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Interaction of 1,2-Dichloroethane with Benzene and other Aromatic Hydrocarbons

Akio Morita, Hiroaki Takahashi, and Keniti Higasi
School of Science and Engineering, Waseda University, Shinjuku, Tokyo

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Experiments to confirm Kubo's conclusion on the complex formation of 1,2-dichloroethane with benzene were carried out following his procedure. Dielectric measurements were carried out with inert solvents hexane and cyclohexane. The interactions between 1,2-dichloroethane and each of the compounds toluene and *p*-xylene were also studied with inert solvents hexane, cyclohexane, and carbon tetrachloride. The results are discussed in relation to complex formation.

It was found that the dipole moment of 1,2-dichloroethane, when measured in benzene solution, is unaccountably high.[1] It was also found that the Raman lines of the same molecule in the same solvent show abnormal behavior.[2] Later investigation led to the conclusion that the gauche isomers of this molecule gain an extra stability in benzene. However, no satisfactory explanation has been offered since for the nature of the extra energy.[3] From ultrasonic and thermodynamic studies it was concluded that there is some interaction between 1,2-dichloroethane and an aromatic hydrocarbon but no evidenc for complex formation between these molecules was obtained.[4]

The complex formation between 1,2-dichloroethane and benzene has been suggested by many workers.[5] First experimental proof was given by Kubo[6] from the dielectric measurements of mixtures of the two molecules in the medium of carbon tetrachloride. He examined a general case of complex formation:

$$CH_2Cl\text{-}CH_2Cl + nC_6H_6 \rightleftarrows CH_2Cl\text{-}CH_2Cl\cdot nC_6H_6$$

and showed that the number *n* should be 1 and not 2. He gave the equilibrium constant $K_c=32$ m*l*/mol and the excess polarization for the solute $\Delta P=97.6$ cm^3 at 20°C. From his ΔP value the dipole moment of the 1 : 1 complex was estimated[7] to be almost equal to the value 2.55 D[8] of the gauche isomer. Thus, we might conclude that the gauche isomer is stabilized in benzene solution through the complex formation, because such formation will certainly result in stronger intensities of the Raman lines of the gauche isomer and give rise to a high dipole moment in benzene solution.

The present paper deals with dielectric measurements on the basis of complex formation; it is in fact an extention of Kubo's work. Three inert solvents were employed, *viz.*, hexane, cyclohexane, and carbon tetrachloride. Benzene, toluene (with polarity), and *p*-xylene (with no polarity) were also chosen as aromatic molecules for the interaction with 1,2-dichloroethane.

Experimental

Dielectric constants of dilute solutions of 1,2-dichloroethane were measured at 25°C with the use of a heterodyne apparatus at 1 MHz. Solvents are mixtures of aromatic and inert solvents. Dielectric constants ε and densities d of dilute solutions can be expressed by linear functions of concentration of the solute (wt. fraction $w<0.05$).

$$\begin{aligned} \varepsilon &= \varepsilon_m + aw \\ d &= d_m + bw \end{aligned} \tag{1}$$

where ε_m, d_m are the dielectric constant and the density, respectively, of the mixture solvent and a, b are the so-called "slopes". With the use of these "slopes" we can obtain the apparent specific polarization ${}_\infty p^*$ of 1,2-dichloroethane (at zero concentration of the solute) in the mixture of two solvents with a given concentration of aromatic molecules.

$${}_\infty p^* = \frac{\varepsilon_m-1}{\varepsilon_m+2}\cdot\frac{1}{d_m}\left[\frac{3a}{(\varepsilon_m-1)(\varepsilon_m+2)}+\frac{d_m-b}{d_m}\right] \tag{2}$$

The apparent polarization ${}_\infty p^*$ is a hypothetical polarization calculated on the assumption of no complex formation. It differs from the specific polarization ${}_\infty p$ obtained in the medium of inert solvent alone. The difference ${}_\infty p^*-{}_\infty p=\Delta p$ is, therefore, a measure of the interaction between the solute and the aromatic solvent. Multiplying Δp by the molecular weight M of 1,2-dichloroethane, we obtain the corresponding molecular polarization ΔP_{obs}. This polarization term has been obtained for the system of 1,2-dichloroehane, aromatic and inert solvents.

$$\Delta P_{obs} = M\Delta p = M({}_\infty p^* - {}_\infty p) \tag{3}$$

The relationship between ΔP_{obs} and the concentration of aromatic solvent under the light of Kubo's equation[6] and the Benesi-Hildebrand[9] equation for complex formation were examined.

