

CHAPTER III

EXPERIMENTAL

SECTION - A

Three cationic dyes viz. Rhodamine B and Rhodamine 6G of Xanthene series and Brilliant cresyl blue (oxazine series) were chosen for the present work.

The description of the above mentioned dyes are being summarised in the following table (1).

Table 1

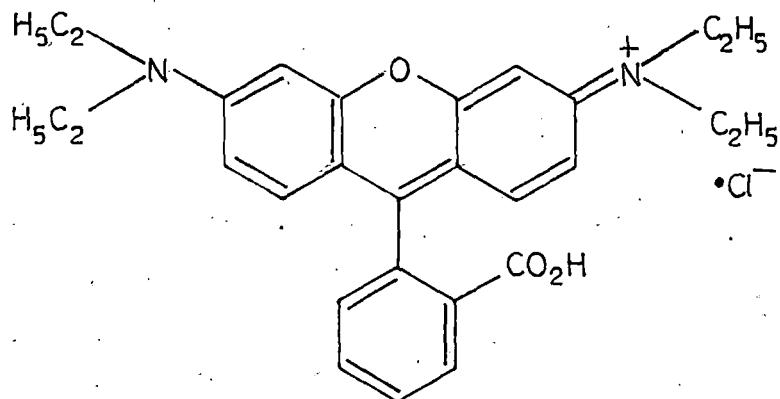
Sample	Symbol used	Description	Source
1. Rhodamine B	RB	Brown crystals hygroscopic	Merck
2. Rhodamine 6G	RG	Reddish brown crystal hygroscopic	Merck
3. Brilliant Cresyl Blue	BB	Dark blue crystal hygroscopic	The British Drug House, England

Preparation of Pure Dye

(a) Recrystallisation of Rhodamine B.

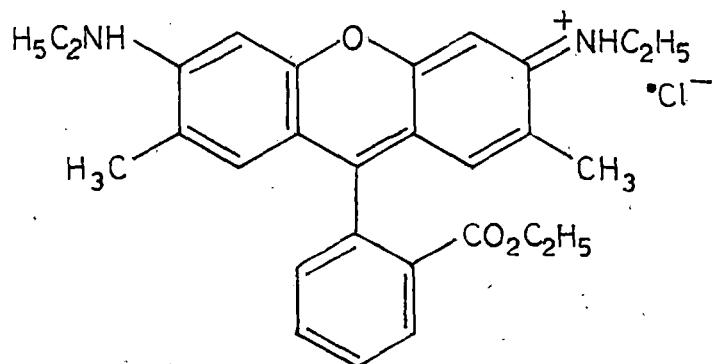
Rhodamine B chloride was purified by adding slowly with stirring about ten volumes of anhydrous ether to a saturated solution of the dye in absolute ethanol. It precipitated in

the form of golden green flakes. The process was repeated and the filtered solution was washed with ether and air dried. The structure of Rhodamine B is



(b) Recrystallisation Rhodamine 6G

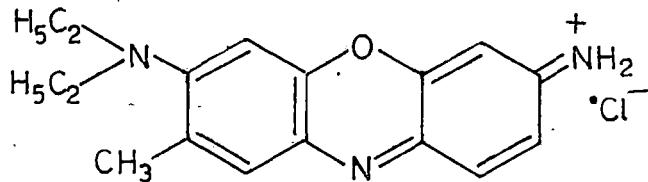
The Rhodamine 6G was obtained from Merck. It was twice recrystallised from ethanol and dried in a vacuum oven. The structure of Rhodamine 6G is



(c) Recrystallisation of Brilliant Cresyl Blue

The dye Brilliant Cresyl Blue was purified by repeated crystallisation from ethanol : water (1:1 v/v) mixture and dried at 80° for 24 hrs. The homogeneity of the samples was tested chromatographically.

The structure of Brilliant Cresyl Blue is :



Preparation of Stock Solution of the Dyes:

Stock solutions of RB, RG and BB were prepared by accurately weighing vacuum dried samples of the dyes and dissolving them in distilled water upto a definite volume. The concentration of these stock solutions, stored in polypropylene bottles, was of the order of 10^{-3} (M) and counter-checked through estimation by Ascorbometric Titration (1).

