

CHAPTER X

SUMMARY AND CONCLUSION

The structures of the clay minerals namely kaolinite, montmorillonite and laponite are briefly discussed. A short review of the earlier studies on the adsorption and desorption of inorganic and organic ions on clay minerals and also other substrates is presented in the introductory Chapter I.

(Pages 1-39)

Chapter II includes the scope and object of the present investigation.

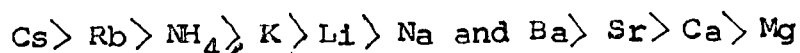
(Pages 40-44)

The methods of analysis and the preparation of materials, experimental details and the preparation of the samples for I.R. spectra, X-ray diffraction analysis are described in Chapter III. Three selected dyes viz. RB, RG, BB belonging in two different categories have been used. All are well established structure recrystallised by usual methods. Their interactions with the above mentioned silicate minerals have been described in order to find out their adsorption and desorption behaviour vis-a-vis the structural characteristics of both the adsorbent and the adsorbate.

(Pages 45-56)

The adsorption isotherms of Rhodamine 6G and Rhodamine B on Na-montmorillonite are of the H-type, indicative of strong sorbate-sorbent interactions, with the species being adsorbed flat on the surface. The adsorption data of both the dyes on Na-montmorillonite are found to fit in well with the Langmuir equation. The Langmuir bonding constant of RB^+ is higher than RG^+ suggesting a stronger binding of the former dye with the Na-montmorillonite. The maximum sorption of both the dyes exceeds the C.E.C. of the clay, RG^+ being adsorbed more than RB^+ . The higher uptake of RG^+ by Na-montmorillonite is due to its greater dimerisation or aggregation tendency than RB^+ in aqueous solution. When adsorption takes place from solutions the former is sorbed with a larger fraction of the aggregates than that of the latter at any particular concentration. Ionic and van der Waals forces are most likely operated during adsorption upto cation exchange capacity and beyond it only van der Waals forces predominates.

The efficiency of the inorganic ions in desorbing the dye molecules from the Na-montmorillonite matrix generally increases with the crystallographic radius of the ions and follows the lyotropic series with few exceptions. The orders of selectivity for the monovalent and bivalent inorganic ions are :



The plots of log (selectivity coefficient) against hydrated ionic radius and the reciprocal of the Debye Huckel parameter, a° yield straight lines in the case of alkaline earth metal cations while for the alkali metal ions the latter plot is only linear. The cause of non linearity in case of alkali metal ions has been attributed to the unequal fixation tendencies of the ions vis-a-vis interlayer collapse of the clay structure. However, the plot of log (selectivity coefficient) vs $\frac{1}{a^\circ}$ is based on the simple ion-exchange model of Pauley, and the above observations suggest that electrostatic attraction between the counterions and the fixed ionic groups is the significant factor in the process of displacement of the dye ions from the clay matrix by the inorganic ions. These plots may be used to correlate and predict the relative affinities of the ions for the mineral in terms of their a° values and hydrated ionic radii.

The exchangeability of organic ions from the respective Na-montmorillonite dye complexes is much higher than that by the inorganic ions and also increases with increasing size of the ions. This is due to increased contribution of the van der Waals forces to the adsorption energy and to changes in the hydration status of the ions in the clay interlayer. The desorption curves of both the dyes with quaternary ammonium

ions on Na-montmorillonite complexes are almost S-shaped which indicates co-operative sorption with solute molecules tending to be adsorbed or packed in rows or clusters. Giles et al, through theoretical treatment have shown recently that S-curve occurs when the activation energy for the desorption of the solute is concentration dependent, and/or is markedly reduced by large negative contributions of the solvent or a second solute. It is apparent from the selectivity data that monovalent long-chain surfactant ions like CP^+ or $CTMA^+$ are more preferred by clay matrix than those of other organic ions studied. Again CP^+ desorbs a large amount of dye than $CTMA^+$ owing to the lower cmc (critical micelle concentration) of the former. From higher values of selectivity coefficients of the monovalent long chain surface active ions it may therefore be concluded that shape and size of these ions and the degree of van der Waals contact between the organic ions and the clay surface are significant factors to be considered during desorption process. Besides, the solubility of the organic cations decreases as the size increases and there is obviously less tendency of the larger ions, once adsorbed, to get desorbed back into the solution. The percentage of desorption of RG^+ from this clay by various electrolytes and their respective distribution and selectivity coefficients are higher than those of RB^+ . So the order of the affinity of the dyes for the mineral surface which is in the reverse order of their desorption is $RB^+ > RG^+$, which

is also reflected in the Langmuir constant value.

