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Solvent Effects on π-π Charge-Transfer Complexations[1]

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Solvent effects on charge-transfer (CT) transition energy, $h\nu_{CT}$, and association constant, K_C, for π-π intermolecular CT complexing were investigated with hexamethylbenzene–p-chloranil, hexamethylbenzene–tetracyanoethylene, and N,N-dimethylaniline–1,3,5-trinitrobenzene systems in various organic solvents. The values of $h\nu_{CT}$ linearly decreased with an increase in refractive index (n) and its function $(n^2-1)/(2n^2+1)$ with high significance, while log K_C was recognized to have some relations to functions of dielectric constant (D) such as log D, $1/D$, and $(D-1)/(2D+1)$ expressed with an parabolic curve exhibiting the minimum K_C value in the solvent with a D of about 6—10. Some discussion was made on these relationships.

Charge-transfer (CT) complexing between organic substances has been of considerable pharmaceutical interest with respect to the mechanism of drug action and stabilization. It has been generally believed that weak intermolecular CT complexes become more stable with increasing refractive index and dielectric constant of the solvent.[3] However, refractive index seems fairly different from dielectric constant as a measure of polarity of solvents upon CT complexations. In the present paper, solvent effects on CT transition energy, $h\nu_{CT}$,[4] and association constant, K_C, for several π-π donor-acceptor systems which formed weak complexes were investigated in terms of refractive index, dielectric constant, and a number of other solvent parameters recently introduced.

Experimental

Materials——Hexamethylbenzene (HMB), p-chloranil (CA), and tetracyanoethylene (TCNE) were of analytical grade, and purified by recrystallization or sublimation. All the solvents were of JIS special grade or the like, and purified by redistillation. Their melting or boiling points were found to be similar to those listed in chemical handbooks and literatures.

Measuremens of the Wave Length of CT Band——The difference spectra of mixtures of HMB (2×10^{-2}—6×10^{-2}M) with CA (5×10^{-4}—4×10^{-3}M) *vs.* CA or with TCNE (5×10^{-4}—1×10^{-3}M) *vs.* TCNE in various organic solvents listed in Table I were recorded with a Shimadzu model MPS-50L multipurpose spectrophotometer in 1 cm or 0.5 cm cells at 30°, and the wave length of CT band, λ_{CT}, was determined. The value of $h\nu_{CT}$ was derived from λ_{CT}.

Determination of Equilibrium Constants——A Hitachi model 139 spectrophotometer was employed for the measurements of absorbances at λ_{CT} for the donor-acceptor mixtures in various solvents at 30°. The concentrations of the donor and the acceptors were as follows: 5×10^{-3}—6×10^{-2}M for HMB, 4×10^{-4}—2×10^{-3}M for CA, and 1×10^{-4}—5×10^{-4}M for TCNE. The calculation of K_C was made by the method previously described.[5]

Measurenemt of Refractive Index——Refractive indices of various solvents were measured at 30° with an Atago model 302 Abbe-type refractometer.

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1) *a*) This forms Part VIII of "Spectroscopic Studies on Molecular Interactions"; *b*) Part VII: I. Moriguchi, S. Fushimi, and N. Kaneniwa, *Chem. Pharm. Bull.* (Tokyo), **19**, 1272 (1971).

2) Location: *Hatanodai, Shinagawa-ku, Tokyo, 141, Japan.*

3) A. Kuboyama, "Denshi Supekutoru," ed. by the Chemical Society of Japan, Maruzen Co., Tokyo, 1965, p. 477.

4) h is the Planck constant, and ν_{CT} the frequency of CT band.

5) I. Moriguchi and N. Kaneniwa, *Chem. Pharm. Bull.* (Tokyo), **17**, 2173 (1969).

Result and Discussion

HMB is known to be a good π-electron donor because of its low ionization potential and high chemical stability. As π-electron acceptors, CA and TCNE are widely used for studies on CT properties.[6] Although they are rather chemically reactive, they form fairly stable outer complexes with HMB in various organic solvents, especially in the case of CA. Thus, HMB-CA system in 19 solvents and HMB-TCNE system in 9 solvents[7] were investigated for the determination of the values of λ_{CT}, $h\nu_{CT}$, and K_C. In these solvents, the complexing was reversible and dissociation of the complexes into free radical ions was not observed spectrophotometrically.