For the equilibrium of 1 : 1 complex formation

$$CH_2Cl\text{-}CH_2Cl + \text{Arom} \rightleftarrows \text{Complex}$$

we have the relation

$$K_c = \frac{\alpha}{(1-\alpha)c_B} \tag{4}$$

where α is the fraction of dichloroethane combined with aromatic solvent and c_B the concentration of the aromatic solvent in equilibrium which is taken as equal to its initial concentration.

The following relation is assumed for fraction.

$$\alpha = \frac{\Delta P_{obs}}{\Delta P} \tag{5}$$

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[1] L. Meyer, *Z. Physik. Chem.*, **B8**, 357 (1930); K. Higasi, *Bull. Inst. Phys. Chem. Res.*, **13**, 186 (1934).

[2] S. Mizushima, Y. Morino, and K. Higasi, *Sci. Pap. Inst. Phys. Chem. Res.*, **25**, 159 (1934).

[3] A. Wada and Y. Morino, *J. Chem. Phys.*, **22**, 1276 (1954).

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[5] H. Müller, *Physik. Z.*, **34**, 689 (1933).

[6] M. Kubo, *Bull. Inst. Phys. Chem. Res.*, **13**, 1221 (1934).

[7] K. Chitoku and K. Higasi, This Bulletin, **40**, 773 (1967).

[8] S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York (1954), p. 35.

[9] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **70**, 2832 (1948); **71**, 2703 (1949).

and

$$\Delta P = P(\mathrm{AB}) - P(\mathrm{A}) - P(\mathrm{B}) \tag{6}$$

where $P(\mathrm{AB})$, $P(\mathrm{A})$, and $P(\mathrm{B})$ are the molecular polarizations of the complex, dichloroethane and aromatic solvent, respectively.

Introducing Eq.(5) into Eq.(4), we get Kubo's formula[6]

$$\frac{\Delta P_{\mathrm{obs}}}{c_{\mathrm{B}}} = K_c(\Delta P - \Delta P_{\mathrm{obs}}) \tag{7}$$

In a similar way Benesi-Hilderband's equation[9] can be derived as

$$\frac{1}{\Delta P_{\mathrm{obs}}} = \frac{1}{K_c \Delta P}\cdot\frac{1}{c_{\mathrm{B}}} + \frac{1}{\Delta P} \tag{8}$$

The following modification of Eq.(8) can be used as well.[10]

$$\frac{c_{\mathrm{B}}}{\Delta P_{\mathrm{obs}}} = \frac{c_{\mathrm{B}}}{\Delta P} + \frac{1}{K_c \Delta P} \tag{9}$$

Plots of $\Delta P_{\mathrm{obs}}/c_{\mathrm{B}}$ against ΔP_{obs} will confirm the validity of Eq. (7); plots of $1/\Delta P_{\mathrm{obs}}$ against $1/c_{\mathrm{B}}$ and those of $c_{\mathrm{B}}/\Delta P_{\mathrm{obs}}$ against c_{B} are related to Eqs.(8) and (9), respectively. If the plots all satisfy the straight-line relationship and provide the consistent values of K and ΔP, we could conclude that 1 : 1 complex is formed between 1,2-dichloroethane and the aromatic solvent. K_c and ΔP are obtained from these plots.

In addition we can estimate the dipole moment μ_{AB} of the complex AB in Debye units from ΔP.

$$P_0(\mathrm{AB}) = \Delta P + P_0(\mathrm{A}) + P_0(\mathrm{B}) \tag{10}$$

$$\mu_{\mathrm{AB}} = 0.0128\sqrt{P_0(\mathrm{AB})T} \tag{11}$$

where $P_0(\mathrm{AB})$, $P_0(\mathrm{A})$, and $P_0(\mathrm{B})$ are the orientation polarizations of the complex, 1,2-dichloroethane, and aromatic solvent, respectively; and $P_0(\mathrm{A}) = P(\mathrm{A}) - P_E(\mathrm{A}) - P_A(\mathrm{A}) = P(\mathrm{A}) - 23.9\ \mathrm{cm}^3$;[8] and $P_0(\mathrm{B}) = 0$ for benzene and *p*-xylene and $P_0(\mathrm{B}) = 3.8\ \mathrm{cm}^3$ for toluene.[2,11]

Materials. Both 1,2-dichloroethane of special grade (Wako) and carbon tetrachloride were kept over calcium chloride for a week before distillation. Benzene, toluene, *p*-xylene, hexane, and cyclohexane were stored over sodium wire and distilled.

