Inorganic Salts as Chromotropes in Metachromasia

Amitabha Saha

Department of Chemistry, Kabi Nazrul Mahavidyalaya, Sonamura, 799131, India

Abstract: Inorganic salts potassium iodide and sodium tungstate induce distinct metachromasia in thiazine dye 1,9-dimethylmethylene blue (DMMB, 2.0×10⁻⁵M). Both potassium iodide and sodium tungstate fail to induce metachromasia in Toluidine blue (TB) and Methylene blue (MB). Both monoanionic potassium iodide and dianionic sodium tungstate are weak chromotropes.

Key words: Metachromasia, Chromotrope, α-band, β-band, µ-band

Introduction

Polyanionic substrates, called chromotropes, are known to induce metachromatometric spectral shifts of suitable cationic dyes. 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[1]. Metachromatic interactions of cationic dyes with chromotrope depend on metachromatic potentialities of cationic dyes and chromotropic abilities of polyanion. Czikkle et. al[2] made a theoretical prediction that polyanion having four to six anionic sites would be able to induce metachromasia in a suitable cationic dye. Pal and Mandal[3] experimentally demonstrated that a poly anionic sites would induce metachromasia.

All the cationic dyes are not metachromatic and all the metachromatic dyes are not potentially equal. Metachromatic dyes are hydrophobic in nature with relatively small hydrophilic cationic charges. 1,9 dimethylmethylene blue (DMMB), Toluidine blue (TB) and Methylene blue (MB) are cationic dyes belonging to the thiazine group. Metachromatic abilities of different thiazone dyes are in the order DMMB>TB>MB[4].

Introduction of two methyl groups in MB at 1 and 9 positions increases its hydrophobic character, which is reflected in greater metachromatic tendency of DMMB. The methyl groups linked with the C-atoms contribute to the hydrophobicity of the dye molecules where methyl groups linked with the amino N-atoms constitute a part of the hydrophilic cationic charge. In DMMB, two methyl groups are linked with the ring C-atoms and four methyl groups are linked with amino N-atoms in comparison with 4-amino N-linked methyl groups are none with ring C in MB, and two amino N-linked methyl groups and one ring C-linked methyl group in TB.

Induction of metachromasia in suitable cationic dyes by polyanionic chromotrope is well reported. We aimed at studying the feasibility of small molecules in inducing metachromasia in different cationic dyes. This paper deals with our observation on spectrometric interaction of mono-anionic salt like potassium iodide and di-anionic salt sodium tungstate with thiazine dyes.

2. Experimental

Potassium iodide (Merck), sodium tungstate (BDH), dimethylmethylene blue (Sigma-Aldrich), toluidine blue (E. Merck), methylene blue (E. Merck) were used. Stock solutions of the dyes dimethylmethylene blue (DMMB), toluidine blue (TB) and methylene blue (MB) 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 500-700nm depending upon the λmax of the dye used) with a Toshniwal digital spectrophotometer and Systronics spectrophotometer.

Result and Discussion:

Figs 1A and 2A show the absorption of 2.0X10⁻⁵M, 1,9 dimethylmethylene blue (DMMB) solution in water with prominent dimer band (β-band) around 590 nm in addition to its monomer band (α-band) around 650nm. Enhanced aggregating tendency of DMMB is evident from the appearance of sharp β-band in addition to its monomer band. Potassium iodide and sodium tungstate induce sharp but multiple banded metachromasia at different salt/dye values (Curves 1B, C &2B, C), µ-band appearing around 560nm with small peak around α-band of the dye. In addition, small peak is found around β-band in case of sodium tungstate. Weak chromotropic nature of both potassium iodide and sodium tungstate are also evident from the lesser magnitude of blue shift. TB, which ranks in between DMMB and MB in metachromatic potentiality, undergoes no distinct metachromatic shift in presence of these salts. Both Potassium iodide and sodium tungstate fail to induce metachromasia in MB.

Dextran sulphate, heparin and chondroitin sulphate[5-6] are polyanions of high charge density and known to induce sharp metachromasia in thiazine dyes DMMB, TB and MB. Orange peel polysaccharide[7] and neem polysaccharide[8] 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.

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 ($\mu$-band) cannot be made since the magnitude of the blue shift of $\lambda_{\text{max}}$ 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.

The following model may, therefore, be suggested to metachromasia induced in different cationic dyes by mono anionic and dianionic substance.

$$\text{Anion with Negative charge} + \text{Dye with Positive charge} \rightleftharpoons \text{Anion with Negative charge} \text{Dye with Positive charge}$$

$$\text{n Anion with Negative charge} \text{Dye with Positive charge} \rightleftharpoons \text{Anion with Negative charge} \text{Dye with Positive charge} \text{n}$$

Where $n$ need not be a large number.

**Fig.X: Mechanistic model of metachromasia**

When a dye cation binds with anionic substance, the cationic charge of the dye is at least partially neutralized, thus facilitating the dye cations bound to the anion leading to blue shifted metachromasia[9].

**Conclusion :** Compounds with favourable anionic site may act as a chromotrope. Anion 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 and also degree of metachromasia is dependent on the nature of dye.

![Absorbance spectra of 2.0x10^{-5} M DMMB in (A) water and in presence of KI (B) 6.37x10^{-3} M (C) 12.74x10^{-3} M](Fig.1).
References:

8. A. Saha, International Journal. of Science and Research,2018,7,1077
9. A. Saha, International Journal. of Science and Research,2020,9,810