Table I. Charge-Transfer Properties for Some Donor-Acceptor Systems in Various Organic Solvents

	Solvents	n_D^{30}	D[a]	HMB-CA			HMB-TCNE			DMA-TNB[b]	
				λ_{CT} (mμ)	$h\nu_{CT}$ (eV)	K_C(30°) (M^{-1})	λ_{CT} (mμ)	$h\nu_{CT}$ (eV)	K_C(30°) (M^{-1})	λ_{CT} (mμ)	K_C(20°) (M^{-1})
1.	hexane	1.374	1.89	511	2.427	11.36	529	2.344	119.4	465	8.2
2.	heptane	1.381	1.92	507	2.446	12.77	530	2.340	119.4	466	8.2
3.	cyclohexane	1.421	2.02	512	2.422	13.64	531	2.335	126.8	470	9.5
4.	1,4-dioxane	1.417	2.21	503	2.465	0.92		c)		465	0.15
5.	carbon tetrachloride	1.455	2.24	519	2.389	5.70	538	2.305	62.5	484	3.4
6.	tetrachloroethylene	1.501	2.30	523	2.371	5.30		c)			
7.	isopropylether	1.363	3.88	504	2.460	4.14	529	2.344	90.0		
8.	chloroform	1.440	4.81	517	2.398	1.65	543	2.284	14.8	486	1.3
9.	butyl acetate	1.390	5.01	497	2.495	1.64		c)			
10.	ethyl acetate	1.368	6.02	496	2.500	1.61		c)			
11.	1,1,2,2-tetrachloroethane	1.489	8.20	525	2.362	1.37	544	2.279	12.3	492	0.2
12.	dichloromethane	1.419	9.08	523	2.371	1.88	543	2.284	12.4		
13.	1,2-dichloroethane	1.440	10.36	521	2.380	1.96	542	2.288	12.1		
14.	2-methoxyethanol	1.398	16.0	494	2.510	2.19		c)			
15.	1-butanol	1.395	17.1	499	2.485	5.07		c)			
16.	2-propanol	1.373	18.3	498	2.490	3.41		c)			
17.	1-propanol	1.381	20.1	498	2.490	5.07		c)			
18.	ethanol	1.358	24.3	495	2.505	4.29		c)			
19.	methanol	1.325	32.6	492	2.520	3.18		c)			

a) J.A. Riddick and E.E. Toops, Jr., "Organic Solvents," Interscience Publishers, Inc., New York, 1955.
b) Ref. 8.
c) The outer complex is not stable at 30°.

The values obtained are listed in Table I, together with those for the system of N,N-dimethylaniline (DMA) with 1,3,5-trinitrobenzene (TNB) in 7 solvents appeared in the literature.[8] At first, the correlations of λ_{CT} and log K_C for HMB-CA system with those for HMB-TCNE system and for DMA-TNB system were examined. The result is shown in Table II, indicating that highly significant correlations exist among those systems both in λ_{CT} and in log K_C. Therefore, further studies were made only on HMB-CA system where the data could be obtained in a relatively large number of solvents.

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[6] W.R. Carper, R.M. Hedges, and H.N. Simpson, *J. Phys. Chem.*, **69**, 1707 (1965); E.M. Voigt, *J. Am. Chem. Soc.*, **86**, 3611 (1964); and earlier references given therein.

[7] The solubility as well as the stability was comparatively poor for TCNE and its outer complex.

[8] R. Foster and D.L. Hammick, *J. Chem. Soc.*, **1954**, 2685.

TABLE II. Correlation Coefficients of λ_{CT} and log K_C for HMB-CA System with those for HMB-TCNE System and for DMA-TNB System in Several Organic Solvents

Systems correlated	Number of samples	Correlation coefficient	
		λ_{CT}	log K_C
HMB-CA with HMB-TCNE	9	0.919 [a]	0.950 [a]
HMB-CA with DMA-TNB	7	0.928 [b]	0.959 [a]

a) highly significant at the 0.001 levels
b) significant at the 0.01 levels

Several intrinsic properties of solvents are known including refractive index, n, and dielectric constant, D, and their functions such as $(n^2-1)/(2n^2+1)$,[9] $1/D$,[10] and $(D\text{-}1)/(2D+1)$[9b,11] have been also employed. Recently a number of solvent parameters such as Brownstein's S value,[12] Brooker's X_R value,[13] Dimroth's E_T value,[14] Kosower's Z value,[15] and solubility parameter, δ,[11] have been introduced as an empirical measure of the effect on an organic reaction of changing solvent. The detailed difinitions and characteristics of these parameters are not reviewed here because they seem unnecessary for the later discussion. Besides these, ionization potential of solvents has been reported to influence on CT com-