Results and Discussion

Results of the dielectric measurements are summarized in Tables 1, 2, and 3. The concentration of the aromatic hydrocarbon c_{B} in the system of three components is shown in the first column in the units of mol/m*l*. The dielectric constant ε_m and the densities d_{m} refer to the mixture solvent (with a given c_{B}). Two slopes a and b are obtained from several solutions with the same c_{B} and with the concentration of the solute w=0.01—0.05. With the use of ε_{m}, d_{m}, a, and b, the apparent specific polarization ${}_\infty p^*$ is calculated from which ΔP_{obs} is easily obtained (*cf.* Eqs. (2) and (3)).

The quantity $\Delta P_{\mathrm{obs}}/c_{\mathrm{B}}$ will be a linear function of ΔP_{obs} if Eq. (7) for the complex formation is satisfied in the system under examination. Plots of $\Delta P_{\mathrm{obs}}/c_{\mathrm{B}}$ are made against ΔP_{obs} for nine systems of 1,2-dichloroethane, aromatic, and inert solvents (see Figs. 1, 2, and 3). Deviations from the linear relation are within experimental error. We see that 1,2-dichloroethane forms 1 : 1 complex with an aromatic molecule, benzene, toluene, and *p*-xylene.

Other plots using the relations given by Benesi-Hildebrand equation (8) and Eq. (9) are repeated for all the systems. No appreciable deviation from the

Table 1. Apparent polarization of 1,2-dichloroethane in mixtures of benzene and inert solvent (25°C)

a) Inert solvent: hexane

Benzene $c_{\mathrm{B}}(\times 10^{-3})$	ε_{m}	d_{m}	a	b	$M_\infty p^*$	ΔP_{obs}
11.18	2.274	0.8735	3.511	0.2578	89.1	26.6
7.69	2.145	0.8063	2.905	0.2827	84.3	21.8
6.08	2.087	0.7756	2.616	0.2874	81.3	18.8
5.64	2.071	0.7672	2.548	0.2955	80.4	17.9
0.00	1.891	0.6627	1.490	0.3053	(62.5)	0.0

b) Inert solvent: cyclohexane

Benzene $c_{\mathrm{B}}(\times 10^{-3})$	ε_{m}	d_{m}	a	b	$M_\infty p^*$	ΔP_{obs}
11.18	2.274	0.8735	3.511	0.2578	89.1	25.0
8.43	2.200	0.8454	3.187	0.2705	86.2	22.1
5.50	2.126	0.8176	2.815	0.2788	81.8	17.7
4.34	2.099	0.8071	2.663	0.2837	79.6	15.5
0.00	2.014	0.7735	1.819	0.2756	(64.1)	0.0

c) Inert solvent: carbon tetrachloride

Benzene $c_{\mathrm{B}}(\times 10^{-3})$	ε_{m}	d_{m}	a	b	$M_\infty p^*$	ΔP_{obs}
11.18	2.274	0.8735	3.511	0.2578	89.1	22.6
9.86	2.270	0.9573	3.737	0.2248	87.1	20.6
8.06	2.266	1.0708	3.898	0.1365	84.0	17.5
5.68	2.259	1.2243	4.141	−0.0161	79.6	13.1
0.00	2.226	1.5855	4.103	−0.4743	(66.5)	0.0

Values in parentheses correspond to $M_\infty p$.

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[10] G. Briegleb, "Electronen-Donator-Acceptor Komplexe", Springer, Berlin (1961).

[11] A. L. McClellan, "Tables of Experimental Dipole Moments," Freeman, San Francisco (1963).

