

## The Effect of Solvents on the Formation of Complexes of Benzene with Iodine and with Iodine Monochloride\*\*

by

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벤젠과 요오드 또는 일염화요오드 사이의錯物에 대한 용매의 영향

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### 要 約

$C_6H_6 \cdot I_2$  및  $C_6H_6 \cdot ICl$ 의 두錯物의安定度에 미치는 용매의 영향을 자외선分光光度法으로研究하였다. 클로로포름, 시크로헥산 및 *n*-헥산 용액에서  $C_6H_6 \cdot I_2$  생성에 대한 실온에서의 평형상수가 각각 0.090, 0.216 및 0.328  $l \text{ mole}^{-1}$ 이고  $C_6H_6 \cdot ICl$  생성에 대한 실온에서의 평형상수가 각각 0.125, 0.676 및 0.689  $l \text{ mole}^{-1}$ 임을 알았다. 이結果로부터 이들 두錯物의安定度가 용매의誘電常數의減少와 더불어增加함을 볼 수 있고 그增加率이  $C_6H_6 \cdot I_2$ 에서 보다  $C_6H_6 \cdot ICl$ 에서 더 큼을 알 수 있다. 이事實로 보아  $C_6H_6^+ \cdots I_2^-$  또는  $(C_6H_6I)^+ \cdots Cl^-$ 型的 이온構造가 이들錯物의共鳴安定化에 참여하는 정도가 크며 또 그 참여도가  $C_6H_6 \cdot I_2$ 에서 보다  $C_6H_6 \cdot ICl$ 에서 더 크다고 생각된다.

### Abstract

The effect of solvents on the stabilities of the  $C_6H_6 \cdot I_2$  complex and the  $C_6H_6 \cdot ICl$  complex has been investigated through ultraviolet spectrophotometric measurements. The equilibrium constants obtained at room temperature for the formation of  $C_6H_6 \cdot I_2$  complex are 0.090, 0.216 and 0.328  $l \text{ mole}^{-1}$  in chloroform, cyclohexane and *n*-hexane, respectively. The corresponding equilibrium constants at room temperature for  $C_6H_6 \cdot ICl$  complex are 0.125, 0.676 and 0.689  $l \text{ mole}^{-1}$ . These results indicate that the stabilities of the two complexes increase with decreasing dielectric constants of the solvents used, the increase in stability being more rapid in the  $C_6H_6 \cdot ICl$  complex than in the  $C_6H_6 \cdot I_2$  complex. This may support the conclusion that the dative ionic structures,  $C_6H_6^+ \cdots I_2^-$  and/or  $(C_6H_6I)^+ \cdots Cl^-$ , play important roles on the resonance stabilization of both the  $C_6H_6 \cdot I_2$  complex and the  $C_6H_6 \cdot ICl$  complex, the roles being more important in the latter complex than in the former complex.

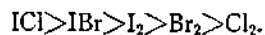
\* The Molecular Complexes. IV.

\*\* Based on a M. S. thesis submitted by Bu Yong Lee to the Graduate School of Hanyang University.

### Introduction

In a previous study of this series,<sup>1)</sup> it was

observed that the solutions of benzene with halogens or interhalogens in carbon tetrachloride showed the presence of absorption maxima in the vicinity of 2900 Å, where none of the component materials had strong absorption. This phenomenon was attributed to the formation of one to one molecular complexes of the type,  $C_6H_6 \cdot X_2$  or  $C_6H_6 \cdot IX$  in solution (X denotes halogen atoms). From spectrophotometric data, we obtained both the equilibrium constants for the complex formation, and the molar absorptivities of the complexes at their absorption maxima. The equilibrium constants at 25° for the benzene complexes were found to decrease in the order,



These complexes were assumed to be formed in solution through an interaction between Lewis base (benzene) and Lewis acids (halogens or interhalogens).<sup>2,3)</sup> The relative magnitudes of the equilibrium constants for the complex formation were then considered as a measure of the relative acidities of the halogens and the interhalogens toward benzene. The results obtained were explained in terms of the relative polarizabilities of halogen molecules and the relative electronegativities of halogen atoms.

