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Differential Refractometric Studies on Some Strong and Weak Molecular Complexes

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A more adequate model has been developed to determine the equilibrium constant (K_1) and stoichiometry of molecular complexes. This model involves the assumption:

$$\Delta\phi_a/C_D^\circ = \{K_1C_A^\circ/\alpha(1+K_1C_A^\circ)\}-\{K_1\Delta\phi_a/(1+K_1C_A^\circ)^2\}$$
$$\Delta\phi_d/C_D^\circ = \{K_1C_A^\circ/\alpha(1+K_1C_A^\circ)\}-\{K_1\Delta\phi_d/(1+K_1C_A^\circ)^2\}$$

where $\Delta\phi_a$ is the difference in the refraction per cm^3 of solution and acceptor; $\Delta\phi_d$ is the difference in the refraction per cm^3 of solution and donor; α is the extent of electronic polarization. C_A° and C_D° are the initial concentrations of acceptor and donor respectively. This model has been verified on some strong and weak complexes and was found better than that of earlier methods. $\Delta\phi_a$, $\Delta\phi_d$, and $\Delta\Omega C_{DA}$ (refraction per cm^3 due to charge-transfer complex) have also been used to Yoshida and Ōsawa's method. The K_1 obtained from the plot of $\Delta\phi_a$ or $\Delta\phi_d$ *versus* molar ratio of solutes were found more reliable for weak complexes than K_1 calculated from Yoshida and Ōsawa's plot. From these plots the percentage of contribution of donor or acceptor in total 30% solute aggregation as proposed by Yoshida and Ōsawa has been calculated. It is also noted that Yoshida and Ōsawa's method may give the reliable value for strong complexes but for weak complexes only differential refractometric method can provide the best values.

In our previous investigations,[1–4)] refractometric[1,4)] and differential refractometric[2–4)] methods have been used to determine the stoichiometry and formation constant of molecular complexes. In our first paper on refractometric technique,[1)] the refraction per cm^3 due to donor (D), acceptor (A) and donor–acceptor (DA) complex, $\delta\phi$, has been collectively considered, but in second paper,[3)] a differential refractometric method has been developed to get the refraction per cm^3 due to donor–acceptor complex, $\Delta\Omega C_{DA}$. In these papers the refractions per cm^3 due to D and DA ($\Delta\phi_d$) and A and DA ($\Delta\phi_a$) have not been considered. The purpose of this paper is to consider these refractions, to determine equilibrium and the results are compared with those of previous techniques.

Recently we have applied $\Delta\Omega C_{DA}$ to Yoshida and Ōsawa's method to calculate the K_1 of weak molecular complexes (phenol–naphthalene) and better results were noted.[2)] The purpose of the present paper is also to use $\Delta\Omega C_{DA}$, $\Delta\phi_a$, and $\Delta\phi_d$ to Yoshida and Ōsawa's method[5)] and to observe the effect on the equilibrium constant. An attempt has also been made to calculate the contribution of donor and acceptor separately in the total 30% solute (donor+acceptor) aggregation as proposed by Yoshida and Ōsawa[5)] for weak complexes.

Theoretical

Consider the condition of equilibrium for 1:1 complex DA, for the interaction of a donor (D) and an acceptor (A), $D+A\overset{K}{\rightleftharpoons}DA$; K is given by Eq. 1:

$$K = K_1K_\gamma\,;K_\gamma = \frac{\gamma_{DA}}{\gamma_D\gamma_A}. \tag{1}$$

In Eq. 1 γ is the Raoult's activity coefficient of species, i. In general, K_1 and $K\gamma$ are not constant but are functions of concentrations of reactants and products. Until recently complexes had been studied almost entirely in solution. It generally has been assumed that $K\gamma$ is unity; so that the calculations of equilibrium constants were based on the Eq. 2.

$$K_1 = C_{DA}/[(C_A^\circ-C_{DA})(C_D^\circ-C_{DA})] \tag{2}$$

where C_A° and C_D° represent the initial concentrations of acceptor and donor respectively and C_{DA} is the equilibrium concentrations of the complex.