Table 2. Apparent polarization of 1,2-dichloroethane in mixtures of toluene and inert solvent (25°C)

a) Inert solvent: hexane

Toluene $c_B(\times 10^{-3})$	ε_m	d_m	a	b	$M_\infty p^*$	ΔP_{obs}
9.35	2.374	0.8618	3.020	0.2669	79.3	16.8
5.74	2.180	0.7852	2.522	0.2956	76.8	14.3
4.38	2.107	0.7562	2.313	0.2962	75.3	12.8
3.32	2.054	0.7333	2.159	0.3061	73.6	11.1
0.00	1.891	0.6627	1.490	0.3053	(62.5)	0.0

b) Inert solvent: cyclohexane

Toluene $c_B(\times 10^{-3})$	ε_m	d_m	a	b	$M_\infty p^*$	ΔP_{obs}
9.35	2.374	0.8618	3.020	0.2669	79.3	15.2
6.73	2.263	0.8314	2.755	0.2739	77.6	13.5
5.92	2.220	0.8258	2.673	0.2772	76.9	12.8
4.40	2.172	0.8109	2.511	0.2761	75.4	11.3
0.00	2.014	0.7735	1.819	0.2756	(64.1)	0.0

c) Inert solvent: carbon tetrachloride

Toluene $c_B(\times 10^{-3})$	ε_m	d_m	a	b	$M_\infty p^*$	ΔP_{obs}
9.35	2.374	0.8618	3.020	0.2669	79.3	12.8
8.03	2.355	0.9642	3.323	0.2121	78.9	12.4
7.39	2.347	1.0135	3.473	0.1771	78.7	12.2
6.62	2.337	1.0733	3.641	0.1345	78.4	11.9
0.00	2.226	1.5855	4.103	−0.4743	(66.5)	0.0

Table 3. Apparent polarization of 1,2-dichloroethane in mixture of *p*-xylene and inert solvent (25°C).

a) Insert solvent: hexane

p-Xylene $c_B(\times 10^{-3})$	ε_m	d_m	a	b	$M_\infty p^*$	ΔP_{obs}
8.065	2.263	0.8562	2.902	0.2674	78.9	16.4
6.05	2.166	0.8096	2.593	0.2882	76.8	14.3
5.37	2.129	0.7940	2.484	0.2739	75.9	13.4
4.55	2.094	0.7750	2.247	0.2448	74.7	12.2
0.00	1.891	0.6627	1.490	0.3053	(62.5)	0.0

b) Inert solvent: cyclohexane

p-Xylene $c_B(\times 10^{-3})$	ε_m	d_m	a	b	$M_\infty p^*$	ΔP_{obs}
8.065	2.263	0.8562	2.902	0.2674	78.9	14.8
6.65	2.208	0.8399	2.712	0.2525	77.8	13.7
5.94	2.184	0.8319	2.644	0.2588	77.1	13.0
5.10	2.154	0.8222	2.573	0.2723	76.2	12.1
0.00	2.014	0.7735	1.819	0.2756	(64.1)	0.0

c) Inert solvent: carbon tetrachloride

p-Xylene $c_B(\times 10^{-3})$	ε_m	d_m	a	b	$M_\infty p^*$	ΔP_{obs}
8.065	2.263	0.8562	2.902	0.2674	78.9	12.4
7.16	2.255	0.9366	3.087	0.2197	77.9	11.4
6.68	2.256	0.9808	3.217	0.2020	77.4	10.9
5.86	2.254	1.0552	3.376	0.1460	76.3	9.8
0.00	2.226	1.5855	4.103	−0.4743	(66.5)	0.0

linearity was observed.

Two unknown quantities K_c and ΔP for each system can be determined by the least square method from the data with the use of any of Eqs.(7), (8), and (9). In Table 4 the equilibrium constant and the excess polarization ΔP thus obtained are recorded. Values calculated by Eq. (9) are omitted since they are very similar. All the K_c and ΔP values thus obtained are consistent with each other.

For the system of 1,2-dichloroethane, benzene, and carbon tetrachloride equilibrium constant K_c is found to be 30.0 m*l*/mol and the excess polarization $\Delta P=$ 90.0 cm^3 at 25°C from Eq. (7). The values are in agreement with Kubo's $K_c=32$ m*l*/mol and $\Delta P=$ 97.6 cm^3 at 20°C.$^{6)}$

We see from Figs. 1—3 that toluene has steeper inclinations. The different behavior of toluene may perhaps be due to the existence of polarity while both benzene and *p*-xylene lack it. The same trend is found in Benesi-Hildebrand's plots.

