Modified Method for the Determination of Stoichiometry and Formation Constant of Molecular Complexes by Differential Refractometry

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A modified method has been proposed for the determination of stoichiometry and formation constant of molecular complexes by Job method using differential refractometry. A more adequate model has been presented and has been verified on some strong, moderate, and weak systems in different solvents at 35 °C. The formation constants obtained by this method are in good agreement with the literature values.

Recently we have applied the differential refractometric method[1,2] in Yoshida and Ōsawa's equation[3,4] to determine the stoichiometry and formation constant of molecular complexes which has yielded better results. In Yoshida and Ōsawa's method[5] two experimental sets are essential to calculate the equilibrium constant of a molecular complex. In this communication an attempt has been made to calculate the equilibrium constant of these complexes by using only one experimental set. For this purpose differential refractometry has been applied in Job method and a model has been developed which has been verified on strong as well as on weak molecular complexes.

We realize that in molecular complexes from acceptor, A, and donor, D, when $1:n$ complex is formed, it usually is accompanied by the formation of $1:1$, $1:2$,---, $1:n-1$ complexes. At this we have,

$$A + nD \underset{}{\overset{K_n}{\rightleftharpoons}} AD_n \quad (n>1) \tag{1}$$
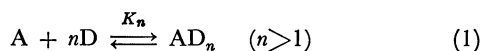
and

$$K_n = C_{ADn}/C_A C_D{}^n = C_{ADn}/(C_A{}^\circ - C_{ADn})(C_D{}^\circ - nC_{ADn})^n. \tag{2}$$

Let us assume, V_A and V_D are the volumes of A and D respectively, and $V=V_A+V_D$. Then the total concentration C_T is given by

$$C_T = 1/V(V_A C_A{}^1 + V_D C_D{}^1) = 1/V[(V-V_D)C_A{}^1 + V_D C_D{}^1], \tag{3}$$

where $C_A{}^1$ and $C_D{}^1$ represent the concentration of the stock solution of A and D, respectively. From Eq. 2 we have

$$C_{ADn} = K_n(C_A{}^\circ - C_{ADn})(C_D{}^\circ - nC_{ADn})^n$$
$$= K_n[(1 - V_D/V)(C_A{}^1 - C_{ADn})] \times [V_D/VC_D{}^1 - nC_{ADn}]^2. \tag{4}$$

Let $V_D/V=v$ and $C_D{}^1/C_A{}^1=r$. Then

$$C_{ADn} = K_n[(1-v)(C_A{}^1 - C_{ADn})](vC_A{}^1 r - nC_{ADn})^n. \tag{5}$$

To find the maximum value of C_{ADn} by varying v, we calculate

$$\frac{1}{C_{AD}} \cdot \frac{\partial C_{ADn}}{\partial v} = \frac{-C_A{}^1 - \partial C_{ADn}/\partial v}{(1-v)C_A{}^1 - C_{ADn}} + n\frac{rC_A{}^1 - n\partial C_{ADn}/\partial v}{vrC_A{}^1 - nC_{ADn}}. \tag{6}$$

Setting $\partial C_{ADn}/\partial v=0$, we obtain

$$C_{ADn}^{n(r-1)} = rC_A{}^1[v - n(1-v)]. \tag{7}$$

We chose $r=1$, then

$$v = n/(1+n); \quad C_T = C_D{}^1 = C_A{}^1. \tag{8}$$

In refractometric measurements, we assumed that the refraction per cm^3 of solution is due to the complexed and free acceptor refractions which may be expressed as,

$$\phi = \left(\frac{C_A{}^\circ - C_{ADn}}{C_A{}^\circ}\right)\phi_{CD} + \frac{C_{ADn}}{C_A{}^\circ}\phi_{AD}. \tag{9}$$

