

Metachromasia Induced in Cationic Dyes by Iodide Salts

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Abstract: *Inorganic salts like NaI and KI induce distinct metachromasia in thiazine dye 1,9-dimethylmethylene blue (DMMB, $2.0 \times 10^{-5} M$) and cyanine dye pinacyanol chloride (PCYN, $2.0 \times 10^{-5} M$). Half plateau values signifying destruction of metachromatic compounds to the extent of 50% correspond to ~22%, and ~30% ethanol for DMMB-NaI, and PCYN-NaI systems respectively. Conductometric titrations reveal that DMMB and PCYN bind with NaI in the molar ratio of 1:1*

Keywords: Metachromasia, Chromotrope, α -band, β -band, μ -band

1. Introduction

Metachromatic compounds are formed of certain cationic dyes and polyanions. They exist in solution in equilibrium with their component cations and polyanions. They have absorption spectra in solution in visible region which differ from those of dilute solution of the dye alone. The metachromatic compound has an absorption peak (μ -band) at a wave length usually 50 to 100nm less than the wave length of the peak of the dye alone in dilute aqueous solution (α - band). The dye cations occupy adjacent sites on the polyanionic substrates and thus are stacked to undergo dye-dye interactions as in dye aggregates to exhibit metachromasia. The dye-dye interaction is due to hydrophobic bonds between neighboring dyes. Chromotropic ability of a polyanion depends on the charge density as well as on the nature of anionic group.

Though the β -band is said to refer to the dimer band, the aggregation of minimum number of dye cations required for the exhibition of metachromatic band (μ -band) is yet to be established finally, in fact a uniform generalization does not seem to fit in all cases since not all cationic dyes are metachromatically alike, nor all the chromotropes behave alike. Czikkley et al.[1] made a theoretical prediction that polyanions having four to six anionic sites would be able to introduce metachromasia in a suitable cationic dye. Pal and Mandal [2] experimentally demonstrated that a polyanion molecule with four anionic sites would induce metachromasia. Bhattacharyya and Saha [3] also reported the metachromatic abilities of tetra, tri, di and mono anionic chromotropes.

In an earlier communication, we reported the metachromatic interaction of neem polysaccharide [4] with different cationic dyes. We report here the chromatic abilities of fluoride, chloride, bromide and iodide salts of sodium and potassium with different cationic dyes.

2. Experimental

Sodium iodide, sodium chloride, sodium fluoride, potassium iodide, potassium bromide, potassium chloride, potassium fluoride (Merck), sodium bromide (SRL), dimethylmethylene blue (Sigma-Aldrich), toluidine blue (E. Merck), methylene

blue (E. Merck) and pinacyanol chloride (Serva) were used. Stock solutions of the dyes dimethylmethylene blue (DMMB), toluidine blue (TB), methylene blue (MB), and pinacyanol chloride (PCYN) were made by dissolving the required amount of the dye in methanol and then making up the volume with double distilled water. The dye solutions and other experimental solutions were stored in dark when they were not used.

Absorbance spectra of different dyes and dye-salt were recorded in visible range (covering the range 450-700nm depending upon the λ_{max} of the dye used) with a Toshniwal digital spectrophotometer and Systronics spectrophotometer.

The effects of co-solvent like ethanol solution on reversal of metachromasy were studied by measuring absorbance of pure dye solution as well as dye-salt mixture at monomeric band (α - band) upon addition of increasing amounts of alcohols (0-60%)

Stoichiometry of dye-salt compound was determined by conductometric titration of dye solution ($\sim 0.05 g/25 ml$) with salt solution ($\sim 0.5 g/25 ml$). Conductances were measured with a Systronics conductivity meter after each small addition of salt solution to the dye solution. The solution was kept under thorough stirring with the help of a magnetic stirrer. Point of intersection of conductance curve gave the stoichiometry of dye-salt compound.

