

Thionine-triethylamine interactions in mixed solvents

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Addition of triethylamine (TEA) to thionine (Th^+) solutions in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9:1, v/v) and $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (9:1, v/v) solvents leads to shift in absorption maxima from 597 nm to 500 nm and from 600 nm to 515 nm respectively. The spectral changes with various TEA concentrations have isosbestic points at 533 nm and 544 nm. Various types of interactions have been analysed to show that the charge transfer initiated redox disproportionation of the dye does not explain the observed data and the interaction in fact involves 1:1 complexation of the lewis acid/base type with $K = 2.60 \times 10^2 \text{ mol}^{-1} \text{ dm}^3$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ and $0.33 \times 10^2 \text{ mol}^{-1} \text{ dm}^3$ in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solvent.

Several reports have appeared on the replacement of a normal blue colour of the solution of phenothiazine dyes such as methylene blue (MB^+) and new methylene blue (NMB^+) by a weak pink colour on the addition of amines, phosphines or arsines in polar aprotic solvents¹⁻⁴. Addition of polar protic solvents to the mixtures has been reported to result in the immediate, but not total, reconversion to the original colour. However, in our opinion no satisfactory explanation has been offered for such a reversible change. McKay¹ suggested the formation of Lewis acid(dye)/base (amine) complexes in MB^+ solutions in the presence of strongly basic amines ($pK_b < 5$) and observed that the absorption bands of red form of the dyes in amines have low molar absorption coefficients which was consistent with the interaction of anion at the terminal group in the dye ion whereby one resonant structure of high dipole moment is stabilized at the expense of another equivalent structure. Sheaffer and Zimmermann² suggested that the colour change is due to a base induced redox disproportionation resulting in the formation of leuco- MB^+ and an oxidised imino form. Hydrolysis of the imino form can demethylate the dye to afford a new coloured species, the basic tautomer of trimethylethionine, whose absorption is blue shifted relative to MB^+ . Blue form is regenerated on protonation of the pink dye by an acid or other weak proton donor.

Similar interaction of NMB^+ with triethylamine (TEA) in dry acetonitrile has been explained by a charge transfer initiated redox disproportionation mechanism. However, the results do not completely conform to this mechanism. The dye is not fully converted to the red product at lower amine concentrations, which requires the establishment of some kind of equilibrium to arrive at an acceptable mechanism for

such colour changes. The present investigation has been carried out on the interaction of another thiazine dye, thionine (Th^+), with TEA in mixed solvents in order to further analyse the observations and arrive at an acceptable mechanism.

Materials and Methods

Th^+ (Aldrich, USA) was purified by repeated crystallisations from ethanol and its purity was checked on the basis of its UV/visible spectrum in water (Doubly distilled). TEA (Ranbaxy, A.R.) was used as such. Solvents acetonitrile (CH_3CN) and methanol (CH_3OH) were purified by distillation. Stock solutions of the dye were prepared in blackened volumetric flasks. Various spectra were recorded in closed quartz cells (1 cm) with the help of a double beam spectrophotometer (U.V. - 190, Shimadzu, Japan). The absorbance measurements were within the Beer's law limit.

Results and Discussion

Addition of TEA to Th^+ solutions in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9:1, v/v) and $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (9:1, v/v) solvents results in blue shift in the absorption maxima from 597 to 500 nm and 600 to 515 nm. The spectral changes with varying TEA concentrations have isosbestic points at 533 and 544 nm respectively for $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ and $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solvents as shown in Figs 1 and 2. The charge transfer initiated redox disproportionation mechanism suggested for such spectral shifts in similar systems^{2,3} and observed results necessitate the consideration of the processes as given in Scheme 1 for Th^+ and TEA interactions.