where $\phi_{CD}=\phi-\phi_D$, and solving Eq. 9 we get,

$$C_{ADn}/C_A{}^\circ = \phi_D/(\phi_{AD} - \phi_{CD}). \tag{10}$$

Now assuming $\phi_{AD}-\phi_{CD}=\Delta\phi_{AD}$; the maximum refraction per cm^3 of complex which may be calculated from the plot of $\Delta\Omega C_{DA}$ *versus* molar ratio of solutes.[†] Thus Eq. 10 becomes,

$$C_{ADn} = \phi_D/\Delta\phi_{AD}C_A{}^\circ. \tag{11}$$

Therefore, if C_{ADn} is a maximum, then $\phi_D/\Delta\phi_{AD}C_A{}^\circ$ would also be maximum at $v=n/(1+n)$. Thus by plotting $\phi_D C_A{}^\circ$ (or $\phi_D/\Delta\phi_{AD}C_A{}^\circ$) against X_D (mole fraction of donor), the maximum will occur at $X_D= n/(1+n)$ (Fig. 1). At this point we have,

Table 1. Equilibrium constant (K_1) data for some strong, moderate and weak molecular complexes at 35 °C

Complex	Solvent	$K_1/\mathrm{dm^3\ mol^{-1}}$		
		From Eq. 12	Spectrophotometric method	
			K_1	$T/°C$
Ethanol–naphthalene	Cyclohexane	2.7 ± 0.2		
Phenol–naphthalene	Cyclohexane	4.0 ± 0.2		
Ph$_3$N–I$_2$	Cyclohexane	9.2 ± 1.0	$12.5(9)$[a]	26
Tryptophan–chloranil	50% aq ethanol	149.0 ± 10.0	$176.0(10)$[a]	25
Dimethyl sulfide–I$_2$	Heptane	178.0 ± 10.0	$200.0(9)$[a]	25
Pyridine–I$_2$	Heptane	257.0 ± 15.0	$290.0(9)$[a]	25
Ph$_3$As–I$_2$	CCl$_4$	714.0 ± 25.0	$790.0(11)$[a]	30

a) Number in parentheses indicates the reference number.

[†] The values of ϕ, ϕ_D, ϕ_A, and $\Delta\Omega C_{DA}$ have been calculated as reported earlier.[6-8]
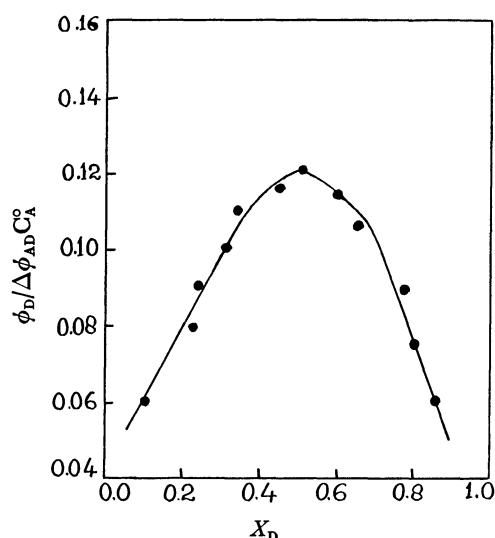
Fig. 1. A plot of X_D versus $\phi_D/\Delta\phi_{AD}C_A^\circ$ indicating 1 : 1 stoichiometry of phenol–naphthalene complex.

$$K_n = (\phi_D/\Delta\phi_{AD})/(C_D^\circ)^n(1-\phi/\Delta\phi_{AD})^{n+1} \qquad (12)$$

where $C_D^\circ = X_D C_T = n/(1+nC_T)$. Equation 12 has been used to calculate equilibrium constant (K_n) after determining n. Thus the K values calculated for some strong and weak 1:1 complexes are listed in Table 1. From this Table it is evident that the K values calculated from Eq. 12 are in good agreement with the spectrophotometric values. The present method involves an experimental simplicity because for one system only one experimental set is sufficient to calculate K but in Yoshida and Ōsawa's and differential refractometric methods, two experimental sets are necessary to get K values.

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