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Study of Molecular Complexes by Refractometry

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The refractive index measurement technique is used to investigate molecular complex formation in liquid solutions and the association constants are determined directly. The association constants at 25 °C and heats of complexation for naphthalene–phenol, benzene–tetracyanoethylene, *p*-xylene–tetracyanoethylene, hexamethylbenzene–tetracyanoethylene, and triethylamine–iodine in cyclohexane are 8.2, 2.2, 8.6, 231, and 4620 $dm^3\ mol^{-1}$ and 19.25, 11.30, 18.00, 32.21, and 51.46 kJ/mol, respectively. These values agree well with the literature data obtained by spectroscopic methods.

The Benesi-Hildebrand equation[1] and their modified equations[2,3] have been widely used in the study of molecular complexes. However, these methods were subject to criticism, particularly in the case of weakly interacting systems, as the valid separation of K and ε from $K\varepsilon$ product may be difficult to attain, the error increasing with the decrease in the strength of the complexes.[4–6] So if one wants to have accurate values of $K\varepsilon$, K, and ε, which are essential in developing and testing theories[7] of electron donor-acceptor interactions, one has to supplement the results obtained by the non-spectral methods to the one obtained by spectral methods. Recently we have shown that the equilibrium constant, K, can be determined directly by the non-spectral methods like surface tension[8] and refractive index measurements[9] and we have felt that in order to establish the suitability of refractometry in obtaining reliable value of K directly, an extensive studies on the applications of this method to various systems is worthwhile to carry out. In the present paper the studies of naphthalene–phenol, methylbenzenes–tetracyanoethylene, and triethylamine–iodine in cyclohexane have been reported as they represent weak, moderate and strong interactions between electron donors and acceptors.

Experimental

Materials. Triethylamine (Riedel de Hainay) was treated with acetic anhydride to remove primary and secondary amines.[10] It was then dried over anhydrous KOH pellets and fractionally distilled (bp 89.5 °C). Iodine (BDH, A.R. grade) was purified by sublimation from a mixture of iodine and potassium iodide (in the ratio of 2.5 : 1). Phenol was crystallized from cyclohexane–ethanol mixture (mp 42.8 °C). Nephthalene, *p*-xylene, and hexamethylbenzene were purified by the standard procedures.[11] Tetracyanoethylene (Du Pont) was purified by crystallization (from chlorobenzene solution) and vacuum sublimation (mp 199.5°C in sealed tube). Benzene and cyclohexane (BDH Spectro quality) were used as such.

Method. The refractive index of solution was measured using Pulfrich refractometer (Adam Hilger No. M 48302/20210).[9] A mercury vapor lamp was used as source of light. The refractive index was obtained by measuring the angle of refraction (θ) for green (546 nm) and yellow (578 nm) lines of mercury, using the formula

$$\eta^2 = \eta_0^2 - \sin^2\theta, \tag{1}$$

where η_0 is the prism constant for a particular wavelength at a particular temperature.

The refractive indices of triethylamine, iodine, benzene, *p*-xylene, hexamethylbenzene, tetracyanoethylene, naphthalene, and phenol in cyclohexane and those of "mixed solutions," keeping the total concentration constant were measured at 25, 30, 35, 40, and 45 °C. The temperature of solution was maintained constant ($\pm$0.1 °C) by circulating water from a thermostat. The refractive index could be determined with an accuracy of $\pm$0.00002.

The refractive index at infinite wavelength can be calculated using Couchy's approximation,[12]

$$n_\infty = \frac{n_y\lambda_y^2 - n_g\lambda_g^2}{\lambda_y^2 - \lambda_g^2}, \tag{2}$$

where n_y, λ_y and n_g, λ_g are refractive index and wavelength of yellow and green line of mercury respectively. The experiments were repeated at least twice and the values obtained were within the experimental error.

The stoichiometry of the complexes was determined by the continuous variation method.[13]

Determination of Equilibrium Constant

The non-linear plot of any physical property of the "mixed solution" against the concentration of pure components, *i.e.*, the deviation from ideal behaviour of the pure components in solution, is an indication of the interaction between the two species, namely the donor D, and the acceptor A, (neglecting the solvent effect). If we can assume that the deviation is entirely due to the complex alone, then the deviation should be proportional to the concentration of the complex. Baur and his co-workers[14] had developed a procedure by which deviations from additivity of the total polarization and refraction of a binary solution can be related to the association constant of a complex (AD) formed from two non-polar molecules. However, the equilibrium constant can be calculated for ternary systems, using the equation proposed by Yoshida and Osawa,[15]

$$K = \frac{2\sqrt{k}[\sqrt{k}(C+C') - (C+kC')]}{(C-kC')^2}, \tag{3}$$

where K is equilibrium constant in $dm^3\ mol^{-1}$, k is the ratio of the maximum deviations for total concentrations of C and C' in two different sets. Here we should note that the results obtained by the continuous variation method must be taken with caution since with this method it is not always possible to observe all the complexes present in the solution, and in such cases the titration method should be followed.[16]

