

CHAPTER - II

Scope and Object of Work

In spite of the wide occurrence and practical applications, adsorption at the interface between the suspended particles of aluminosilicates and an aqueous solution of Cationic dyes still presents one of the complicated problems in surface Chemistry. It is in this context that an attempt has been made to study the Physico-Chemical aspects on the interaction of different cationic dyes with clay minerals and allied aluminosilicates. The term interaction has been applied to mean mainly the sorption and desorption phenomena along with other effects as may accrue from or be related to them. In studies of clay-dye interaction adsorption data will be meaningful only when both adsorbates and adsorbents are well characterized. Small organic cations are seen to be taken up by aluminosilicates upto the extent corresponding to cation exchange capacity while large ions may be adsorbed in excess being held up by van der Waal's and/or hydrophobic forces. It has been observed that the sorption of organic molecules takes place on the surface of aluminosilicates of the fixed lattice group viz. kaolinite when they penetrate between the unit layer of montmorillonite or the clays of the expanding lattice group. This complicated process of interaction of organic ions with clays is accompanied by significant variation of properties of the solid which needs thorough investigation in

any attempt to interpret the data on equilibrium and also to explain different types of adsorptive forces involved such as (1) Chemisorption (2) Ion-exchange (3) Hydrogen bond (4) Hydrophobic bonding (5) van der Waal's forces, etc. Several approaches both qualitative and quantitative have been made to understand the equilibria between ion-exchangers and solution.

Dye desorption measurements were used by earlier workers mainly to estimate the surface areas and c.e.c. of the adsorbents. Not always could satisfactory results be obtained. A proper knowledge of the interaction of the adsorbate with adsorbent was lacking in most of the studies, unless this is known in reasonable details, an appreciation of the adsorption measurements may be difficult. It is therefore appropriate to carry out systematic study of sorption phenomenon for which adsorbates of known structures and adsorbents with well defined surface characteristics would be most convenient. The clay minerals montmorillonite, kaolinite and laponite (a synthetic trioctahedral hectorite) used in the present study provide more or less known features.

Rhodamine B and Rhodamine 6G (Xanthene series), Brilliant cresyl blue (oxazine series) are dye compounds of known structures used in the present investigation as adsorbates. Some basic data regarding these dyes are known. Being structurally similar with like charge delocalisation the two Xanthene dyes differ from each other only in the position of alkyl substituents, whereas

oxazine dye differs in structure and molecular weight from the xanthane dyes. As such, it is an excellent opportunity to study the effect of shape and size of the adsorbate on sorption and desorption phenomena as well as to compare the sorption behaviour of xanthane dyes with that of an oxazine.

The main object of the present investigation is to study in fundamental detail the physico-chemical aspects of ion exchange equilibrium of the above dye cations onto the exchangers mentioned in the preceding paragraph with a view to derive some insight into the factors that govern and influence the exchange processes. For this purpose, the study of interaction has been approached from three different angles : sorption-desorption forming the main bulk of the thesis, heat of adsorption and the metachromatic behaviour of the dye spectra due to adsorption. The adsorption isotherms have been studied and analysed in the light of Langmuir equation for Rhodamine B, Rhodamine 6G and Brilliant cresyl Blue on the adsorbents mentioned above. Further, in order to investigate the influence of the type of clay mineral on ion exchange behaviour, natural and synthetic clays having widely different structural characteristics, charge densities and swelling properties have been chosen. Although large amount of work is recorded in the literature on the adsorption of dyes on clay minerals, the desorption characteristics of the dyes have not been studied thoroughly with different inorganic and organic ions by previous workers. So the desorption

of Rhodamine B and Rhodamine 6G from their respective clay complexes have been studied with monovalent, divalent inorganic ions as well as with tetraalkyl ammonium and long chain surface active ions of varying sizes in order to acquire a better knowledge of the nature of adsorbate-adsorbent interaction relative strength of binding of the adsorbents, cation specificity etc. Such studies also reveal the extent of extractibility of the dye cation from the adsorbent surfaces from which we can have an idea of the affinity of the ions for the minerals vis-a-vis the relative desorbing efficiency of the ions with size, shape and charge of the ions. An attempt has also been made to analyse the desorption data obtained with the inorganic ions in the electrostatic model of Pauley. There exists sufficient scope for a further use of these experimental data to test and develop different existing theoretical models and equations, describing ion-exchange equilibria.

The heats of adsorption of selected xanthane dyes onto montmorillonite and kaolinite have been calculated from measurement of adsorption at three different temperatures. This parameter provides useful information for the interpretation of the adsorption process and on the strength of bonding of the adsorbed species with the adsorbent surface.

In view of the conflicting theories reported in literature about the causes of metachromasy when cationic dyes are sorbed

onto clay minerals, the present study has been carried out to throw further light in this area by investigating the spectral behaviour of selected dyes exchanged onto montmorillonite, kaolinite and laponite. X-ray diffraction data have been used to supplement the observations. This study may lead to an important insight into the mechanism of the interaction between the adsorbate and the adsorbent. The correlation of the spectral shifts with the surface concentration may be an interesting study. A direct determination of surface concentration may ^{also} be possible, from which the surface area of the substrate can be easily derived.