In refractometric investigation, the refraction per cm^3 due to solution (donor+acceptor), ϕ; donor, ϕ_D; acceptor, ϕ_A, have been calculated as reported earlier.[1–4)] The difference in the refraction per cm^3 of solution and acceptor, $\Delta\phi_a$, may be calculated using the method of Colter and Grunwald.[6)]

$$10^3(\phi-\phi_A) = 6000(n-n_A)n_A/(n_A^2+2)^2 = \Delta\phi_a \tag{3}$$

Similarly $\Delta\phi_d$, the difference in the refraction per cm^3 of solution and donor may be calculated as:

$$10^3(\phi-\phi_D) = 6000(n-n_D)n_D/(n_D^2+2)^2 = \Delta\phi_d. \tag{4}$$

Now it can be assumed that the extent of charge-transfer from donor will measure the concentration of the complex and hence it will be proportional to the difference in the refraction per cm^3 of solution and acceptor, $\Delta\phi_a$, or donor, $\Delta\phi_d$. Now taking the case of $\Delta\phi_a$ we have,

$$C_{DA} = \alpha\Delta\phi_a, \tag{5}$$

where α is a constant determined by the extent of electronic polarization due to incidence of light. Hence Eq. 2 becomes,

$$K_1 = \alpha\Delta\phi_a/(C_A^\circ-\alpha\Delta\phi_a)(C_D^\circ-\alpha\Delta\phi_a). \tag{6}$$

On solving Eq. 6 as it was done in NMR,[7)] spectrophotometric,[8)] refractometric[1)] and differential refractometric[3)] techniques, Eq. 7 is obtained:

$$\Delta\phi_a/C_D^\circ = \{K_1C_A^\circ/\alpha(1+K_1C_A^\circ)\} - \{K_1\Delta\phi_a/(1+K_1C_A^\circ)^2\}. \tag{7}$$

Similarly, Eq. 8 can be obtained when $\Delta\phi_d$ was considered:

$$\Delta\phi_d/C_D^\circ = \{K_1C_A^\circ/\alpha(1+K_1C_A^\circ)\} - \{K_1\Delta\phi_d/(1+K_1C_A^\circ)^2\}. \tag{8}$$

Equations 9 and 10 as derived earlier[1,3)] have also been used to calculate K_1 for strong and weak molecular complexes.

$$\delta\phi/C_D^\circ = \{K_1C_A^\circ/\alpha(1+K_1C_A^\circ)\} - \{K_1\delta\phi/(1+K_1C_A^\circ)^2\} \tag{9}$$

$$\Delta\Omega C_{DA}/C_D^\circ = \{K_1C_A^\circ/\alpha(1+K_1C_A^\circ)\} - \{K_1\Delta\Omega C_{DA}/(1+K_1C_A^\circ)^2\} \tag{10}$$

As expected a plot of $\Delta\phi_a$ *versus* $\Delta\phi_a/C_D^\circ$, $\Delta\phi_d$ *versus* $\Delta\phi_d/C_D^\circ$, $\delta\phi$ *versus* $\delta\phi/C_D^\circ$ and $\Delta\Omega C_{DA}$ *versus* $\Delta\Omega C_{DA}/C_D^\circ$ gave a straight line with a slope $-\{K_1/(1+K_1C_A^\circ)^2\}$ and intercept, $K_1C_A^\circ/\alpha(1+K_1C_A^\circ)$ (Fig. 1).

