(\mathrm{PVP}\cdot\mathrm{I}_{i/2})^{i/2+}\cdot(\mathrm{I}_{3i/2})^{i/2-}}$$

$$\mathrm{Py}+\mathrm{I_2} \rightleftharpoons \underset{\text{(outer complex)}}{\mathrm{Py}\cdot\mathrm{I_2}} \rightleftharpoons \underset{\text{(inner complex)}}{(\mathrm{Py}\cdot\mathrm{I}_{1/2})^{1/2+}\cdot(\mathrm{I}_{3/2})^{1/2-}}$$

In these reactions outer complexes once formed are immediately converted into inner complexes in polar media.

The constant K appeared generally dependent on the size of the donor molecules, and therefore the complexation between PVP and iodine may be attributed to van der Waals forces[13] or the like as well as charge-transfer forces.

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13) It was reported that the binding of anions to PVP was probably due in part to van der Waals forces (G. Oster, *et al.*, Ref. 3*a*)).