Mulliken<sup>3)</sup> explained the nature of the bonding between electron donor D and electron acceptor B by considering resonance between a non-bonded structure ( $D \cdots B$ ) and a dative, ionic structure ( $D^+ \cdots B^-$ ). Thus, the ionic structure ( $D^+ \cdots B^-$ ) seemed to play an important role on the stabilities of the complexes. Hence, it appeared of interest to see if a variation of solvents might affect the attraction between  $D^+$  and  $B^-$ , and hence, affect the stabilities of the complexes. In fact, Benesi and Hildebrand found a considerable difference in equilibrium constant for the  $C_6H_6 \cdot I_2$  complex between the two solvents used, carbon tetrachloride and *n*-heptane.<sup>4)</sup>

We undertook the studies on the effect of solvents on the stabilities of the  $C_6H_6 \cdot I_2$  complex

and the  $C_6H_6 \cdot ICl$  complex, both being selected as typical examples of the benzene—halogen complexes and the benzene—interhalogen complexes, respectively. Thus, the present study involved the spectrophotometric investigations at room temperature on the  $C_6H_6 \cdot I_2$  complex and the  $C_6H_6 \cdot ICl$  complex in various solvents, chloroform, cyclohexane and *n*-hexane.

### Experimental

**Materials.**—Benzene and iodine were purified by the methods reported in our previous paper.<sup>1)</sup> Chlorine was prepared by dropping concentrated hydrochloric acid onto bleaching powder, and the evolving gas was washed successively with water and concentrated sulfuric acid to remove contaminated hydrogen chloride.<sup>5)</sup>

Chloroform (reagent grade, Wako, Japan), cyclohexane (reagent grade, Merck, Germany) and *n*-hexane (reagent grade, Merck, Germany) were dried over calcium chloride and distilled through a 100-cm. distillation column packed with glass helices. The reflux ratio was kept at approximately 1:10. The middle portions of the distillates were collected. The boiling points observed were as follows: chloroform, 61.3°; cyclohexane, 81.3°; and *n*-hexane, 68.0°.

**Spectrophotometric Measurements.**—The solutions of benzene and iodine in various solvents were prepared by the procedures described previously.<sup>1)</sup> The solutions of the iodine monochloride were prepared by dissolving an equivalent amount of elemental iodine into chlorine solutions whose concentrations had already been determined. The absorbancies of the solutions thus prepared were measured over the wave lengths ranging from 2700 to 6000 Å, using each solvents as the blank.

Then, the solutions of benzene were mixed at appropriate ratio with the solutions of iodine or iodine monochloride. The absorbancies of the resulting solutions were immediately measured at room temperature. The prolonged keeping of

the mixture solutions was avoided in order to discriminate a possibility of any chemical changes in solution. The blanks in this case were the carbon tetrachloride solutions of benzene with the same concentrations as those of the solutions containing iodine or iodine monochloride.

A Beckman DU Spectrophotometer and a set of 1-cm. quartz cells were used for the absorbancy measurements. All the measurements were carried out at room temperature ( $23 \pm 3^\circ\text{C}$ ).

### Results and Discussion

The absorption spectra of the solutions of iodine, iodine monochloride or benzene in chloroform, cyclohexane and *n*-hexane did not show the presence of maximum absorption peaks in the vicinity of 2900 Å. On the other hand, the absorption spectra of the solutions of a mixture of benzene with iodine or iodine monochloride did indicate the presence of absorption maxima in the region of wave lengths near 2900 Å. The maximum absorptions observed are attributed to the formation of the complexes of benzene with iodine or iodine monochloride in solution. The complexes of this type are assumed to be one to one molecular complexes, as was discussed previously.<sup>1)</sup>



where D denotes the benzene molecules, B the molecules of iodine or iodine monochloride, and C the one to one complexes, D·B. The equilibrium constants *K* for the complex formation (equilibrium 1) and the molar absorptivities,  $a$ , of the complexes at their absorption maxima were evaluated by the method described previously.<sup>1)</sup> This calculation required to know the molar absorptivities,  $a_0$ , of the free iodine or iodine monochloride in each solvents. The values of  $a_0$  determined experimentally are summarized in Table I.