TABLE III. Correlation Coefficients of Various Parameters for Solvents with $h\nu_{CT}$ and with log K_C in HMB-CA System

Parameters for solvents	Number of samples	Correlation coefficient	
		$h\nu_{CT}$	log K_C
n_D^{30}	19	-0.832 [a]	-0.171
$(n^2-1)/(2n^2+1)$ [b]	19	-0.833 [a]	-0.172
log D	19	0.496 [c]	-0.291
$1/D$	19	-0.388	0.480 [c]
$(D-1)/(2D+1)$	19	0.402	-0.452
δ	18	0.471 [c]	-0.233
S value	16	0.566 [c]	-0.339
χ_R value	15	0.357	0.513
E_T value	13	0.674 [c]	0.026
Z value	8	0.979 [a]	0.856 [d]
Ionization potential [e]	15	-0.109	-0.026

a) highly significant at the 0.001 levels
b) $n=n_D^{30}$
c) significant at the 0.05 levels
d) significant at the 0.01 levels
e) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957); C.E. Meloan and R.W. Kiser, Ref. 23

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9) *a*) H.A. Lorentz and L.V. Lorenz, through W.J. Moor, "Physical Chemistry," Prentice-Hall, Inc., Edgewood Cliffs, 1962, Chapter 14; *b*) Y. Ooshika, *J. Phys. Soc. Japan*, **9**, 594 (1954); *c*) E.G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

10) A.H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).

11) H.F. Herbrandson and F.R. Neufeld, *J. Org. Chem.*, **31**, 1140 (1966).

12) S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960).

13) L.G.S. Brooker, A.C. Craig, D.W. Heseltine, P.W. Jenkins, and L.L. Lincoln, *J. Am. Chem. Soc.*, **87**, 2443 (1965).

14) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Ann. Chem.*, **661**, 1 (1963); *idem*, *ibid.*, **669**, 95 (1963).

15) E.M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253, 3261, 3267 (1958); C. Walling and P.J. Wagner, *ibid.*, **86**, 3368 (1964); E.M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York, 1968, Chapter 2.

plexing.[16] Relations of these parameters for solvents to $h\nu_{\mathrm{CT}}$ and to $\log K_{\mathrm{C}}$ were investigated. Their correlation coefficients are tabulated in Table III, exhibiting that $h\nu_{\mathrm{CT}}$ is correlated with n, $(n^2-1)/(2n^2+1)$, and Z value with high significance, and that $\log K_{\mathrm{C}}$ is also significantly correlated with Z value. Fig. 1, 2, and 3 show some of these relationships. Besides, functions of dielectric constant such as $\log D$, $1/D$, and $(D-1)/(2D+1)$ have some relations to $\log K_{\mathrm{C}}$ expressed with parabolic curves as shown in Fig. 4 for the case of $\log D$.

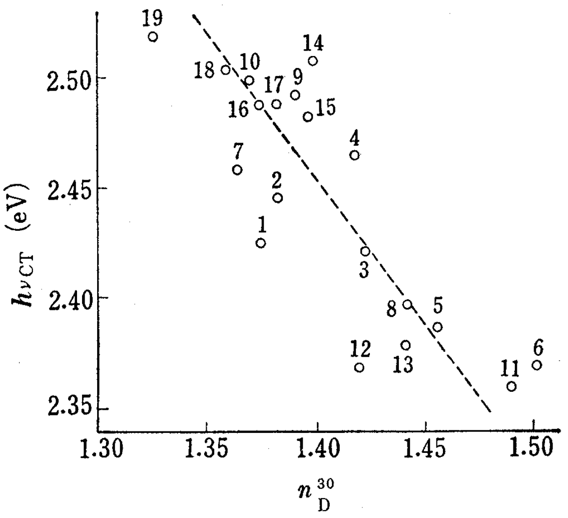

Fig. 1. Relation of $h\nu_{\mathrm{CT}}$ for HMB-CA System to Refractive Index of the Solvent[a]

[a] For numbering, see Table I.