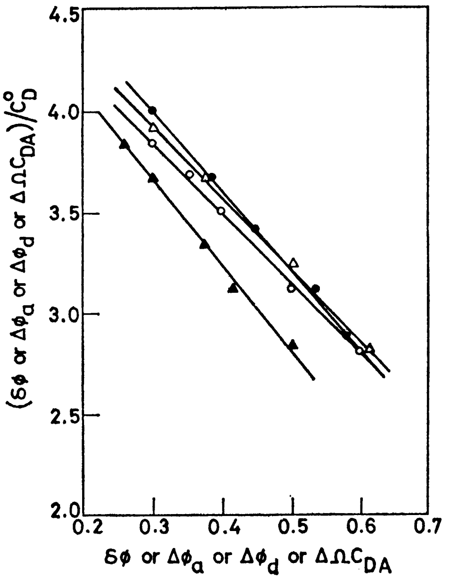

Fig. 1. Plots of $\delta\phi$ *versus* $\delta\phi/C_D^\circ$ (▲-▲-▲), $\Delta\phi_a$ *versus* $\Delta\phi_a/C_D^\circ$ (△-△-△), $\Delta\phi_d$ *versus* $\Delta\phi_d/C_D^\circ$ (●-●-●), and $\Delta\Omega C_{DA}$ *versus* $\Delta\Omega C_{DA}/C_D^\circ$ (○-○-○) for phenol-naphthalene complex in cyclohexane at 35 °C.

The equilibrium constant have also been calculated by Yoshida and Ōsawa's[5)] method using Eq. 11.

$$K_1 = 2\sqrt{k}\{\sqrt{k}(C+C')-(C+kC')\}/(C-kC')^2 \tag{11}$$

where C and C' are the maximum concentrations of both the systems and k is the maximum deviation from additive or base line when molar ratio of solutes is plotted against n^2 or $\Delta\phi_a$ or $\Delta\phi_d$ or $\Delta\Omega C_{DA}$. Equation 11 has also been used to calculate K_1 after getting more reliable value of k through the plots of $\Delta\phi_a$ or $\Delta\phi_d$ *versus* molar ratio of solutes. Differential refractometric[2)] method has also been used to calculate K_1. In this method, the refraction per cm^3 due to charge-transfer, $\Delta\Omega C_{DA}$ has been plotted against molar ratio of solutes.

Experimental

The method of experimentation was essentially the same as it was reported earlier.[1–4)]

Results and Discussion

Strong Interaction. The equilibrium constant (K_1) calculated for some strong complexes from Eqs. 7, 8, 9, and 10 are listed in Table 1. From this table it is clear that K_1 calculated from these equations are almost the same. Their percentage deviation from the spectrophotometric value comes under the experimental error (10—15%). For strong complexes, the concentration of solutes was kept low (10^{-3} mol dm^{-3}). Therefore the possibility of solute aggregation becomes quite low. The difference noted in K_1's values, obtained from these equations may be due to the bet-

TABLE 1. EQUILIBRIUM CONSTANT (K_1) AND SOLUTE AGGREGATION DATA FOR 1:1 MOLECULAR COMPLEXES IN DIFFERENT SOLVENTS AT 35 °C

Complex	Solvent	K_1/dm^3 mol^{-1}						SA_d	SA_a
		Refractometric methods				Spectrophotometric method			
		Eq. 9	Eq. 7	Eq. 8	Eq. 10		T/°C		
Phenol-naphthalene	Cyclohexane	5.8	6.2	5.2	4.6			11.25	18.75
Ethanol-naphthalene	Cyclohexane	5.2	4.8	3.8	3.2			9.00	21.00
Indole-chloranil	CCl_4	3.8	3.2	3.0	2.3	2.86(15)	25	14.0	16.0
Ph_3As-I_2	CCl_4	1100	840	830	770	790(12)	30		
Ph_3As-I_2	$CHCl_3$	8540	7530	7510	7142(3)	8330(12)	26		
Ph_3Sb-I_2	$CHCl_3$	1140	1020	1000	909(3)	1700(12)	26		
Et_3N-I_2	Cyclohexane	3250	2850	2820	2500(3)				
Et_3N-I_2	Heptane	2800	2350	2310	2000(3)	1740(13)			
Tryptophan-chloranil	50% (aq) Ethanol	221(4)	208	200	156(4)	176(14)	25		
Tyrosine-chloranil	50% (aq) Ethanol	172(4)	168	166	142(4)				
Phenylalanine-chloranil	50% (aq) Ethanol	166(4)	164	151	131(4)				