**The Benzene-Iodine Complex in Various Solvents.**—Data obtained at room temperature

**Table I**

Molar Absorptivities of Iodine and Iodine Monochloride in Various Solvents at Room Temperature.

Solvent	Halogen	Concn., $10^{-3}$ mole $l^{-1}$	Wave length (Å)	Absorbancy (A)	Molar absorptivity ( $a_0$ )	Average
Chloroform	I <sub>2</sub>	2.20	2930	0.126	57	57
		3.14	"	0.187	57	
		3.93	"	0.224	57	
		9.41	"	0.621	58	
Cyclohexane	I <sub>2</sub>	2.88	2910	0.203	70	69
		9.68	"	0.649	69	
<i>n</i> -Hexane	I <sub>2</sub>	1.48	2900	0.103	70	70
		1.85	"	0.129	70	
Chloroform	ICl	2.27	2850	0.138	61	61
		3.28	"	0.202	61	
		4.54	"	0.282	62	
Cyclohexane	ICl	1.10	2790	0.212	193	193
		3.16	"	0.527	193	
<i>n</i> -Hexane	ICl	0.602	2780	0.171	318	318
		0.843	"	0.269	319	
		1.21	"	0.384	319	

on the system of benzene with iodine in chloroform, cyclohexane and *n*-hexane are summarized in Table II, III and IV. The data result in good linearities between  $\{D\}_0[B]_0 / \{A - a_0[B]_0\}$  and  $\{D\}_0$ , where *A* denotes the absorbancies measured at the absorptoin maxima, and  $\{ \}$ .

**Table II**

Formation of  $C_6H_6 \cdot I_2$  in Chloroform at  $22^\circ\text{C}$ .

$C_6H_6$ , mole/l ( $\{D\}_0$ )	$I_2$ , $10^{-4}$ mole $l^{-1}$ ( $\{B\}_0$ )	Absorbancy at 2930 Å (A)	$\frac{\{D\}_0[B]_0}{A - a_0[B]_0}$ , $10^{-4}$ mole $l^{-1}$	Average, $10^{-4}$ mole $l^{-1}$
2.18	1.12	0.336	7.40	7.46
	1.68	0.501	7.44	
	2.24	0.660	7.54	
2.45	1.12	0.369	7.56	7.63
	1.68	0.545	7.68	
	2.24	0.730	7.65	
2.83	1.12	0.413	7.79	7.84
	1.68	0.614	7.86	
	2.24	0.820	7.86	
3.21	1.12	0.458	7.95	8.01
	1.68	0.679	8.06	
	2.24	0.910	8.01	

$$K = 0.090 \text{ l mole}^{-1}$$

$$a = 17600$$

the initial molar concentrations (Figs. 1 to 3). These linearities indicate the assumption of the formation of one to one molecular complex  $C_6H_6 \cdot I_2$  being correct, as was discussed previously.<sup>1)</sup>

Table III

Formation of  $C_6H_6 \cdot I_2$  in Cyclohexane at 26°C.