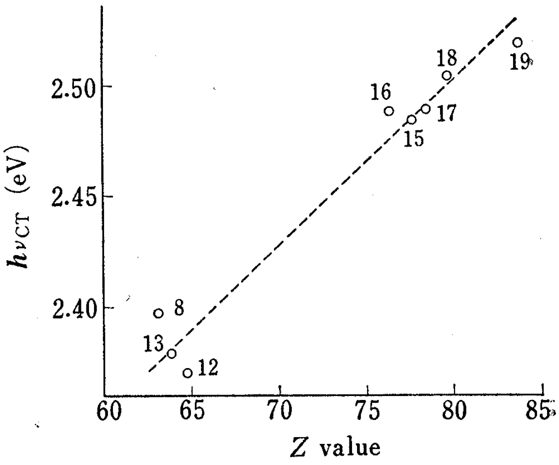

Fig. 2. Relation of $h\nu_{\mathrm{CT}}$ for HMB-CA System to Z Value for the Solvent[a]

[a] For numbering, see Table I.

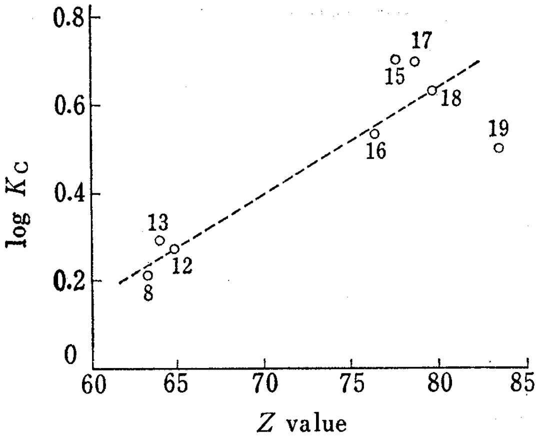

Fig. 3. Relation of $\log K_{\mathrm{C}}$ for HMB-CA System to Z Value for the Solvent[a]

[a] For numbering, see Table I.

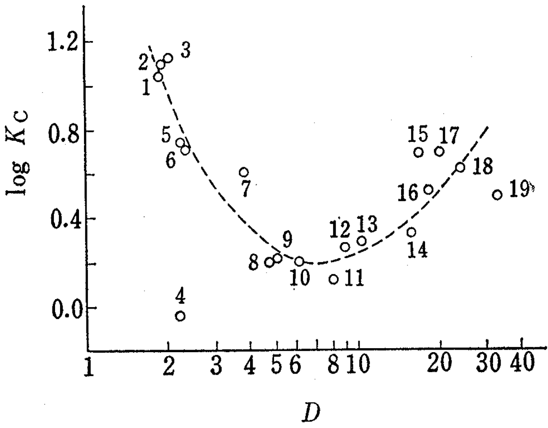

Fig. 4. Relation of $\log K_{\mathrm{C}}$ for HMB-CA Complexing to $\log D$ for the Solvent[a]

[a] For numbering, see Table I.

In such circumstance, it seems to be needed to clarify the relations among n, D, and Z value. Fig. 5 shows the relations. It is seen that Z value is linear in $\log D$, and also in n because a straight line relationship[17] is recognized between n and $\log D$ in the region of higher D values where Z values for the solvents used are known. In addition, a number of

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[16] L.J. Andrews and R.M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, 1964, Chapter 4.

[17] Correlation coefficient was 0.944 (9 samples) for n with $\log D$ in the region of D higher than 8.

Z values appeared in the literature[14] were found to be highly correlated with log D with a correlation coefficient of 0.774 (28 samples) at the 0.001 levels. For these reasons, it does not seem necessary to discuss on Z value exclusively.

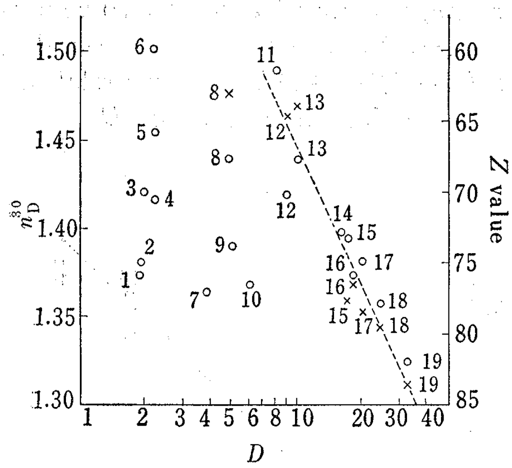

Fig. 5. Relations of log D to n_D^{30} and Z Value for Various Solvents[a)]

○: n_D^{30} *vs.* log D

×: Z value *vs.* log D

a) For numbering, see Table I.