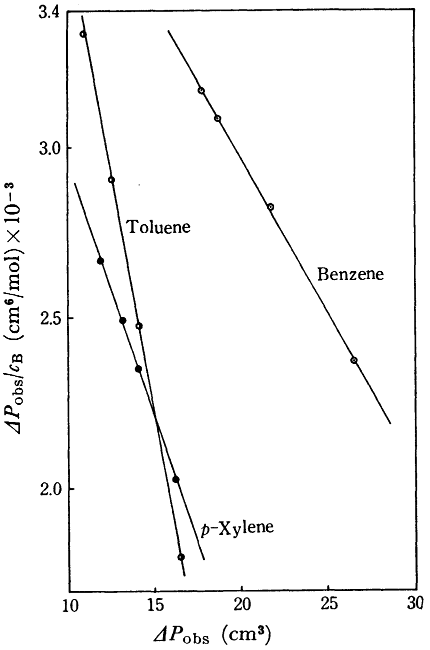

Fig. 1. Interaction of 1,2-dichloroethane with benzene, toluene, and p-xylene, in the inert medium of hexane. ⊙: Benzene, ○: Toluene, •: p-Xylene

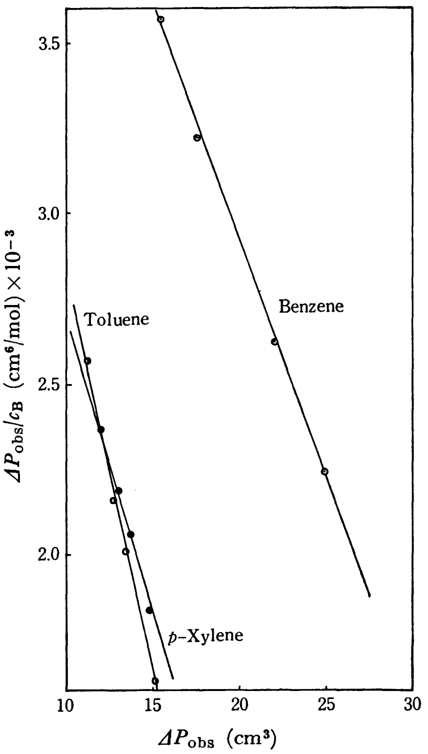

Fig. 2. Interaction as in Fig. 1, in the inert medium of cyclohexane.

From Table 4 we see that K_c in carbon tetrachloride is comparatively high with toluene and low with both benzene and p-xylene. Carbon tetrachloride may not be a perfectly inert solvent, some interaction with a solute often being suspected when this solvent is employed.[12,13] However, we have no means to decide the most ideal inert solvent among these non-polar solvents.

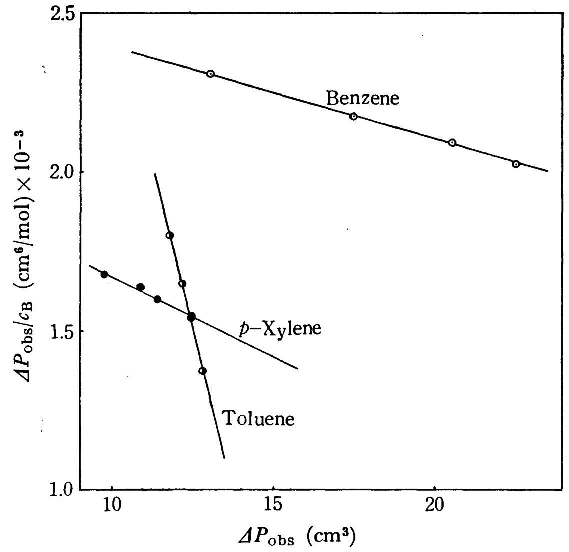

Fig. 3. Interaction as in Fig. 1, in the inert medium of carbon tetrachloride.

TABLE 4. K_c AND ΔP OBTAINED BY Eqs. (7) AND (8)

Inert solvent	Hexane	Cyclohexane	Carbon tetrachloride	
Intraction with Benzene				
K_c	90.7	139	30.0	(7)
(ml/mol)	90.4	140	30.6	(8)
ΔP	52.9	41.0	90.0	(7)
(cm^3)	52.9	40.8	88.5	(8)
Interaction with Toluene				
K_c	272	240	480	(7)
(ml/mol)	271	242	476	(8)
ΔP	23.4	21.9	15.6	(7)
(cm^3)	23.5	21.8	15.8	(8)
Interaction with p-Xylene				
K_c	155	196	51.0	(7)
(ml/mol)	154	200	53.1	(8)
ΔP	29.5	24.2	42.5	(7)
(cm^3)	29.6	24.0	41.5	(8)

The equilibrium constant K_c (Table 4) increases in the order

benzene<p-xylene<toluene

while the excess polarization varies in the order

toluene<p-xylene<benzene.