$C_6H_6$ , mole $l^{-1}$ ( $[D]_0$ )	$I_2$ , $10^{-4}$ mole $l^{-1}$ ( $[B]_0$ )	Absorbancy at 2910 Å (A)	$\frac{[D]_0[B]_0}{A - a_0[B]_0}$ , $10^{-4}$ mole $l^{-1}$	Average, $10^{-4}$ mole $l^{-1}$
2.14	0.745	0.303	5.35	5.31
	1.24	0.512	5.28	
	1.74	0.712	5.32	
	2.24	0.919	5.30	
2.36	0.745	0.326	5.48	5.48
	1.24	0.544	5.47	
	1.74	0.763	5.47	
	2.24	0.979	5.48	
2.78	0.745	0.361	5.82	5.79
	1.24	0.602	5.81	
	1.74	0.851	5.76	
	2.24	1.10	5.75	
3.34	0.746	0.401	6.26	6.31
	1.24	0.664	6.30	
	1.74	0.928	6.31	
	2.24	1.18	6.38	

$$K = 0.216 \text{ l mole}^{-1}$$

$$a = 12100$$

Table IV

Formation of  $C_6H_6 \cdot I_2$  in *n*-Hexane at 25°C.

$C_6H_6$ , mole $l^{-1}$ ( $[D]_0$ )	$I_2$ , $10^{-4}$ mole $l^{-1}$ ( $[B]_0$ )	Absorbancy at 2900 Å (A)	$\frac{[D]_0[B]_0}{A - a_0[B]_0}$ , $10^{-4}$ mole $l^{-1}$	Average, $10^{-4}$ mole $l^{-1}$
1.64	0.634	0.230	4.62	4.62
	1.11	0.399	4.65	
	1.43	0.518	4.60	
2.01	0.634	0.269	4.87	4.93
	1.11	0.452	5.03	
	1.43	0.591	4.94	
2.42	0.634	0.293	5.32	5.32
	1.11	0.512	5.33	
	1.43	0.665	5.30	
2.79	0.634	0.312	5.76	5.76
	1.11	0.543	5.78	
	1.43	0.702	5.75	

$$K = 0.328 \text{ l mole}^{-1}$$

$$a = 10300$$

From the values of slopes and intercepts of the plots, the values of  $K$  and  $a$  are calculated.

These results are compared with those of our previous, similar study in carbon tetrachloride (Table V). Since larger values of  $K$  indicate greater stabilities of the complex, it is concluded that the stability of the  $C_6H_6 \cdot I_2$  complex increases with decreasing dielectric constants,  $\epsilon$ , of the solvents utilized. It can also be seen from Table V that the values of both  $\lambda_{max}$  and  $a$

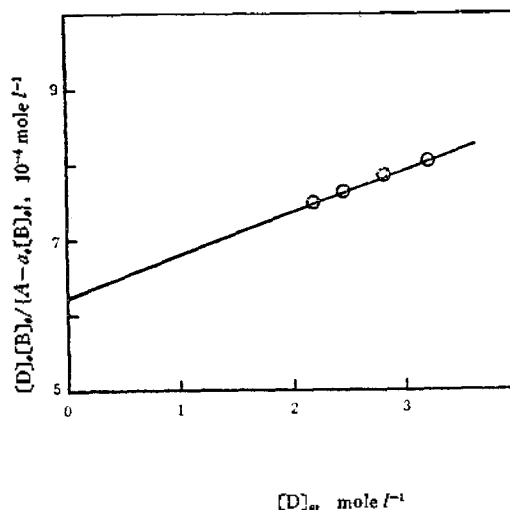


Fig. 1 Plot of  $[D]_0[B]_0 / \{A - a_0[B]_0\}$  versus  $[D]_0$  of the benzene-iodine-chloroform system at 22°C.

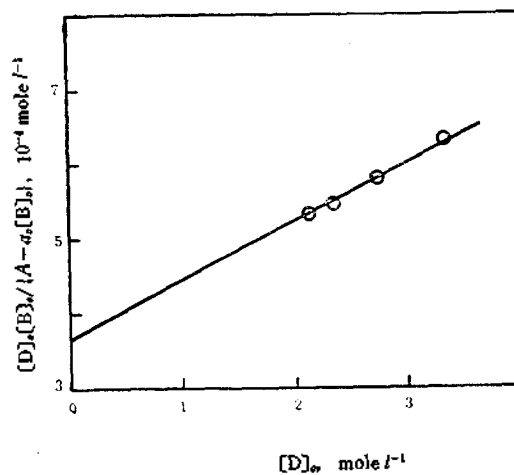


Fig. 2 Plot of  $[D]_0[B]_0 / \{A - a_0[B]_0\}$  versus  $[D]_0$  of the benzene-iodine-cyclohexane system at 26°C.