Number in parenthesis indicates the reference number.

terment of respective equations. The K_1 calculated from Eq. 9, in which refraction per cm^3 due to solvent was considered, show maximum percentage of error. But for the same complex if Eq. 7, in which the refraction per cm^3 of solution and acceptor was considered, the percentage error is less. The value of K_1 calculated from Eq. 8 were noted to be the same as calculated from Eq. 7. This indicates that the contribution of donor or acceptor in the solute aggregation is almost negligible. The best values have been obtained when Eq. 10 has been used in which differential refractometric method has been applied to evaluate $\Delta\Omega C_{DA}$.

The equilibrium constant calculated from Yoshida and Ōsawa's plot[5] and from the plot of $\Delta\phi_a$ or $\Delta\phi_d$ or $\Delta\Omega C_{DA}$ *versus* molar ratio of solutes are listed in Table 2. The K_1 calculated from the plot of n^2 *versus* molar ratio of solutes and from the plot of $\Delta\Omega C_{DA}$ *versus* molar ratio of solutes, show slight difference. This difference may again be interpreted due to the betterment of the differential refractometric method. Consequently for strong complexes Yoshida and Ōsawa's method can give the reliable value of K_1, but to get accurate results, the differential refractometric method should be used. We could not get different values for the maximum deviation from the base line (k), when plotted $\Delta\phi_a$ or $\Delta\phi_d$ *versus* molar ratio of solutes. Thus, it was not possible to calculate the different K_1 values through these plots. This was due to the limited accuracy of the instrument.

In strong complexes, a positive deviation was observed at 1:1 molar ratio of solutes indicating 1:1 stoichiometry of these complexes (Fig. 2). But in case of $Et_3N–I_2$ system a negative deviation was observed (Fig. 3). A similar observation was also made by Singh and Bhat.[9] After applying the differential refractometric method, negative $\Delta\Omega C_{DA}$ values were calculated and have been plotted against molar ratio of solutes (Fig. 4). From this figure it is clear that the deviation is large which indicates strong interaction between Et_3N and I_2. The molar refraction is a measure of deformability of the electronic seath. The decrease in refractive index of $Et_3N–I_2$ complex shows the increase of molar refractivity. Thus the complex is more polar. Similar results was obtained earlier through dipole moment studies on this system.[10]

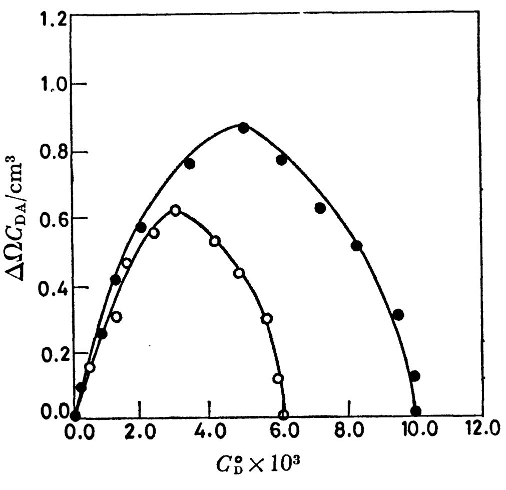

Fig. 2. Plot of $\Delta\Omega C_{DA}$ *versus* molar ratio of solutes indicating 1:1 stoichiometry of $Ph_3Sb–I_2$ complex in $CHCl_3$ at 35 °C.

