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# Determination of Stoichiometry and Formation Constant of Molecular Complexes by Differential Refractometry

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**Synopsis.** A more adequate method has been proposed to determine the stoichiometry and equilibrium constant of molecular complexes by Job method using differential refractometry in modification of Yoshida and Ōsawa method. This method has been verified on phenol-naphthalene system in cyclohexane at 35 °C. The equilibrium constant ($K_1$=4.9±0.20 dm$^3$ mol$^{-1}$), obtained by this method is in good agreement with the literature value.

In our previous investigations to determine the formation constants of molecular complexes, nuclear magnetic resonance,1) spectrophotometric,2) refractometric,3,4) and differential refractometric5) methods have been used. Yoshida and Ōsawa6) have also used the refractometric method to determine the equilibrium constant of 1:1 molecular complexes by Job method. In their approach they have plotted $n^2$ *versus* molar ratio of the solutes [donor(D) and acceptor(A)] and observed the maximum deviation from the additive line ($k$). As they have pointed out that due to limited accuracy of the instrument, they could not get the reliable value of the equilibrium constant ($K_1$) because of increased solute concentration (10$^{-1}$ mol dm$^{-3}$). In this communication an alternate method has been suggested to get the reliable value of $K_1$ under the conditions of Yoshida and Ōsawa, using the differential refractometry in Job method.

Reagent grade (BDH) phenol, naphthalene were used after further purification. A. R. grade cyclohexane was purified by standard procedures.7) Stock solutions of phenol (0.10 mol dm$^{-3}$) and naphthalene (0.10 mol dm$^{-3}$) were prepared by weighing on an analytical balance and then diluted to the required volume in volumetric flask by cyclohexane.

The refractive indices have been measured by Bausch and Lomb refractometer with an accuracy of ±0.0002. All the measurements were carried out at 35±0.1 °C. The experiment has been carried out for two sets. Firstly, the refractive indices of phenol and naphthalene (0.0 mol dm$^{-3}$—0.6 mol dm$^{-3}$) were observed separately and then the refractive indices of mixed solution (phenol+naphthalene), keeping the total concentration constant (0.6 mol dm$^{-3}$). Secondly, the refractive indices of phenol and naphthalene (0.0 mol dm$^{-3}$—1.0 mol dm$^{-3}$) were measured separately and then the refractive indices of mixed solution (phenol+naphthalene), keeping the total concentration constant (1.0 mol dm$^{-3}$). The refraction per cm$^3$ due to charge-transfer ($\Delta\Omega C_{DA}$) has been calculated for each set by using Eq. 1 as suggested by Sahai and Singh.5)

$$10^3(\phi-\phi_D) - \Omega_A C_A^\circ = 6000(n-n_D)n_D/(n_D^2+2)^2 - \Omega_A C_A^\circ = \Delta\Omega C_{DA}. \tag{1}$$

In Eq. 1 $\Omega_A C_A^\circ$ may be calculated by Eq. 2.

$$\Omega_A C_A^\circ = 10^3(\phi_A-\phi_0) = 6000(n_A-n_0)n_0/(n_0^2+2)^2 \tag{2}$$

The quantity $\Omega_j$ for the jth solute is defined as $\Omega_j=R_j-V_j\phi_0$; where $R_j$ is the apparent molar refraction and $V_j$ the apparent molar volume of the jth solute.5) The refraction per cm$^3$ of solvent ($\phi_0$), acceptor ($\phi_A$), donor ($\phi_D$), and solution ($\phi$) may be calculated by the relations: $\phi_0=(n_0^2-1)/(n_0^2+2)$; $\phi_A=(n_A^2-1)/(n_A^2+2)$; $\phi_D=(n_D^2-1)/(n_D^2+2)$; $\phi=(n^2-1)/(n^2+2)$, where $n_0$, $n_A$, $n_D$, and $n$ are the refractive indices of solvent, acceptor, donor and solution (donor+acceptor) respectively.3) A plot of $\Delta\Omega C_{DA}$ *versus* molar ratio of solutes for phenol naphthalene complex has been shown in Fig. 1 which suggests 1:1 stoichiometry of this complex. After getting a more reliable value of $k$ from this plot, the equilibrium constant ($K_1$) has been calculated by Yoshida & Ōsawa's6) equation (Eq. 3).