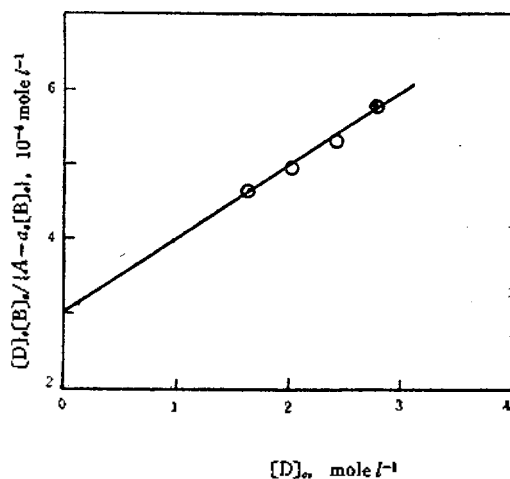


Fig. 3 Plot of  $[D]_0[B]_0 / \{A - a_0[B]_0\}$  versus  $[D]_0$  of the benzene-iodine-*n*-hexane system at 25°C.

decrease with decreasing dielectric constants of the solvents.

Table V

Summary of Data Obtained at Room Temperature for  $C_6H_6 \cdot I_2$  in Various Solvents.

Solvent	Wave length of absorption maxima, Å ( $\lambda_{max}$ )	Molar absorptivity ( $a$ )	Equilibrium const., $l \text{ mole}^{-1}$ ( $K$ )	Free energy change, kcal $\text{mole}^{-1}$ ( $-\Delta F^\circ$ )	Dielectric const. at 20° ( $\epsilon$ )
$CHCl_3$	2930	17600	0.090	-1.41	5.05
$CCl_4^{(1)}$	2930	15500	0.173	-1.04	2.24
Cyclo- $C_6H_{12}$	2910	12100	0.216	-0.80	2.05
<i>n</i> - $C_6H_{14}$	2900	10300	0.328	-0.66	1.87

<sup>(1)</sup> Ref. 1.

<sup>(2)</sup> Ref. 6.

Standard free energy changes,  $-\Delta F^\circ$ , for the formation of the  $C_6H_6 \cdot I_2$  complex (equilibrium I) are calculated from a knowledge of  $K$  values, and included in Table V. According to Mulliken,<sup>3)</sup> the  $C_6H_6 \cdot I_2$  complex should be stabilized by resonance between a non-bonded structure,



and a dative structure,



Since the energy of attraction between the two opposite charges in structure II should be prop-

portional to  $1/\epsilon$  of the solvents, the values of  $-\Delta F^\circ$  should be correlated directly with the values of  $1/\epsilon$ , if it is assumed that all factors other than the ionic interaction are identical in all the solvents used. Actually, the plots of  $-\Delta F^\circ$  versus  $1/\epsilon$  give a fairly good straight line (Fig. 7). It appears reasonable, therefore, to conclude that the ionic structure II may play an important role on the resonance stabilization of the  $C_6H_6 \cdot I_2$  complex.\*

**The Benzene-Iodine Monochloride Complex in Various Solvents.**—In view of the existence of apparent effect of solvents on the stability of the  $C_6H_6 \cdot I_2$  complex, studies were extended to the system of benzene with iodine monochloride in chloroform, cyclohexane and *n*-hexane. The results obtained at room temperature are summarized in Table VI, VII and VIII. Here also good linearities exist between  $[D]_0[B]_0 / \{A - a_0[B]_0\}$  and  $[D]_0$  (Figs. 4 to 6), and hence, the values of both  $K$  and  $a$  are calculated

Table VI

Formation of  $C_6H_6 \cdot ICl$  in Chloroform at 21°C.