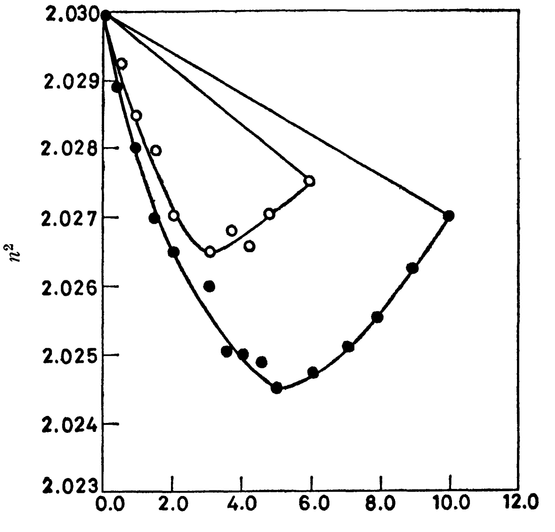

Fig. 3. Plot of n^2 *versus* molar ratio of solutes indicating 1:1 stoichiometry through negative deviation of $Et_3N–I_2$ in cyclohexane at 35 °C.

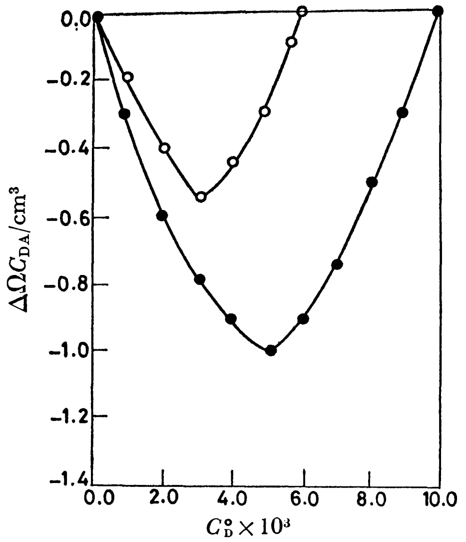

Fig. 4. Plot of $\Delta\Omega C_{DA}$ *versus* molar ratio of solutes indicating 1:1 stoichiometry through negative deviation of $Et_3N–I_2$ complex in cyclohexane at 35 °C.

Weak Interaction. From Table 1 it is evident that K_1 calculated for weak complexes from Eqs. 7, 8, 9, and 10 show greater difference. In order to get appropriate variation in scale due to limited accuracy of the instrument and low K_1 values, the solute concentration was raised (10^{-1} mol dm^{-3}).[2,5,11] As pointed out by Yoshida and Ōsawa[5] that at such a higher concentration, the solute aggregation occurs (about 30%) which prevents to give the reliable value of K_1. Therefore K_1 calculated from Eq. 9 shows maximum percentage of error. This error becomes less when Eq. 7 or 8 has been used but the best values were noted when Eq. 10 was used.

TABLE 2. EQUILIBRIUM CONSTANT (K_1) AND SOLUTE AGGREGATION DATA FOR 1:1 MOLECULAR COMPLEXES OBTAINED ON THE BASIS OF YOSHIDA AND ŌSAWA'S EQUATION IN DIFFERENT SOLVENTS AT 35 °C

Complex	Solvent	K_1/dm^3 mol^{-1} Refractometric methods				SA_d	SA_a
		1[a]	2[b]	3[c]	4[d]		
Phenol-naphthalene	Cyclohexane	6.2	5.6	5.2	4.9(2)	6.93	23.07
Ethanol-naphthalene	Cyclohexane	5.2	4.6	4.1	3.2	13.50	16.50
Indole-chloranil	CCl_4	3.6	3.1	2.8	2.3	11.53	18.47
Ph_3As-I_2	CCl_4	842	—	—	746.00		
Ph_3As-I_2	$CHCl_3$	8730	—	—	8710.00		
Ph_3Sb-I_2	$CHCl_3$	2127	—	—	1830.00		
Et_3N-I_2	Heptane	2550	—	—	2000.00		
Et_3N-I_2	Cyclohexane	2917	—	—	2552.00		
Tryptophan-chloranil	50% (aq) Ethanol	208(4)	—	—	157.54(4)		
Tyrosine chloranil	50% (aq) Ethanol	191.30(4)	—	—	140.72(4)		
Phenylalanine-chloranil	50% (aq) Ethanol	157.54(4)	—	—	127.16(4)		

