

Use of Refractometry in the Study of Stoichiometries & Equilibrium Constants of Molecular Complexes: Triethylamine-Iodine & Phenol-Naphthalene Complexes

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Refractive index measurement technique can be used to investigate molecular complex formation in liquid solution. The association constant, K , for triethylamine-iodine 1:1 complex is 2.25×10^3 litre mole⁻¹ and for phenol-naphthalene it is 6.35 litre mole⁻¹ at 35° in cyclohexane.

ALTHOUGH spectroscopic method has been used extensively to study the molecular interactions, this technique is not feasible when there is only a slight perturbation of either the donor or acceptor absorption bands due to weak interactions¹⁻³. In such cases it is not only difficult to get the correct stoichiometry of the complex formed but also to get the accurate value of K_c and ϵ_c of the weak complexes⁴. Though the possibility of nonspectral methods to study the complexation is mentioned in the literature, hardly any attempt has been made in this direction^{5,6}. Presently we have employed refractive index measurement technique to study the molecular complexes of triethylamine with iodine and naphthalene with phenol.

Triethylamine, iodine and the solvent cyclohexane were purified by the standard procedures⁷. The refractive indices of pure and mixed solutions keeping the total concentration of mixed solutions constant (6 and 10 millimoles in two sets), were measured at 35° ± 0.1° using a Pulfrich refractometer with an accuracy of 0.00002. A mercury lamp was used as the light source.

The refractive index of triethylamine in cyclohexane decreases, while that of iodine increases with increase in concentration; the decrease or increase is linear in the concentration range 0.5–10 × 10⁻³M. When iodine solution is mixed with triethylamine, a neutral complex is formed in the experimental range of concentration. The plot of Δn , difference in refractive indices of the calculated and observed values, against [complex] is linear indicating that there is no interaction between the complex and the individual species. The plot of n^2 versus [donor] shows only one minimum at half the [donor] (Fig. 1), indicating the formation of only 1:1 complex. We could not detect any other minimum in the plot. From this, it looks to us that triethylamine forms only one 1:1 complex and no other complexes as suggested by Schulback⁸ in the concentration range used.

The deviation from ideal behaviour of the pure components is due to the interaction of the two species, namely the donor and the acceptor, and the deviation is proportional to the concentration of the complex. Assuming that the deviation is entirely due to the complex alone, the equilibrium constant, K , can be calculated using the equation proposed

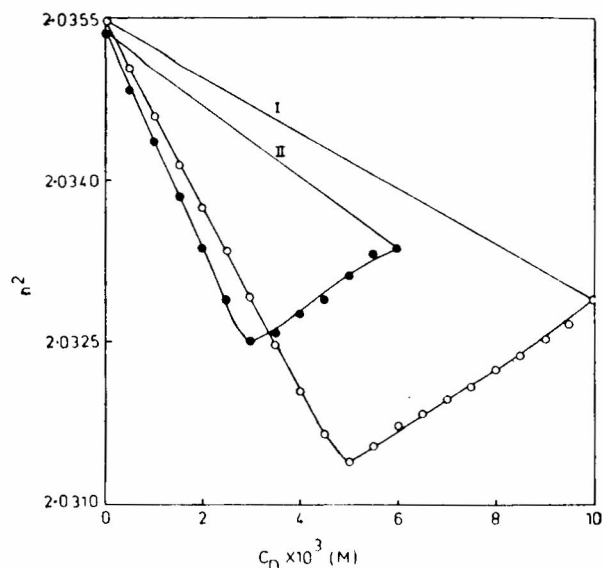


Fig. 1 — Variation of n^2 with the concentration of triethylamine for the mixed solutions in cyclohexane [I, total concentration = 10×10^{-3} M; and II, total concentration = 6×10^{-3} M]

by Yoshida and Osawa⁹,

$$K = \frac{2\sqrt{k}\{\sqrt{k}(c+c') - (c+kc')\}}{(c-kc')^2} \quad \dots(1)$$

where K is equilibrium constant in litre mol⁻¹, k is ratio of the maximum deviations for total concentrations of c and c' and c and c' are total [donor] in mol litre⁻¹ in two different sets.

The value of K thus calculated comes out to be 2.25×10^3 litre mol⁻¹ at 35°, which can be compared to the value reported by spectroscopic methods^{1,10}. The molar refraction is a measure of deformability or electron polarizability of the electronic sheath. In the case of triethylamine-iodine complex, the refractive index decreases, the molar refractivity increases, i.e. the complex is more polar or the system is less tightened. This observation goes in parallel with the observation made earlier on the dipole moment of triethylamine-iodine complex¹¹.

The small deviation in refractive index of the mixed systems 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 6.35 litre mol⁻¹ at 35° which is slightly higher compared to the value calculated from available data¹⁰. As the refractive index (molar refraction) for visible light varies with the wavelength, the electron polarization is somewhat uncertain. So the K values obtained by this method must be accepted with care. However, this technique can be used to indicate the formation of a complex and give some idea as to the relative strength of the interaction. It is a good method for studying the interaction between polar components.