$C_6H_6$ , mole $l^{-1}$ ( $[D]_0$ )	$ICl$ , $10^{-4}$ mole $l^{-1}$ ( $[B]_0$ )	Absorbancy at 2850 Å ( $A$ )	$[D]_0[B]_0 / \{A - a_0[B]_0\}$ , $10^{-4}$ mole $l^{-1}$	Average, $10^{-4}$ mole $l^{-1}$
1.47	2.08	0.350	9.04	9.17
	4.15	0.681	9.29	
	6.23	1.04	9.17	
2.12	2.08	0.453	9.99	9.89
	4.15	0.922	9.81	
	6.23	1.38	9.87	
2.56	2.08	0.530	10.3	10.3
	4.15	1.07	10.2	
	6.23	1.58	10.3	
2.93	2.08	0.585	10.6	10.8
	4.15	1.16	10.6	
	6.23	1.65	11.3	

$$K = 0.146 \text{ l mole}^{-1}$$

$$a = 9150$$

\* Although the temperatures examined for the complex formation are different from 20°C, it is considered that such a small difference in temperature may not alter appreciably the discussions described here as to the correlations of  $K$  or  $-\Delta F^\circ$  with  $\epsilon$ .

from slopes and intercepts of the straight lines.

Table VI

Formation of  $C_6H_6 \cdot ICl$  in Cyclohexane at  $26^\circ C$ .

$C_6H_6$ , mole $l^{-1}$ ( $[D]_0$ )	$ICl$ , $10^{-4}$ mole $l^{-1}$ ( $[B]_0$ )	Absorbancy at 2790 Å (A)	$\frac{[D]_0[B]_0}{A - a_0[B]_0}$ , $10^{-4}$ mole $l^{-1}$	Average, $10^{-4}$ mole $l^{-1}$
1.76	0.835	0.333	4.63	4.61
	1.67	0.674	4.57	
	2.50	1.01	4.61	
	3.34	1.33	4.64	
2.15	0.835	0.365	5.14	5.14
	1.67	0.735	5.11	
	2.50	1.10	5.13	
	3.34	1.45	5.19	
2.53	0.835	0.387	5.69	5.73
	1.67	0.770	5.72	
	2.50	1.15	5.75	
	3.34	1.53	5.77	
2.92	0.835	0.406	6.25	6.24
	1.67	0.819	6.20	
	2.50	1.21	6.31	
	3.34	1.64	6.20	

$$K = 0.676 \text{ l mole}^{-1}$$

$$a = 7240$$

Table VII

Formation of  $C_6H_6 \cdot ICl$  in *n*-Hexane at  $23^\circ C$ .

$C_6H_6$ , mole $l^{-1}$ ( $[D]_0$ )	$ICl$ , $10^{-4}$ mole $l^{-1}$ ( $[B]_0$ )	Absorbancy at 2780 Å (A)	$\frac{[D]_0[B]_0}{A - a_0[B]_0}$ , $10^{-4}$ mole $l^{-1}$	Average, $10^{-4}$ mole $l^{-1}$
1.59	1.03	0.394	4.54	4.54
	1.72	0.659	4.55	
	2.41	0.926	4.51	
	3.10	1.18	4.57	
1.86	1.03	0.430	4.95	4.88
	1.72	0.707	4.90	
	2.41	1.00	4.84	
	3.10	1.29	4.85	
2.41	1.03	0.463	5.77	5.71
	1.72	0.790	5.64	
	2.41	1.10	5.70	
	2.10	1.40	5.75	
2.89	1.03	0.489	6.52	6.43
	1.72	0.831	6.41	
	2.41	1.16	6.41	
	3.10	1.50	6.40	