Number in parenthesis indicates the reference number. a) Calculated from the plot of n^2 *versus* molar ratio of solutes. b) Calculated from the plot of $\Delta\phi_a$ *versus* molar ratio of solutes. c) Calculated from the plot of $\Delta\phi_d$ *versus* molar ratio of solutes. d) Calculated from the plot of $\Delta\Omega C_{DA}$ *versus* molar ratio of solutes.

The K_1 calculated for weak complexes from the plots of n^2 or $\Delta\phi_a$ or $\Delta\phi_d$ or $\Delta\Omega C_{DA}$ *versus* molar ratio of solutes are listed in Table 2. For weak complexes we could get different K values for the same system when plotted $\Delta\phi_a$ or $\Delta\phi_d$ *versus* molar ratio of solutes. Thus for the same system, different K_1 values calculated from these plots are noted in Table 2. It was not observed for strong complexes. For weak complexes, the best K_1 values have been observed when differential refractometric method was used in which the refraction per cm^3 due to charge-transfer complex ($\Delta\Omega C_{DA}$) is plotted against molar ratio of solutes. The present study indicates that the contribution of refraction per cm^3 of donor, acceptor and solvent is more important for moderate and weak complexes than that for strong complexes. Now, we can conclude that Yoshida and Ōsawa's method[5)] can give satisfactory results for strong complexes only and not for weak complexes. But more accurate values for strong complexes can be obtained by using differential refractometric method.[2)] For weak complexes only the differential refractometric method[2)] can provide the best values.

Assuming that K_1 calculated from the plot of $\Delta\Omega C_{DA}$ *versus* molar ratio of solutes are absolute, and that the K_1 calculated from the plot of n^2 *versus* molar ratio of solutes incorporates 30% solute aggregation, then the contribution of donor or acceptor in the total 30% solute aggregation may be calculated as:

$K_n2=K_1$ calculated from the plot of n^2 *versus* molar ratio of solutes or from Eq. 8.

$K_{\Delta\phi_a}=K_1$ calculated from the plot of $\Delta\phi_a$ *versus* molar ratio of solutes or from Eq. 7.

$K_{\Delta\phi_d}=K_1$ calculated from the plot of $\Delta\phi_d$ *versus* molar ratio of solutes or from Eq. 9.

$K_{\Delta\Omega C_{DA}}=K_1$ calculated from the plot of $\Delta\Omega C_{DA}$ *versus* molar ratio of solutes or from Eq. 10.

Thus,

$\Delta K_{da}=K_n2-K_{\Delta\Omega C_{DA}}$=Total 30% solute aggregation.

$\Delta K_a=K_n2-K_{\Delta\phi_d}$=Solute aggregation due to acceptor.

$\Delta K_d=(\Delta K_{da}-\Delta K_a)$=Solute aggregation due to donor.

Thus the contribution of acceptor (SA_a) and donor (SA_d) in total 30% solute aggregation may be expressed by Eqs. 12 and 13 respectively.

$$SA_a = 30\times\Delta K_d/\Delta K_{da} \tag{12}$$

$$SA_d = 30\times\Delta K_a/\Delta K_{da} \tag{13}$$

The values of SA_d and SA_a calculated from Eqs. 12 and 13 are listed in Tables 1 and 2. From these tables it is evident that in case of weak complexes the contribution of donor in total 30% solute aggregation is less than that of acceptor.

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