On the basis of steady state approximation, Scheme 1 involving equilibrium between steps 1 and 2 (K) and steps 4 and 5 (K'), yields,

$$k_3 K K' / 2 (k_4 - K' k_5) \times [\text{Th}^+] [\text{TEA}] = [\text{I}]^2 \quad \dots (1)$$

In the event of direct formation of ThH and I from the complex $[\text{Th}^+ - \text{TEA}]$ without the intervention of Th^- and TEA^+ , steady state treatment yields,

$$\sqrt{K' K} [\text{Th}^+] [\text{TEA}] = [\text{I}] \quad \dots (2)$$

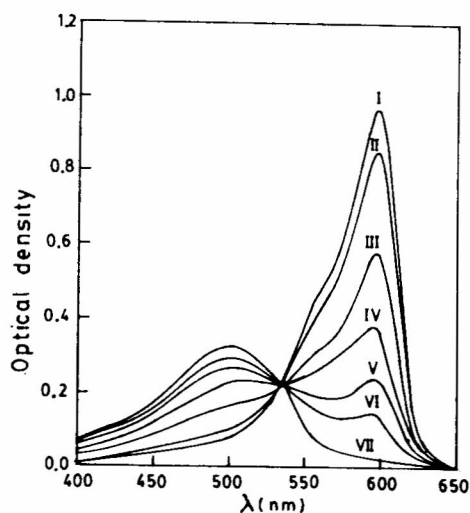
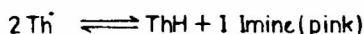
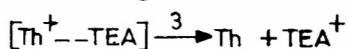
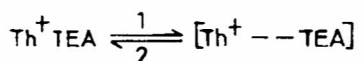
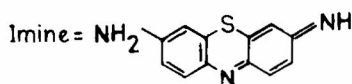


Fig. 1—Spectra of Th^+ at different TEA concentrations {Solvent = $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9:1, v/v); $[\text{Th}^+] = 1.42 \times 10^{-5} \text{ mol dm}^{-3}$; curve I for $[\text{TEA}] = 0 \text{ mol dm}^{-3}$, curve II for $[\text{TEA}] = 0.0001 \text{ mol dm}^{-3}$, curve III for $[\text{TEA}] = 0.001 \text{ mol dm}^{-3}$, curve IV for $[\text{TEA}] = 0.005 \text{ mol dm}^{-3}$, curve V for $[\text{TEA}] = 0.01 \text{ mol dm}^{-3}$, curve VI for $[\text{TEA}] = 0.05 \text{ mol dm}^{-3}$ and curve VII for $[\text{TEA}] = 0.1, 0.5, 1.0$ and 2.0 mol dm^{-3} }



$\text{ThH} = 1 \text{ euco-thionine}$



SCHEME 1

Equation (1) predicts a linear plot of $[\text{TEA}]$ versus $[\text{I}]^2$ at constant $[\text{Th}^+]$ with zero intercept while equation (2) predicts linear relationship between $[\text{TEA}]$ and $[\text{I}]$. Such linearities are not observed and hence the observed data rule out the possibility of such chemical interactions in this system.

Here McKay's explanation of lewis acid (dye)/base (amine) complex formation appears to hold good. TEA is a good electron donor and a large number of examples of charge transfer complex formation between TEA and compounds similar to these dyes are known⁵⁻⁹. Such interactions have also been reported in $\text{Th}^+ - \text{Fe(II)}$ systems^{10,11}. Generally, 1:1 and 1:2 complexes are formed. For the present system the interactions can be:

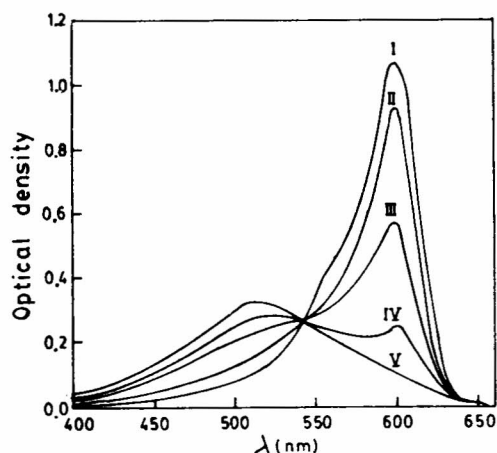
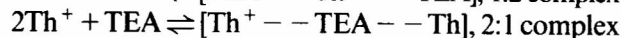
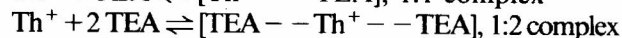
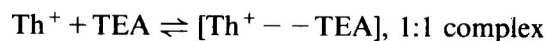