(Pages 57-88)

The adsorption isotherms of RG^+ and RB^+ onto Na-kaolinite are of the high affinity class. Both RG^+ and RB^+ are adsorbed upto a maximum, well in excess of the c.e.c. of the clay mineral. This is due to the sorption of aggregated dye-ions and/or the unionised dye molecules by the mineral. The desorption isotherms of the two dyes for Na-kaolinite complexes differ in two aspects for those two other complexes of the clays studied here viz. the percentage of desorption of the dyes from their Na-kaolinite complexes by monovalent and bivalent inorganic ions is the highest while it is the lowest for the larger organic ions. The extent of desorption however, increases with the size of the ions in both the cases. This behaviour towards inorganic ions is due to the fact that the binding strength to this clay mineral is weak as compared to the other minerals, since the exchange sites in Na-kaolinite are located only on the external surface of the crystal.

The desorption isotherm of both the dyes from their aqueous Na-kaolinite complexes are S-shaped for some of the surfactant ions like CP^+ , $CTMA^+$, DDP^+ . Similar explanation can be given as in case montmorillonite system. Plot of \log (selectivity coefficient) vs hydrated ionic radius and $1/a^0$ for monovalent and bivalent inorganic ions are similar to

systems already studied. As in other adsorbent systems used in earlier studies, the affinity of the dye ions for Na-kaolinite surface have the order $RB^+ > RG^+$.

(Pages 89-109)

The adsorption isotherms of RG^+ and RB^+ on Na-laponite, a synthetic hectorite also belongs to the H-class of isotherm and the exchange data obey Langmuir equation. The amount of exchange here for RG^+ are in excess of c.e.c. of the mineral RG^+ being adsorbed more than RB^+ . Sorption of dyes in aggregates as well as bilayer formation tendency of the dye ions in the interlamellar space, due to unlimited swelling of Laponite having lower charge density may account for this observation. A higher fraction of aggregated RG ions is sorbed onto the mineral surface due to higher dimerisation tendency of this dye. As a result of which, the extent of adsorption of RG^+ is greater than RB^+ . Like the other two minerals the desorption isotherm in Na-laponite system is similar in nature. The extent of desorption here by inorganic ions is much lower than that observed in montmorillonite system. This can be explained in the light of wider spacing between the exchange spots in the Laponite minerals, as a result of which small sized inorganic desorbing ions are unable to approach these sites as effectively as in montmorillonite to displace the adsorbed dye ions.

The relationship of hydrated ionic radii and $1/a^{\circ}$ with \log (selectivity coefficient) is the same as that in montmorillonite and kaolinite. The obedience of the exchange data to Pauley's model demonstrates that coulombic interaction between the counter ions and the fixed ionic groups is the important factor in this type of exchange reactions.

The desorption of both the dyes by various organic ions increases with size of the ions which is usually found in expanding type of clay mineral and is ascribed to the increased contribution of van der Waals forces to the adsorption energy and also to the changes in the hydration status of the ions in the clay interlayer. Here also the affinity of these dyes to laponite surface is $RB^{+} > RG^{+}$. This is also reflected in the higher Langmuir bonding constant of RB.

(Pages 110-132)

On varying at three different temperatures it may be concluded from the respective adsorption isotherm that the adsorption process of both the selected xanthene dyes on to Na-montmorillonite and Na-kaolinite is exothermic with heats of adsorption lying between 1 and 5 Kcal/mole and that the nature of the isotherm is unaffected by temperature variations. The experimental heat of adsorption may be regarded due to the net result of several processes such as solubility of the dyes, association of the dye molecules etc. where heat may be evolved or adsorbed.

It has been found that the heat of adsorption is not a constant quantity but changes with the amount of dye adsorbed, showing a minimum at a certain value of the dye adsorbed. The minimum point probably may occur to a situation when the monolayer is just complete or when the adsorption value approaches the c.e.c. of the mineral. In case of kaolinite the plot of heat of adsorption does not show a distinct minimum, but tends to increase regularly with adsorption. The result may be explained on the basis of adsorption of aggregated species by the clay minerals.