3. Results and Discussion

Figs. 1A and 2A show the absorption spectra of $2.0 \times 10^{-5} M$ 1,9-dimethylmethylene blue (DMMB) and pinacyanol chloride (PCYN) solution in water. Exhibition of prominent dimer band (β -band) around 600nm and 550 nm in addition to monomer band (α - band) around 650 nm and 600 nm for DMMB and PCYN respectively reflect strong aggregating tendency of DMMB and PCYN. DMMB and PCYN show distinct metachromasia in presence of sodium iodide (Fig.1 and Fig.2) and potassium iodide (Figures not shown). TB does not give distinct metachromasia with NaI. Sodium chloride, sodium bromide, sodium fluoride, potassium bromide, potassium chloride, potassium fluoride fail to show metachromasia in DMMB, TB, MB and PCYN.

Dextran sulphate, heparin and chondroitin sulphate[5] are polyanions of high charge density and known to induce sharp metachromasia in thiazine dyes DMMB, TB and MB. Orange peel polysaccharide [6] and neem polysaccharide[4] are polyanions of relatively lower charge density and are known to induce metachromasia in the stronger metachromatic dye DMMB but not MB. TB undergoes only modest metachromatic shift in presence of these polyanions. Ammonium molybdate [7] has been reported to bind with MB in the molar ratio of 1:6 and to induce sharp metachromasia in it. Inorganic salts like potassium ferrocyanide, potassium ferricyanide ammonium metavanadate induce metachromasia in DMMB and PCYN but fail to do so in MB. TB, which ranks in between DMMB and MB in metachromatic potentiality, undergoes no distinct metachromatic shift in presence of these salts [3].

Metachromatic colour change of a suitable cationic dye is associated with cooperative aggregations of the cations. The dye cations are said to be aggregated to dimer, trimer, tetramer and higher multimer. But generalization about the aggregation of minimum number of dye cations required for exhibition of metachromatic band (μ -band) can not be made since the magnitude of the blue shift of λ_{max} of a dye associated with aggregation depends on the number of dyes aggregated as well as on the distance of separation of monomers and it is also not necessary either.

Role of disruptive factor like ethanol [8] has been studied and half-plateau[9] values signifying destruction of metachromatic compound to the extent of 50% and their stabilities, corresponding to 22% and 30% ethanol, respectively for DMMB-NaI (Fig.3) and PCYN-NaI system (Fig. 4). Stabilities of metachromatic compounds evaluated on the basis of disruptive role of ethanol are found in the order: PCYN-NaI > DMMB-NaI.

Stoichiometry[10] determination through conductometric titration reveals that DMMB (Fig.5) and PCYN (Fig.6) bind with NaI in the molar ratio 1:1.

Mechanistic model

The accepted model for metachromasia induced in suitable cationic dye by a polyanionic chromotrope is represented in Fig.X, where D^+ stands for dye cation.

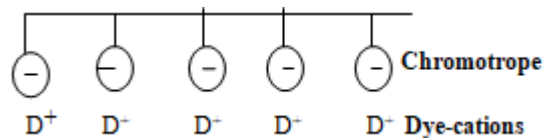
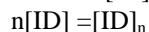
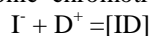


Figure X: Mechanistic Model of Metachromasia

Now the question of interpretation of metachromasia by iodide naturally arises. The following model may be suggested to metachromasia induced in different cationic dyes by monoanionic chromotrope like iodide.



Where, n need not be a large number and D^+ stands for dye cation.

More over spreading of anionic charge of monoanionic chromotrope like iodide over larger area possibly assists interaction with dye cations leading to their aggregation.

4. Conclusion

It may be concluded that chromotrope neither be a macromolecule nor be polyanion to induce metachromasia; even monoanionic substance may induce metachromasia which of course depends on the nature of monoanion. Monoanion enjoying the scope of spreading the anionic charge over larger area appears to facilitate the approach of dye cations leading to their co-operative aggregation, responsible for exhibition of metachromasia.