The equilibrium constant, K, can also be obtained as described earlier.[8]

Consider the interaction of A with D,

$$A + D \rightleftharpoons AD.$$

Let C_A, C'_A, C_D, and C'_D be the initial concentrations of the acceptor and donor respectively for the two sets of solutions, and C_{AD}, C'_{AD} be the concentration of the complexes. For the first set,

$$K = \frac{C_{AD}}{[(C_D - C_{AD})(C_A - C_{AD})]}, \quad (4)$$

and for the second set,

$$K = \frac{C'_{AD}}{[(C'_D - C'_{AD})(C'_A - C'_{AD})]}, \quad (5)$$

therefore,

$$\frac{C_{AD}}{[(C_D - C_{AD})(C_A - C_{AD})]} = \frac{C'_{AD}}{[(C'_D - C'_{AD})(C'_A - C'_{AD})]}. \quad (6)$$

If there is a linear relationship between Δn and the concentration of the complex (*i.e.*, similar to the test of Beer's law), we can conclude that if the two solutions show the same deviations of refractive indices, then they must have the same concentration of the complex. Therefore if

$$\Delta n_1 = \Delta n_2, \text{ then } C_{AD} = C'_{AD}.$$

From the above equations, we get

$$K = \frac{(C'_A C'_D - C_A C_D)[(C'_A + C'_D) - (C_A + C_D)]}{[(C'^2_A + C_A C_D) - C'_A(C_A + C_D)][(C'^2_D + C_A C_D) - C'_D(C_A + C_D)]}. \quad (7)$$

The K values thus calculated agree well with the values calculated using Eq. 3.

Results and Discussion

Naphthalene–Phenol System. The refractive indices of naphthalene and phenol in cyclohexane increase linearly with the increase in concentration of the solute in the experimental range of concentrations (0.01—0.10 mol dm^{-3}). The plot of n^2_∞ against the concentration of naphthalene in the "mixed solutions" of naphthalene–phenol shows only one maximum at a position

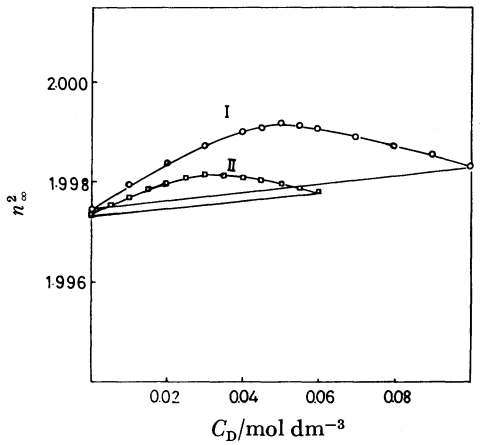

Fig. 1. Plot of n^2_∞ *vs.* concentration of naphthalene in naphthalene–phenol system (solvent : cyclohexane). Total concentration: I: 0.10 mol dm^{-3}, II; 0.06 mol dm^{-3}.

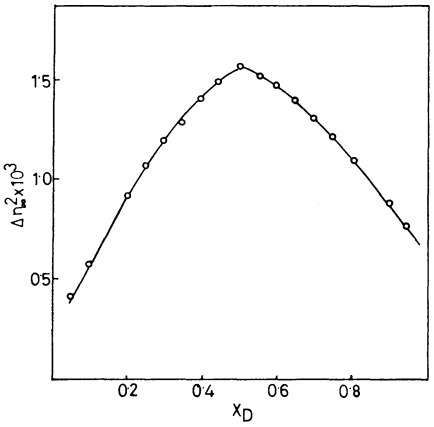

Fig. 2. Plot of Δn^2 *vs.* mole fraction of naphthalene in naphthalene–phenol in cyclohexane.

