AIM AND OUTLINE OF THE PRESENT REPORT

There have been some reports on the metachromatic color changes of some dyes caused only by the presence of some inorganic salts. Spek (1940) reported the intense metachromatic color change induced by small ions like I⁻ and CNS⁻. Wells (1950) suggested the formation of complex salt by the interactions of some iso-and heteropolyacids with organic compounds resulting in metachromastic spectral shifts. He obtained precipitates with azure A. According to West and Geddes (1964) silver iodide induces metachromatic color changes in dyes while silver chloride and bromide fail. Tsubouchi (1971) reported the formation of 1:1 stoichiometric complex between iodide ion and neutral red. Sylven (1954) also reported that several simple inorganic salts like potassium iodide, thiocyanate, tungstate, mercuric chloride induce metachromatic color changes in some dyes and gives precipitates. Apparently metachromasia induced by these salts, which are apparently not polyanions, can not be explained by the aggregation theory. The purpose of the present study is to investigate in more details these curious reports of simple inorganic salts acting as chromotropes in inducing metachromasia in dyes. Unfortunately the metachromasia induced by these salts could not be studied in details due to the precipitation always associated with it. As already mentioned in the introduction there exist two interpretations of metachromatic color changes - counter ion binding theory and the aggregation theory, though the
experimental results points to the aggregation theory to be the more reasonable explanation. We have been interested in the present study in view of finding reasonable interpretation of the chromotropic abilities of the inorganic salts, which eventually could give additional support to one of the two interpretations of metachromasia or even could make it necessary to think of a different interpretation. As we shall see later that the metachromasia induced by mercuric chloride and sodium tungstate, the chromotropic abilities of the two salts we studied in details, could nicely be interpreted by the aggregation theory. Above this the metachromasia induced in mixtures of two dyes induced by these two salts could reasonably be interpreted only by the aggregation theory.

Mercuric chloride gives immediate red colored precipitate when added to an aqueous solution of the dye methylene blue, an observation that eventually had some application in the determination of the stoichiometry of the mercuric chloride - dye compounds, but which stood in the way of studying the system spectrophotometrically. But we could overcome this difficulty by the observation that methylene blue has the metachromatic color without immediate precipitation if an excess of mercuric chloride be present in the solution. The excess mercuric chloride helps only in keeping the dye-mercuric chloride metachromatic compound in solution without disrupting it as is shown by the almost identical shapes of the reflectance spectrum of the red precipitate.
of dye-mercuric chloride that is obtained when a limited amount of mercuric chloride is added to the dye solution and the visible spectrum of the aqueous solution of the dye-mercuric chloride compound obtained in the presence of a large excess of mercuric chloride. Similar were the behaviours of the other cationic dyes studied. Ultraviolet spectra of the dye-mercuric chloride systems are also studied in comparison with that of the aniline-mercuric chloride system to probe into the nature of the bond between dye and mercuric chloride.

In contrast to the observation of Sylvén (1954) we found that $\text{Na}_2\text{WO}_4$ itself does not induce metachromasia in a dye like methylene blue (not even any red precipitate); however tungstate acts as a good chromotrope in inducing metachromasia in many dyes in the presence of a suitable amount of an acid. Our results indicate that the chromotropic ability of tungstate ion is due to the formation of polytungstate in the presence of acid, which eventually acts as the chromotrope.

Potassium iodide also gives red colored precipitate with the dye methylene blue, but we could not find any condition where the precipitate goes in solution without destroying the developed metachromasia. So the chromotropic ability of iodide unfortunately could not be studied further.

The stoichiometry of the dye-mercuric chloride has been studied conductometrically and analytically. The results show
that each dye is associated with its chloride ion in the dye-mercuric chloride compounds, and that in the presence of an excess of dye, the compound has the stoichiometry of 2 moles methylene blue chloride per mole of mercuric chloride, whereas in the presence of an excess of mercuric chloride the stoichiometry changes to one mole of dye chloride per mole of mercuric chloride.

Finally the metachromasia of mixtures of pairs of dyes have been studied with both mercuric chloride and acidified tungstate as chromotropes. Results are quite similar to when polyanions are used as chromotropes and indicate the formation of heteroaggregates of the dyes (Pal and Schubert (1963)).

All the findings have reasonably been interpreted by the aggregation theory.