5. Acknowledgement

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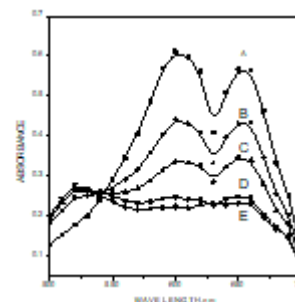


Figure 1: Absorbance spectra of 2.0×10^{-5} M DMMB in (A) water and in presence of NaI (B) 6.95×10^{-3} M; (C) 13.9×10^{-3} M; (D) 20.85×10^{-3} M; (E) 27.8×10^{-3} M

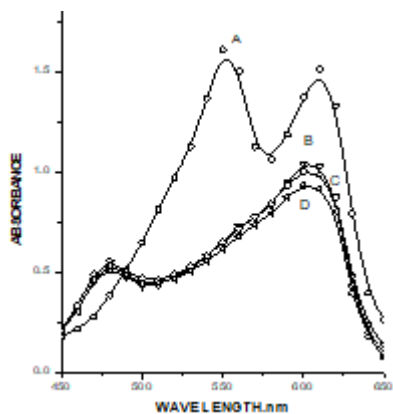


Figure 2: Absorbance spectra of 2.0×10^{-5} M PCYN in (A) water and in presence of NaI (B) 6.71×10^{-3} M; (C) 13.42×10^{-3} M; (D) 20.13×10^{-3} M

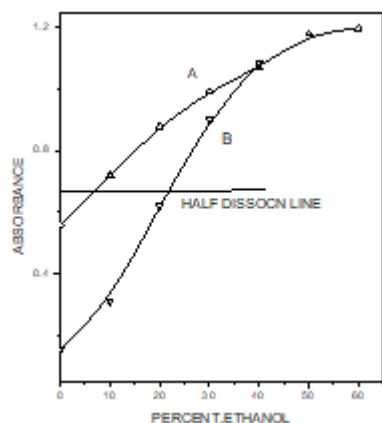


Figure 3: Plots of absorbance at α – band of 2.0×10^{-5} M DMMB Vs percent ethanol in (A) water and in presence of (B) NaI (20.85×10^{-3} M)

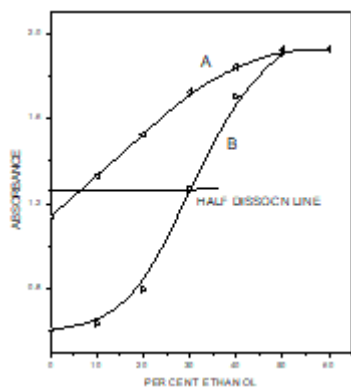


Figure 4: Plots of absorbance at α – band of 2.0×10^{-5} M PCYN Vs percent ethanol in (A) water and in presence of (B) NaI (20.85×10^{-3} M)

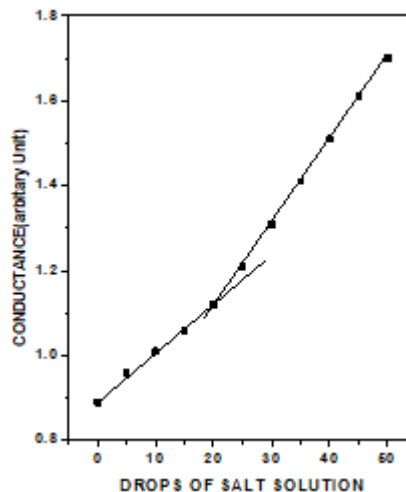


Figure 5: Conductometric titration plot of DMMB (0.0523 g / 25ml) with NaI (0.5202 g / 25ml)

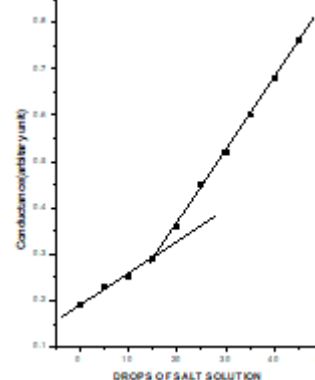


Figure 6: Conductometric titration plot of PCYN (0.0516 g / 25ml) with NaI (0.5071 g / 25ml)