$$K = 0.689 \text{ l mole}^{-1}$$

$$a = 7120$$

The results indicate that the stability of the  $C_6H_6 \cdot ICl$  complex also increases with decreasing dielectric constants of the solvents, and both  $\lambda_{max}$  and  $a$  decrease correspondingly (Table K). Standard free energy changes,  $-\Delta F^\circ$ , for the formation of the  $C_6H_6 \cdot ICl$  complex are calculated, and listed in Table K. Here again a fairly good linearity can be seen between the values of  $-\Delta F^\circ$  and those of  $1/\epsilon$  of the solvents (Fig.

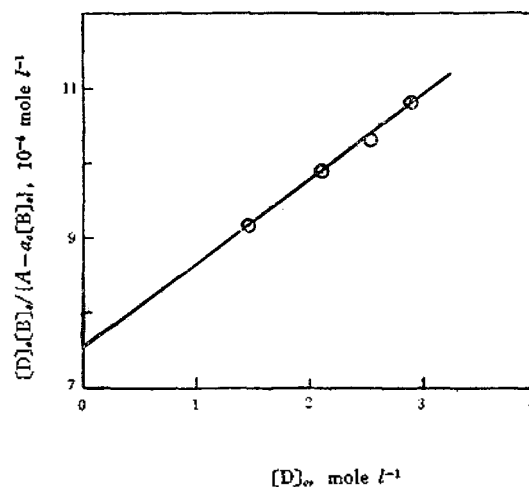


Fig. 4 Plot of  $[D]_0[B]_0 / \{A - a_0[B]_0\}$  versus  $[D]_0$  of the benzene-iodine monochloride-chloroform system at  $21^\circ C$ .

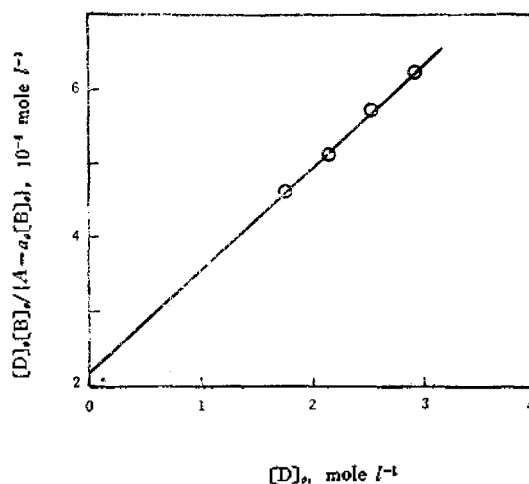


Fig. 5 Plot of  $[D]_0[B]_0 / \{A - a_0[B]_0\}$  versus  $[D]_0$  of the benzene-iodine monochloride-cyclohexane system at  $26^\circ C$ .

7), indicating ionic structures to play major role on the resonance stabilization of the  $C_6H_6 \cdot ICl$  complex\*.

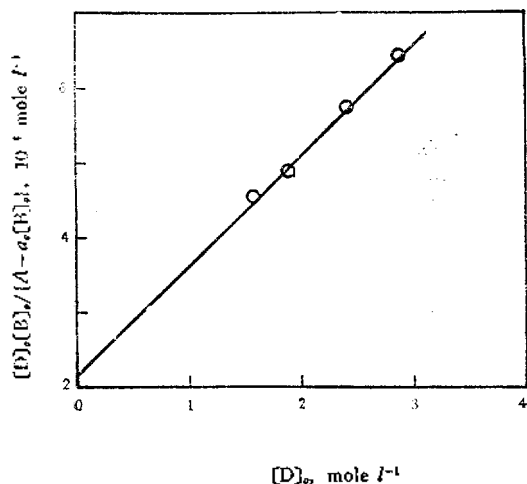


Fig. 6 Plot of  $[D]_0[B]_0/(A - \alpha_e[B]_0)$  versus  $[D]_0$  of the benzene-iodine monochloride-*n*-hexane system at 23°C.