According to Kuboyama,[18] CT bands should shift to the longer wave length with an increase in refractive index of the solvent. Tsubomura and Kuboyama[19] have explained that, because of the more polar structure of the excited state compared with that of the ground state of CT complexes, the excited state becomes more stable with increasing polarity, *i.e.*, increasing n, of the solvent in the case of non-polar media.

More generally, solvent effects on frequency shifts of electronic spectra, $\Delta\nu$, are quantitatively expressed in terms of refractive index and dielectric constant by the following equation developed by McRae.[9c]

$$h\Delta\nu = (AL_0+B)\frac{n^2-1}{2n^2+2} + C\left(\frac{D-1}{D+1}-\frac{n^2-1}{n^2+2}\right) + F\left(\frac{D-1}{D+2}-\frac{n^2-1}{n^2+2}\right)^2$$

In this equation, h is the Planck constant, and AL_0+B, C, and F, relating to the oscillator strength of the transition, the isotropic polarizability of the excited state, *etc.*, are substantially constant. Approximately, both C and F are zero in non-polar solvents, and F can be neglected compared with the other terms even in polar solvents.[20] In the range of values for usual solvents, both $(n^2-1)/(2n^2+1)$ and $(n^2-1)/(n^2+2)$ are linear in n, and $(D-1)/(D+2)$ is linear in log D.[21] Moreover, n is linear in log D in polar media.[17] Consequently, it can be said that $h\Delta\nu$ is approximately linear in n both in polar and non-polar solvents. Thus the significant correlation of $h\nu_{CT}$ with n or $(n^2-1)/(2n^2+1)$ may be reasonable on the assumption that the difference in tangent of the linearity of $h\Delta\nu$ with n between polar and non-polar solvents is not so large.

The solvent effect on K_C may be more complicated in comparison with that on $h\nu_{CT}$ because, in addition to pure CT forces, there may be a number of forces contributing to CT complex formation such as van der Waals forces, multipolar interactions, hydrogen bonding, and solvations, in general. Among these, contributions of multipolar interactions and hydrogen bonding may decrease, those of solvations and CT forces may increase, and van der Waals forces may not change, with an increase in dielectric constant of the solvent. Hence, a possible explanation for the parabolic relations of log K_C to log D, $1/D$, and $(D-1)/(2D+1)$, as shown in Fig. 4 for the case of log D, would be that electrostatic forces such as multipolar interactions *etc.* are dominant in the solvents of lower dielectric constant, and CT forces and solvations are dominant in those of higher dielectric constant. The fact that the minimum K_C values were observed in the solvents with a dielectric constant of about 6—10 may be similar to the case of stability of an ion, where it is said that the effect of electrostatic forces

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18) A. Kuboyama, *Nippon Kagaku Zasshi*, **81**, 558 (1960); *Idem*, *Tokyo Kogyo Shikensho Hokoku*, **57**, 546 (1962).

19) H. Tsubomura and A. Kuboyama, *Kagaku To Kogyo* (Tokyo), **14**, 537 (1961).

20) W.W. Robertson, A.D. King, Jr., and O.E. Weigang, *J. Chem. Phys.*, **35**, 464 (1961).

21) Correlation coefficient was 0.999 both for $(n^2-1)/(2n^2+1)$ and $(n^2-1)/(n^2+2)$ with n, and 0.985 for $(D-1)/(D+2)$ with log D for 19 solvents used.

should be at least compatible to that of solvating action in media of dielectric constant less than 10 or so.[22] The reason for the deviation of 1,4-dioxane from the curve shown in Fig. 4 is uncertain. The relatively low value of the ionization potential[23] may account for the low value of K_C by participation of the solvent in the CT complexing as an electron donor.

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[22] L.P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1970, Chapter 8.

[23] Ionization potential of 1,4-dioxane is 9.13, the lowest of 19 solvents used (C.E. Meloan and R.W. Kiser, "Problems and Experiments in Instrumental Analysis," C.E. Merrill Books, Inc., 1963, p. 309).