The heats of adsorption of RB > RG in the two minerals studied suggesting a stronger binding of the former dye to the mineral surfaces.

(Pages 133-143)

From the structure of the dye molecules it is clear that BB molecule can enter into an exchange type of sorption through $\overset{+}{-O-}$ group or through $\overset{+}{>N}$ - group and RB, RG through $\overset{+}{>N}$ - group, which become positive charge centres by resonance and can arrange themselves flat or in end-on or dye-on position. The resonance structure of the dye ion indicate three positive charge centers on BB and three on RB and RG. The structural consideration assigns to the dyes predominantly flat orientation on to clay surface. However other possibilities are not entirely excluded.

The probability of distribution among the different orientations is conditioned by various factors such as the basicity of Nitrogen group, the number of resonating structures, the molecular geometry of the dye cation, the nature of exchange sites etc. It is however to be noted that the flat position is possibly attended with minimum potential energy. The excess uptake of the dyes may be explained largely by assuming the sorption of aggregated dye cations onto montmorillonite surface and partially by the intercalation of the unionized dye molecules by the interlamellar space. Since the dye molecules are not staggered and can approach each other close enough, the adsorption of the dyes on montmorillonite probably imparts greater mobility to bring them in optimum proximity and proper orientation for micellation.

In the case of kaolinite BB^+ is adsorbed well in excess of c.e.c. as compared to RB and RG. The adsorption isotherm of BB^+ onto Na-kaolinite as onto other minerals studied are of high affinity class. The excess uptake may be due to sorption of aggregated dye ions and/or the unionised dye molecule by the mineral.

The adsorption isotherm of BB^+ on Na-laponite are of Langmuir type and the amount of the dye exchange are far in excess of the c.e.c. of the mineral compared to that of RB and RG. This higher adsorption of BB^+ is possibly due to its lesser size compared to RB^+ or RG^+ and stronger tendency of BB

molecules to form aggregates in solution as well as in the adsorbed state. The influence of the size of the dye is also significant during adsorption to the mineral.

From the values of the bonding constants obtained from intercepts of the Langmuir plots, it is noticed that the values of the constants for each mineral increase in the order RB > RG > BB.

Since Langmuir constants increased proportionately to the heat of adsorption, the higher value of the constant indicates greater heat of adsorption and also binding of the dyes to the higher energy sites of the adsorbent in the above order of the dyes.

Desorption studies on the sorbed xanthene dyes with various inorganic and organic cations also supports the view that dyes are attached to the minerals with increasing bond strength in the order RB > RG.

(Pages 144-147)

The adsorption spectra of the selected cationic dye by different aluminosilicates have been studied by visible spectroscopy. Adsorption of dyes takes place by the mechanism of cation exchange. The adsorbed cationic dye is located in the interlayer space. A study of the effect of varying concentration of different clay in a constant volume of specific dye on the location and intensity of bands proved to be useful in determining the adsorption capacity of the clay. Adsorbent

surfaces imparts mobility to the sorbed dye molecules and hence bring them in optimum proximity and proper orientation for dimerization or a higher degree of aggregation. Steric hindrance is assumed to be responsible for the lesser tendency towards aggregation. However, adsorption on clay surface can modify this effect. The change in spectral shift in RG, RB and BB in all systems studied here indicates their respective behaviour towards aggregation.

(Pages 148-173)

From the above summary discussion it may be concluded that various attempts has been made to present a comprehensive picture on different aspects of exchange equilibrium and the interaction of the selected dyes with clay minerals. It is observed that the adsorption of dye ions, although taking place through ion exchange, is associated with a number of factors such as molecular sizes, molecular geometry, dye-dye interaction and the surface characteristic of sorbents.

Abilities for desorption by various inorganic and organic ions from clay-dye complexes according to the order of preference are being summarised in table 21 (page 186). The sequences of desorbing ions have been justified in terms of size, shape, charge and steric hindrance of the adsorbates and the desorbing ions as well as the charge density and swelling properties of the aluminosilicates. The architectural dissimilarities of the aluminosilicates, specificities of certain

ions, hydrophobicity, hydration energy of the ions, give rise to occasional differences in the exchange behaviour of the clay minerals as discussed earlier.