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Dissociation Constant of 1-(2,3-Dihydroxy-4-pyridylazo)-benzene-4-sulphonic Acid (DHP-4S) & Stability Constants of Its Complexes with Mn(II), Cd(II), Co(II), Ni(II), Zn(II), Fe(II) & UO_2^{2+}

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Dissociation constant of 1-(2,3-dihydroxy-4-pyridylazo)-benzene-4-sulphonic acid (DHP-4S) and stability constants of its complexes with UO_2^{2+} , Ni(II), Co(II), Fe(II), Zn(II), Cd(II) and Mn(II) have been determined potentiometrically in aqueous medium at different ionic strengths and temperatures. The order of stability constants of the complexes of the various metal ions is: $\text{Mn(II)} < \text{Cd(II)} < \text{Co(II)} < \text{Zn(II)} < \text{Ni(II)} < \text{Fe(II)}$. In the case of UO_2^{2+} , only $\log K_2$ could be determined. Values of δH and E_r (Mn-Zn) have been calculated.

DISSOCIATION constant of 2,3-dihydroxypyridine (DHP) has been reported earlier¹. 1-(2,3-Dihydroxy-benzene-4-pyridylazo)-4-sulphonic acid (DHP-4S) has been used as an analytical reagent for the complexometric determination of Zn(II), Cd(II), Hg(II)² and Co(II), Ni(II), Cu(II)³. Garg *et al.*⁴ have used the reaction for the formation of DHP-4S, as a sensitive test for nitrite ion. The present note deals with the determination of dissociation constant of the DHP-4S and stability constant of its complexes with Mn(II), Cd(II), Co(II), Ni(II), Zn(II), Fe(II) and UO_2^{2+} , in aqueous medium and at different ionic strengths and temperatures.

1-(2,3-Dihydroxy-4-pyridylazo)-benzene-4-sulphonic acid was prepared by diazotizing sulphanilic acid and

subsequently coupling the diazotized product with 2,3-dihydroxypyridine. Purity of the ligand was checked by TLC and elemental analyses.

Melting point of the purified DHP-4S is high, i.e. above 360°. Solution of the ligand was prepared in doubly distilled water. All the metal ion solutions were prepared from the corresponding nitrates or sulphates (BDH, AR) and were standardized by conventional methods wherever necessary. Chemically pure sodium perchlorate (Riedel) was used to keep the ionic strengths constant (0.005, 0.06, 0.1 and 0.2M).

A 0.05M solution of tetramethylammonium hydroxide (TMAH) (E. Merck) in doubly distilled water was used as the titrant. It was standardized with a solution of potassium hydrogen phthalate. Titrations were carried out in an inert atmosphere (by bubbling oxygen-free pre-saturated nitrogen through the solutions). A Beckman expandometric pH-meter, SS-2, with glass electrode (0-14 pH range) was used for pH measurements.

Titration procedure—The experimental method of Bjerrum and Calvin as modified by Irving and Rossotti⁵ was used to determine $\bar{n}$ and pL values. The following mixtures (total volume 20 ml, ionic strength adjusted with 2M NaClO_4) were titrated potentiometrically against standard 0.05M tetramethylammonium hydroxide (TMAH).

(i) 4.00 ml HClO_4 (0.01M) + 1.00 ml of metal ion solution (0.01M).

(ii) 4.00 ml HClO_4 (0.01M) + 7.5 ml of ligand ($M/150$) + 1.00 ml of metal ion solution (0.01M).

(iii) 4.00 ml HClO_4 (0.01M) + 7.5 ml of ligand ($M/150$) + 1.00 ml of metal ion solution (0.01M).

In all the cases corrections for changes in volumes, which take place during the course of titrations due to the addition of TMAH, were made.

A tentative structure (I) has been assigned to the ligand. Its IR spectrum in KBr shows $\nu_{\text{N}=\text{N}}$, $\nu_{\text{S}=\text{O}}$ and $\nu_{\text{O}-\text{H}}$ at 1585, 1180 and 3250 cm^{-1} respectively. The metal ions are expected to form five-membered chelates by coordination through the azo nitrogen and OH group in the ortho position to it (I). Since only one proton per ligand molecule is liberated on complexation, $Y = 1$ in all the cases.

From the titration curves (i) and (ii) of acid alone and in the presence of ligand, $\bar{n}H$ values of the ligand at various pH values were calculated and the pK values of the ligand at different ionic strengths and temperatures were evaluated by plotting $\log \bar{n}H/(1-\bar{n}H)$ versus pH, when linear plots of intercept equal to pK_a and slope equal to 1 were obtained. The values of proton-ligand stability constants are given in Table 1.

From the titration curves of the solutions (ii) and (iii), $\bar{n}$ values of the metal complexes were determined at various pH values. From a knowledge of practical pK_a values and $\bar{n}$ value at a particular pH, the corresponding value of pL was then calculated. The $\bar{n}$ values are plotted against the