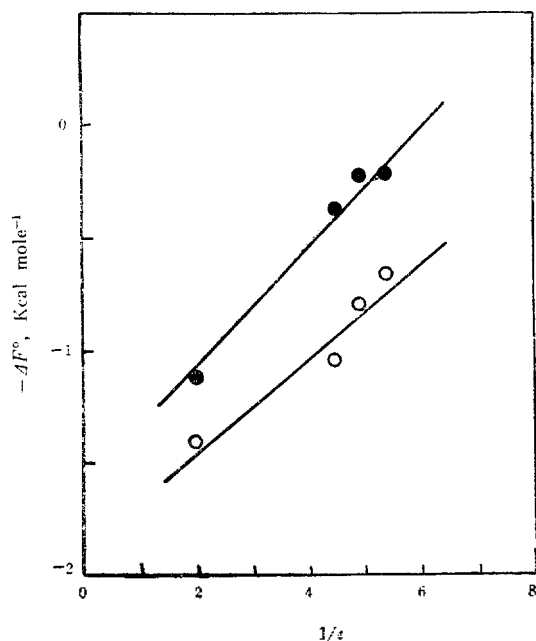


Fig. 7 Correlation of  $-\Delta F^\circ$  values for the formation of the  $C_6H_6 \cdot ICl$  complex (upper line) and  $C_6H_6 \cdot I_2$  complex (lower line) with  $1/\epsilon$  of the solvents at room temperature.

Table X

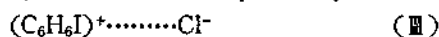
Summary of Data Obtained at Room Temperature for  $C_6H_6 \cdot ICl$  in Various Solvents.

Solvent	Wave length of absorption maxima, Å ( $\lambda_{max}$ )	Molar absorptivity (a)	Equilibrium const., $l$ mole <sup>-1</sup> (K)	Free energy change, kcal mole <sup>-1</sup> ( $-\Delta F^\circ$ )	Dielectric const. (ε) at 20°C
$CHCl_3$ (a)	2850	9150	0.146	-1.12	5.05
$CCl_4$	2820	8130	0.54	-0.37	2.24
Cyclo- $C_6H_{12}$	2790	7240	0.676	-0.23	2.05
<i>n</i> - $C_6H_{14}$	2780	7120	0.689	-0.22	1.87

(a) Ref. 7

(b) Ref. 6

The values of  $-\Delta F^\circ$  for the  $C_6H_6 \cdot ICl$  complex are now compared with those for the  $C_6H_6 \cdot I_2$  complex. It can be seen from Tables V and IX that the  $C_6H_6 \cdot ICl$  complex exhibits greater  $-\Delta F^\circ$  value than the  $C_6H_6 \cdot I_2$  complex in each solvents examined. This is explained by considering an additional contribution of structure III to the resonance stabilization of the  $C_6H_6 \cdot ICl$  complex, as was discussed previously.<sup>10</sup>



We can also see from Fig. 7 that the slope of the plots of  $-\Delta F^\circ$  versus  $1/\epsilon$  is steeper in the  $C_6H_6 \cdot ICl$  complex than in the  $C_6H_6 \cdot I_2$  complex. As mentioned above, energy of attraction between the opposite charges in the ionic structures II and III of each complex may be proportional to  $1/\epsilon$  of the solvents used. Hence, the slope of the straight lines observed between  $-\Delta F^\circ$  and  $1/\epsilon$  should be related directly with the extent of contribution of the ionic structures to the resonance stabilization of each complex. The greater the contribution of the ionic structures is, the steeper the slope of the straight lines must be. Therefore, it appears reasonable from the present study to conclude that the dative structures II and/or III play more important role on the resonance stabilization of the  $C_6H_6 \cdot ICl$  complex than  $C_6H_6 \cdot I_2$  complex.

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\* See foot-note on p. 165.

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