Table 1. Square of refractive indices, n^2_∞, of naphthalene–phenol system of different compositions in cyclohexane

Concentration/mol dm^{-3}		Square of refractive indices, n^2_∞,		
Naphthalene	Phenol	Obsd	Calcd	Difference ($\Delta n^2 \times 10^3$)
1st set: Total concentration=0.10 mol dm^{-3}.				
0.000	0.100	2.03528	—	—
0.005	0.095	2.03551	2.03514	0.37
0.010	0.090	2.03570	2.03514	0.56
0.020	0.080	2.03604	2.03514	0.90
0.025	0.075	2.03620	2.03514	1.06
0.030	0.070	2.03633	2.03514	1.19
0.035	0.065	2.03644	2.03514	1.30
0.040	0.060	2.03654	2.03514	1.40
0.045	0.055	2.03661	2.03514	1.47
0.050	0.050	2.03670	2.03514	1.56
0.055	0.045	2.03664	2.03514	1.50
0.060	0.040	2 03661	2.03514	1.47
0.065	0.035	2.03653	2.03514	1.37
0.070	0.030	2.03644	2.03514	1.30
0.075	0.025	2.03633	2.03514	1.19
0.080	0.200	2.03622	2.03514	1.08
0.090	0.100	2.03602	2.03514	0.88
0.095	0.005	2.03590	2.03514	0.76
0.100	0.000	2.03579	—	—
2nd set: Total concentration=0.06 mol dm^{-3}				
0.000	0.060	2.03494	—	—
0.005	0.055	2.03522	2.03496	0.26
0.010	0.050	2.03550	2.03497	0.53
0.015	0.045	2.03570	2.03497	0.73
0.020	0.040	2.03592	2.03496	0.96
0.025	0.035	2.03610	2.03496	1.14
0.030	0.030	2.03627	2.03496	1.31
0.035	0.025	2.03616	2.03497	1.19
0.040	0.020	2.03607	2.03497	1.10
0.045	0.015	2.03593	2.03496	0.97
0.050	0.010	2.03579	2.03497	0.82
0.055	0.005	2.03563	2.03497	0.66
0.060	0.000	2.03545	—	—

of half the concentration of naphthalene (Fig. 1; Table 1); similarly the plot of Δn^2, difference in square of refractive indices of the calculated and observed values against the concentration of donor (in mole fraction) shows only one maximum at 0.5 mole fraction (Fig. 2). These indicate that naphthalene forms only 1 : 1 complex with phenol in the experimental range of concentrations.

By knowing the maximum deviation in Δn^2 for two sets of different total concentrations (10.0 and 6.0×10^{-2} mol dm^{-3}) the equilibrium constants for different temperatures were calculated. The equilibrium constant at 25 °C and the enthalpies are 8.20 ± 0.50 mol dm^{-3} and 19.25 ± 1.25 kJ/mol respectively (Table 2). These data indicate that equilibrium constant and enthalpy obtained by the above mentioned procedure are reasonably in good agreement with the literature values.

Methyl Benzenes–Tetracyanoethylene Systems. The refractive indices of benzene, *p*-xylene, hexamethylbenzene, and tetracyanoethylene in cyclohexane increase linearly with an increase in concentration of the solute in the experimental concentration range (0.01—0.15 mol dm^{-3}). When tetracyanoethylene is mixed with benzene, *p*-xylene or hexamethylbenzene solutions, stable neutral complex is formed, A plot of Δn, the difference in refractive indices of the calculated and observed values against the calculated concentration of the complex is linear; this indicates that there is no interaction between the complex and the individual species. A plot of n_∞^2 against the concentration of the donor shows only one maximum at a position of half the donor concentration, indicating that there is predominantly one type of complex, *i.e.* 1 : 1, when the donor concentration is comparable to that of the acceptor. Higher order molecular complexes may be formed only when the concentration of either one of the two components is very high.[17]

The values of K_c and $-\Delta H^\circ$ thus obtained are summarised in Table 2 along with the literature data. In the case of benzene–TCNE, the literature data are under different conditions. From the data, it is evident that the values of K_c and $-\Delta H^\circ$ obtained by refractometry are in good agreement with the literature data except for the HMB–TCNE system. It has been shown recently that the value of K_c, based on the assumption that only 1 : 1 complex is formed in HMB–TCNE, is much lower than the value of K_c reported earlier in the literature, which includes other types of complexes.[17] Here it must be noted that the literature data are under different sets of conditions,[3,18] and that the value of K_c depends on the experimental conditions such as whether A$\gg$D, D$\gg$A, or A$\approx$D, and also on the nature of solvents.

The values of K_c (at only one temperature, for the sake of brievity), ΔH° and the other thermodynamic parameters thus obtained for methylbenzenes–tetracyanoethylene in cyclohexane are given in Table 2 along with the literature data. From the data, it is evident that the relative enthalpies and free energies obtained from a series of donors, increase with the increased methylation of the donor. These observations are consistent with charge-transfer theory[7] and go in parallel with the literature data for similar π-π complexes and the values of K_c and ΔH° obtained by refractometry are thus in good agreement with the data obtained by spectroscopic methods. Here it must be worth mentioning that ΔH° values are more reliable than the equilibrium constants obtained by separating K and ε from $K\varepsilon$. As ΔH° values which are more reliable than K values, are in very good agreement with the literature data, we feel our values of K which are obtained directly, are probably more acceptable than the literature data.