Attempts have been made throughout the present investigation to explain the data in the light of various theories and models.

Table 23.

The order of preference of the various ions for the aluminosilicate surface against RG and RB ions.

Na-montmorillonite-RG complex	Na-montmorillonite-RB complex
a) $\text{Na}^+ \angle \text{Li}^+ \geq \text{K}^+ \angle \text{NH}_4^+ \angle \text{Rb}^+ \angle \text{Cs}^+$	a) $\text{Li}^+ \angle \text{Na}^+ \angle \text{K}^+ \angle \text{NH}_4^+ \angle \text{Rb}^+ \angle \text{Cs}^+$
b) $\text{Mg}^{2+} \angle \text{Ca}^{2+} \angle \text{Sr}^{2+} \angle \text{Ba}^{2+}$	b) $\text{Mg}^{2+} \angle \text{Ca}^{2+} \angle \text{Sr}^{2+} \angle \text{Ba}^{2+}$
c) $\text{TMA}^+ \angle \text{TEA}^+ \angle \text{TPA}^+ \angle \text{TBA}^+$	c) $\text{TMA}^+ \angle \text{TEA}^+ \angle \text{TPA}^+ \angle \text{TBA}^+$
d) $\text{DDTMA}^+ \angle \text{DDP}^+ \angle \text{CTMA}^+ \angle \text{CP}^+$	d) $\text{DDTMA}^+ \angle \text{DDP}^+ \angle \text{CTMA}^+ \angle \text{CP}^+$
Na-kaolinite-RG complex	Na-kaolinite-RB complex
a) $\text{Li}^+ \angle \text{Na}^+ \angle \text{K}^+ \leq \text{NH}_4^+ \angle \text{Rb}^+ \angle \text{Cs}^+$	a) $\text{Li}^+ \angle \text{Na}^+ \angle \text{K}^+ \angle \text{NH}_4^+ \angle \text{Rb}^+ \angle \text{Cs}^+$
b) $\text{Mg}^{2+} \angle \text{Ca}^{2+} \angle \text{Sr}^{2+} \angle \text{Ba}^{2+}$	b) $\text{Mg}^{2+} \angle \text{Ca}^{2+} \angle \text{Sr}^{2+} \angle \text{Ba}^{2+}$
c) $\text{TMA}^+ \angle \text{TPA}^+ \angle \text{TEA}^+ \angle \text{TBA}^+$	c) $\text{TMA}^+ \angle \text{TPA}^+ \angle \text{TEA}^+ \angle \text{TBA}^+$
d) $\text{DTMA}^+ \angle \text{DDTMA}^+ \angle \text{CTMA}^+ \angle \text{CP}^+$	d) $\text{DTMA}^+ \angle \text{DDTMA}^+ \angle \text{CTMA}^+ \angle \text{CP}^+$
Na-Laponite-RG complex	Na-Laponite-RB complex
a) $\text{Li}^+ \angle \text{Na}^+ \angle \text{K}^+ \leq \text{NH}_4^+ \angle \text{Rb}^+ \angle \text{Cs}^+$	a) $\text{Li}^+ \angle \text{Na}^+ \angle \text{K}^+ \angle \text{NH}_4^+ \angle \text{Rb}^+ \angle \text{Cs}^+$
b) $\text{Mg}^{2+} \angle \text{Ca}^{2+} \angle \text{Sr}^{2+} \angle \text{Ba}^{2+}$	b) $\text{Mg}^{2+} \angle \text{Ca}^{2+} \angle \text{Sr}^{2+} \angle \text{Ba}^{2+}$
c) $\text{TMA}^+ \angle \text{TEA}^+ \angle \text{TPA}^+ \angle \text{TBA}^+$	c) $\text{TMA}^+ \angle \text{TEA}^+ \angle \text{TPA}^+ \angle \text{TBA}^+$
d) $\text{DDTMA}^+ \angle \text{DDP}^+ \angle \text{CTMA}^+ \angle \text{CP}^+$	d) $\text{DDTMA}^+ \angle \text{DDP}^+ \angle \text{CTMA}^+ \angle \text{CP}^+$