The trend is of interest since it will explain the apparently contradicting behavior of the relaxation times and the dipole moments obtained in benzene and p-xylene.[7]

The average relaxation time τ_0 and the Cole-Cole distribution parameter α of 1,2-dichloroethane increase from 3.69 psec and 0.13 in benzene to 4.53 psec and 0.19 in p-xylene. The increase seems parallel to the increase in the equilibrium constant. The ampler the complex, the greater the values of K_c and

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[12] T. Shibuya and Y. I'Haya, This Bulletin, **37**, 896 (1964).
[13] K. Chitoku and K. Higasi, *ibid.*, **39**, 2160 (1966).

also of τ_0, since the average relaxation time becomes greater when the contribution from the complex with larger size is more important. The same contribution will give rise to an increase in α.

The dipole moment of 1,2-dichloroethane is found to be 1.63 D in *p*-xylene which is much less than the value 1.80 D in benzene.[7] This apparent decrease seems to be parallel to the decrease of ΔP from benzene to *p*-xylene. It reveals that the dipole moment of the complex with *p*-xylene becomes smaller compared with the moment of the complex with benzene.

In Table 5 the dipole moments of 1 : 1 complexes between 1,2-dichloroethane and aromatic solvents calculated from ΔP (Kubo's method) are recorded.

TABLE 5. DIPOLE MOMENT OF 1,2-DICHLOROETHANE-AROMATIC HYDROCARBON COMPLEXES OBTAINED BY Eq. (11)

Aromatic Hydrocarbon	Inert solvent		
	Hexane	Cyclohexane	CCl_4
Benzene	2.11D	1.99D	2.54D
Toluene	1.79	1.79	1.74
p-Xylene	1.82	1.77	2.04

The dipole moment of the complex with benzene obtained in carbon tetrachloride is 2.54D, which is almost the same as the moment 2.55D presumed by Mizushima[8] as the moment of the gauche isomer. The equilibrium constant $K_c=30.0$ m*l*/mol (Kubo's method) gives $\alpha=0.25$ in benzene at 25°C (*viz.*, $c_B=11.18\cdot10^{-3}$ mol/m*l*).

From the ratio of the intensities of the Raman lines I(gauche)/I(trans), we can estimate the number of the gauche isomers in benzene and hexane at room temperature.[2] The mole fraction x_g of the gauche isomers increases from 0.16 (hexane) to 0.39 (benzene). On the other hand we find the increase in x_g is about 0.21 from dipole moment measurements, *viz.*, x_g in hexane 0.276, in carbon tetrachloride 0.289 and in benzene 0.491.[7]

It should be noted that the fraction of the complex 0.25 can be considered equal to the apparent increase 0.21—0.23 in x_g of the gauche isomers when transferred to benzene from a non-aromatic solvent.

This would imply that the extraordinary increase in numbers of the gauche isomers in benzene which is the so-called benzene effect is due to the formation of a complex which has the gauche conformation in the part of 1,2-dichloroethane. In the system of 1,2-dichloroethane - benzene - carbon tetrachloride the above statement appears to be valid since the complex has the same polarity as the gauche isomer. However, the situation is more complicated in other systems. The same problem will be discussed more in detail.[14]

From the dielectric measurements based on Kubo's procedure we get a similar evidence for complex formation between 1,2-dichloroethane and an aromatic hydrocarbon, *viz.*, benzene, toluene, or *p*-xylene, and we find that the so-called "benzene effect" might be related to the complex formation. It should be pointed out that both the equilibrium constant and the polarity of the complex are affected by the choice of inert solvents, hexane, cyclohexane, and carbon tetrachloride.

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[14] K. Higasi, H. Takahashi, K. Chitoku, and A. Morita, in press. *Memo. Sch. Sci. Eng., Waseda Univ.*, **35** (1971).