Fig. 2—Spectra of Th^+ at different TEA concentrations. {Solvent = $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (9:1, v/v); $[\text{Th}^+] = 1.42 \times 10^{-5} \text{ mol dm}^{-3}$; curve I for $[\text{TEA}] = 0 \text{ mol dm}^{-3}$, curve II for $[\text{TEA}] = 0.005 \text{ mol dm}^{-3}$, Curve III for $[\text{TEA}] = 0.05 \text{ mol dm}^{-3}$, curve IV for $[\text{TEA}] = 0.5 \text{ mol dm}^{-3}$ and curve V for $[\text{TEA}] = 5 \text{ mol dm}^{-3}$.}

Table I—Calculated values of equilibrium constants for complexation between Th^+ and TEA

Sr. No.	[TEA] (mol dm^{-3})	$K_{1:1} \times 10^{-2}$ (mol dm^{-3}) ⁻¹		$K_{1:2} \times 10^{-4}$ (mol dm^{-3}) ⁻²		$K_{2:1} \times 10^{-7}$ (mol dm^{-3}) ⁻²	
		a	b	a	b	a	b
1	5×10^{-3}	2.32	0.31	5.78	0.75	4.71	0.61
2	1×10^{-2}	3.04	—	3.04	—	8.20	—
3	5×10^{-2}	2.30	0.38	0.47	0.62	6.20	1.06
4	1×10^{-1}	2.89	—	0.23	—	3.74	—
5	5×10^{-1}	—	0.30	—	0.08	—	0.48
6	5.00	—	0.34	—	0.02	—	0.08
	Average	2.64	0.33	—	—	—	—

a = $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9:1, v/v)

b = $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (9:1, v/v)

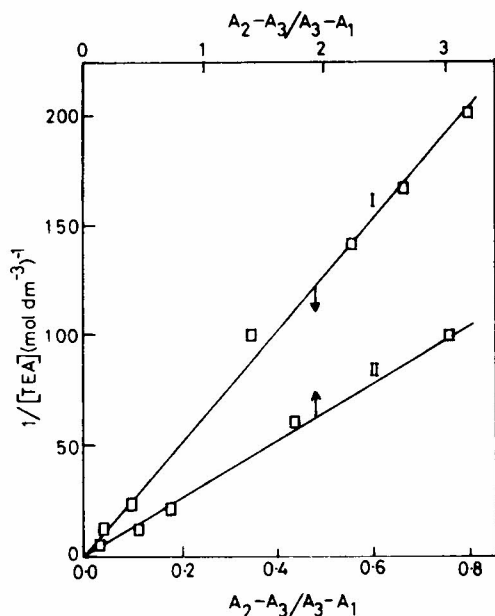


Fig. 3—Plots of results from Eq. (3). [Plot I for Fig. 1 and plot II for Fig. 2]

Equilibrium constants for each of the above possibilities were calculated at various [TEA]'s at constant $[\text{Th}^+]$ and these are given in Table 1. The data clearly fit the 1:1 complex case.

The isosbestic points at 533 nm and 544 nm (c.f. Figs 1 and 2) correspond to equal molar absorption coefficients for Th^+ and the complex at these wavelengths. It is apparent that the total concentration of Th^+ and the complex is constant for all the curves and this argument leads to a simple relationship for 1:1 complexation^{12,13},

$$\begin{aligned} 1/[\text{TEA}] &= K \times [\text{Th}^+]/[\text{COMPLEX}] \\ &= K \times A_2 - A_3/A_3 - A_1 \end{aligned} \quad \dots (3)$$

where A_1 , A_2 and A_3 are the absorbances of Th^+ in the absence of TEA, complex (Th^+ in the presence of excess TEA) and mixture solution at 597 nm and 600 nm for $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ and $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ respectively. Plots of $1/[\text{TEA}]$ versus $A_2 - A_3/A_3 - A_1$ are shown in Fig. 3. These are good straight lines with zero intercept. The slopes of straight lines give $K = 260 \text{ mol}^{-1} \text{ dm}^3$ and $33 \text{ mol}^{-1} \text{ dm}^3$ for $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ and $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solvents respectively, which is in good agreement with the results of Table 1. The present analysis and data thus support the formation of 1:1 complex.

Acknowledgement

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