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Differential Refractometry of Molecular Complexes: A Reinvestigation

Short Communication

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A modified plot method is used to calculate equilibrium constants of molecular complexes. This method (*Sahai* and *Singh*'s plot) is compared with the method of *Yoshida* and *Osawa*.

(Keywords: Charge-transfer complexes; Differential refractometry; Tetracyanoethylene)

Differentielle Refraktometrie von Molekülkomplexen: Eine Neuuntersuchung (Kurze Mitteilung)

Eine modifizierte refraktometrische Methode zur Berechnung von Gleichgewichtskonstanten von Molekülkomplexen wird verwendet und diese mit der Methode von *Yoshida* und *Osawa* verglichen.

Several investigators have used the refractometric method to calculate the equilibrium constant and stoichiometry of molecular complexes[1–10]. Recently *Singh* and *Bhat*[4] have also used this technique to calculate the equilibrium constant (K_1) and stoichiometry of charge-transfer complexes of tetracyanoethylene (*TCNE*) with benzene, *p*-xylene and hexamethylbenzene (*HMB*). They have calculated the value of K_1 by means of *Yoshida* and *Osawa*'s[2] eq. (1) in which n^2 is plotted against the molar ratio of solutes (C and C') and observed the maximum deviation from the additive line (k).

$$K_1 = 2\sqrt{k}\,[\sqrt{k}\,(C + C') - (C + kC')]/(C - kC')^2 \qquad (1)$$

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In the present communication a modified *Yoshida* and *Osawa*'s plot as suggested by *Sahai* and *Singh*[8] has been used to calculate the equilibrium constant for the molecular complexes studied by *Singh* and *Bhat*[4]. In this method instead n^2, $\Delta\Omega\, C_{DA}$, the refraction per cm^3 due to the charge-transfer complex is plotted against the molar ratio of solutes and the maximum deviation from the base line (k) is observed. The values of $\Delta\Omega\, C_{DA}$ were calculated as reported earlier[6–10]. A representative plot of molar ratio of solutes vs. $\Delta\Omega\, C_{DA}$ indicating 1:1 stoichiometry of the complexes is shown in Fig. 1.

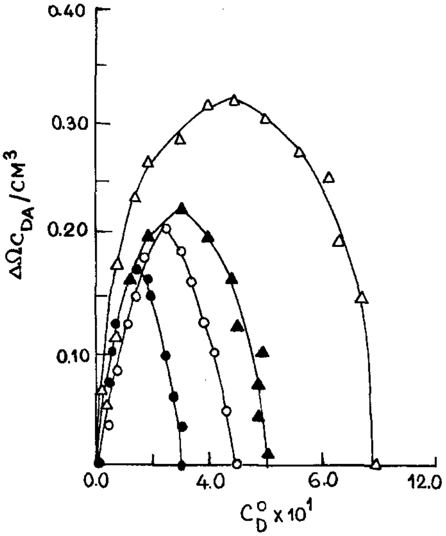

Fig. 1. Plots of molar ratio of solutes vs. the refraction per cm^3 due to charge-transfer complex, $\Delta\Omega\, C_{DA}$ indicating 1:1 stoichiometry of benzene—*TCNE* (●—●—● and ○—○—○) and *p*-xylene—*TCNE* (▲—▲—▲ and △—△—△) complexes in cyclohexane at 35 °C

The K_1 obtained from the plot of molar ratio of solutes vs. n^2 and $\Delta\Omega\, C_{DA}$ are listed in Table 1. From this table it is evident that K_1 obtained by *Sahai* and *Singh*'s method[8] are more reliable than that of *Yoshida* and *Osawa*'s method[2]. Due to the limited accuracy of the instrument, the solute concentration was raised (0.3 mol/l—0.010 mol/l) in order to get a k value sufficient to fit in eq. (1). At this higher concentrations a solute aggregation occurs which prevents to get a reliable value for K_1. The difference in K_1 values for the same system obtained from *Yoshida* and *Osawa*'s[2] and *Sahai* and *Singh*'s[8] methods may be interpreted due to solute aggregation. Thus the problem of solute aggregation was solved in the approach of *Sahai* and *Singh*. In this scheme, the refraction per cm^3 due to solvent, acceptor and donor has been considered whereas in *Yoshida* and *Osawa*'s plot[2] the n^2 of the solution (donor + acceptor) was taken in account only. Therefore, the data obtained from *Sahai* and *Singh*'s plot[8] were more reliable than

Table 1. *Equilibrium constants (K_1) for* 1:1 *molecular complexes of benzene and methylbenzenes with TCNE in cyclohexane at 35* °C

	Spectrophotometric		Refractometric Methods	
	K_1	T/°C	*Yoshida* and *Osawa*'s Plot	*Sahai* and *Singh*'s Plot
Benzene—*TCNE*	1.54	35	1.70 ± 0.20	1.30 ± 0.20
p-xylene—*TCNE*	5.97	35	6.40 ± 0.30	5.60 ± 0.30
HMB—*TCNE*	215.6	35	317 ± 10	264 ± 10

Equilibrium Constant (K_1) l mol^{-1}

that of *Yoshida* and *Osawa*'s[2] method. It seems therefore that the present scheme may prove better to calculate the K_1 of weak complexes within the limited accuracy of the instrument for which the concentration of the solutes was too high.

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