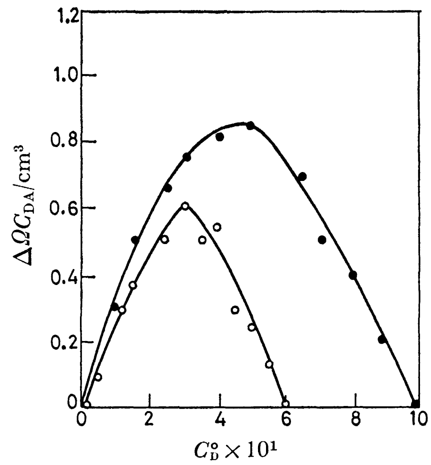

Fig. 1. A Plot of the refraction per cm$^3$ due to charge-transfer, $\Delta\Omega C_{DA}$/cm$^3$ *versus* molar ratio of solutes indicating 1:1 stoichiometry of phenol-naphthalene complex.

$$K_1 = 2\sqrt{k}\{\sqrt{k}(C+C')-(C+kC')\}/(C-kC')^2, \tag{3}$$

where $k$ is the maximum deviation from the base line for two different concentrations of solutes ($C$ and $C'$).

The refractive index of phenol as well as that of naphthalene increases in cyclohexane with concentration. When phenol solution is mixed with naphthalene, a neutral complex is formed. The plot of $\Delta n$, the difference in refractive indices of calculated and observed values, against (complex) is linear indicating that there is no interaction between the complex and individual species.

A change in electron cloud density in the neutral atom or molecule will lead to a change in the polarizability. Since the complex is generally more polar than the components, the electronic polarizability or refractive index increases and the deviation depends upon the extent of interaction between the donor and acceptor. Therefore stronger the complex, the larger the deviation in the refractive index value.

The small deviation in refractive index of the mixed system of phenol and naphthalene in cyclohexane shows that the interaction between phenol and naphthalene is weak. In the present case the deviation is positive and the maximum is observed at 1:1 molar ratio. The $K$ value obtained thus is $5.8\pm0.20$ dm$^3$ mol$^{-1}$ at 35 °C which is slightly higher compared to the value calculated from the available data.[8] But the $K$ value obtained from the plot of $\Delta\Omega C_{DA}$ *versus* molar ratio of solutes is $4.9\pm0.20$ dm$^3$ mol$^{-1}$ at 35 °C which is almost comparable with that of the calculated value. As the refractive index for visible light varies with the wavelength, the electron polarization is somewhat uncertain. So the $K$ value obtained by the plot of $n^2$ *versus* molar ratio of solutes must be accepted with care.

Due to the limited accuracy of the instrument, the solute concentration was raised (0.10 mol dm$^{-3}$) in order to get $k$ value sufficient to fit in Eq. 3. At this higher concentration, the solute aggregation occurs which prevents to get the reliable value of $K_1$. But this problem has been resolved in the present scheme in which instead of the plot of $n^2$ *versus* molar ratio, the refraction per cm$^3$ due to charge-transfer, ($\Delta\Omega C_{DA}$), has been calculated and plotted against molar ratio. The equilibrium constant obtained by the plot of $\Delta\Omega C_{DA}$ *versus* molar ratio of solutes ($K_1=4.9\pm0.20$ dm$^3$ mol$^{-1}$) is more reliable than that of $K_1$ obtained by the plot of $n^2$ *versus* molar ratio of the solutes ($K_1=5.8\pm0.20$ dm$^3$ mol$^{-1}$) which is in agreement with that of literature value.[9] In the present scheme, the refraction per cm$^3$ due to solvent, acceptor and donor has been considered whereas in the earlier methods[6,10,11] the square of refractive indices ($n^2$) of solution was taken into account only. Thus the data obtained by the present scheme are more reliable than that of earlier one. It, therefore, appears that the present method may prove better to calculate the equilibrium constant ($K_1$) of the weak complexes within the limited accuracy of the instrument for which the concentration of the solutes is ought to be high. Though the present scheme involves a lot of complexity in the experimental procedure but the data obtained are more reliable compared to the earlier method.[6]

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