Triethylamine–Iodine System. The refractive index of triethylamine in cyclohexane decreases whereas that of iodine increases with the concentration of solute in the experimental range of concentration ($0.5—10.0\times10^{-3}$ mol dm^{-3}). The total concentrations of triethylamine–iodine (6.0 and 10.0×10^{-3} mol dm^{-3}) are such that when they are mixed, neutral complex is formed which was confirmed spectroscopically.[19]

The plot of n_∞^2 against the concentration of triethylamine in triethylamine–iodine, shows one maximum at a position of half the donor concentration; similarly the plot of Δn^2, difference in square of refractive indices of the calculated and observed values against the concentration of donor (in mole fraction) shows only one maximum at 0.5 mole fraction. These indicate that

Table 2. Equilibrium constant, K_C, and other thermodynamic parameters for naphthalene–phenol, methylbenzenes–tetracyanoethylene, and triethylamine–iodine in cyclohexane

System	K(25 °C) / dm^3 mol^{-1}	$-\Delta H^\circ$ / kJ mol^{-1}	$-\Delta G^\circ$ / kJ mol^{-1}	$-\Delta S^\circ$ / J K^{-1} mol^{-1}
Naphthalene–Phenol	8.2 ± 0.5 (5.0[a])	19.25 ± 1.25	5.02	47.7
Benzene–TCNE	2.2 ± 0.2 (2.0[b])	11.30 ± 1.25 (10.46[c])	2.10	30.9
p-Xylene–TCNE	8.6 ± 0.5 (7.6[c])	18.00 ± 2.10 (14.22[b])	5.02	43.5
Hexamethylbenzene–TCNE	231 ± 10 (263[c]) (417[d]) (219[e])	32.21 ± 2.10 (32.2[b])	12.55	66.6
Triethylamine–Iodine	4620 ± 50 (4690[f])	51.46 ± 0.6 (51.04[f])	20.50	103.8

The values in the parentheses refer to the literature data. Solvent : CH_2Cl_2 a) A. S. N. Murthy and C. N. R. Rao, *Appl. Spectrosc. Revs.*, **2**, 69 (1969). b) P.H. Emslie and R. Foster, *Tetrahedron*, **21**, 2851 (1965). c) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958). d) D. Dodson, R. Foster, A. A. S. Bright, M. I. Foreman, and J. Gorton, *J. Chem. Soc., B*, **1971**, 1283. e) R. A. Singh, S. P. Mishra, and S. N. Bhat, *Proc. Ind. Acad. Sci.*, **89**, 139 (1980). f) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).

triethylamine forms only 1 : 1 complex with iodine in the experimental range of concentrations. From this it appears that triethylamine forms only one 1 : 1 complex with iodine and not any other complexes as suggested by Schmulback.[20] The higher order complexes are invariably formed only when the concentration of one of the two components is in very much excess (*i.e.* D⋙A or A⋙D), but in the present case, as the concentration of donor and acceptor are comparable, the higher order complexes seem to be improbable.

The plot of Δn^2 against the concentration of complex (calculated using the equilibrium constant for different initial donor and acceptor concentrations in all the cases) is linear. This justifies the assumption that the deviation is proportional to the concentration of the complex and there is no interaction between the complex and individual species.

The equilibrium constant and enthalpy value for triethylamine–iodine system are given in Table 2. It is evident from the data that the equilibrium constant and other thermodynamic parameters determined from refractometry are in very good agreement with the literature data.

The increment in the dipole moment is directly related to charge-transfer and the dipole moment of a complex depends on the total polarizability of the complex. However, in the calculation of the dipole moment of complex, so far, the electronic and atomic (which is about 5—10% of electronic) polarizability has been neglected on the ground that the electronic and atomic polarization of the complex is equal to the sum of the electronic and atomic polarization of individual molecules.[17,21,23] As can be seen from the above data and figures, whenever there is any interaction between the molecules, the electronic polarizability exceeds the additive value. Therefore the contribution of the electronic polarizability cannot be neglected if one wants to determine the exact dipole moment of the complex.

Thus as shown earlier, our present observations confirm our earlier suggestive evidences that the refractive index measurement method can be used for not only detecting the formation of the complex but also to determine its equilibrium constants directly even in the case of very weak complexes

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