Ascorbometric Titration of Dyes:

2 ml of dye solution was mixed with 2 ml of 4(M) HCl in a glass vessel and kept in water bath at 70°C , CO_2 was passed into the solution to prevent aerial oxidation. The dye

solution was treated with standard ascorbic acid solution of the order of 10^{-2} (M) and the course of titration followed potentiometrically with Pt. indicator electrode. At the equivalent point the dye lost its colour and the potential attained a constant value.

SECTION - B

The alumino-silicates used for the interaction with the Cationic dyes discussed above, are described below in Table (2).

Table 2

Sample	Description	*Cation exchange capacity meq/100g	Source
1. Montmorillonite	Light grey powder	86*	Evans Medical Ltd., Liverpool, England
2. Kaolinite	White powder	5.4*	BDH, England
3. Laponite, XLG	White powder	88**	Supplied by Laponite Industries Ltd., England, as gift.

* Determined by $\text{BaCl}_2 - \text{Ba}(\text{OH})_2$ method

** Reported from source.

The clay fractions of minerals 1 and 2 having particle size $\angle 2.00 \text{ m}\mu$ were isolated by the usual method of dispersion and fraction by sedimentation. The fractions so collected were then treated several times with dilute HCl and after removal of acid, warmed with 6% H_2O to remove trace of any

organic matter present. Excess H_2O_2 was decomposed by heating the samples over water bath. The iron present in the clay minerals was then removed by treating the clay sample with sodium metabisulphide and sodium dithionite in acetate buffer solution ($pH \approx 5$) at $60^{\circ}C$ followed by centrifugation, washing etc. as recommended by Bromfield (2). Finally the clay residues were washed to dispersion and dialysed. The clay suspension was then converted into Na-form by stirring an approximately 2 per cent suspension of the clay with ion-exchange resin (Dowex 50W x 8) in the Na-form for about four hours. The process was repeated once again to ensure complete conversion of the clay mineral to Na-form. Na-clays ($pH 7$) so formed were used for adsorption and desorption studies.

Preparation of Na-laponite:

The synthetic hectorite clay used in this investigation was Na-laponite XLG. To ensure complete saturation with sodium, the Na-laponite was brought into dialysis bags and washed several times with 1(N) NaCl solutions, before dialysing against distilled water until free of chloride.

Adsorption Studies:

10 ml portions of the suspensions of known clay content, were pipetted into separate stoppered polypropylene bottles (3) and dye solution of known concentration, was added in increasing amount. The total volume was brought to 20 ml by quantitatively adding the necessary amount of distilled water. The bottles, with their contents, were shaken for three hours

and allowed to stand for at least 24 hours to attain exchange equilibrium. Experiments with several days equilibration produced the same results indicating that 24 hours were sufficient for attaining equilibrium. The resulting exchanged clays were then centrifuged (10,000 r.p.m.) for 10 minutes or so, and the supernatant liquids were analysed spectrophotometrically using spekol of Carl Zeiss. From the difference between the initial concentration and the equilibrium concentration, the amount adsorbed was determined. All operations were carried out at constant room temperature.

The clay content of the suspension was measured by evaporating a known volume of the clay suspension to dryness at 100° C to 105° C in an air oven. The contents expressed in g/100 ml are given in Table 3.

Table 3

Sample	Clay content in g/100 ml
1. Na-montmorillonite	1.0
2. Na-Kaolinite	0.70
3. Na-Laponite	0.722

Desorption Studies:

For studying desorption, the clay mineral suspensions were mixed with dye solution of such a concentration that the equilibrium concentration was maintained at 1×10^{-5} (M) or so to ensure monomer sorption (4) as far as possible. The mixtures were shaken for four hours and allowed to equilibrate overnight at constant temperatures. The excess dye was washed off with distilled water by repeated centrifugation of the clay-dye complex till the leachate gave zero optical density. The resulting clay dye complex was then resuspended in distilled water and used for desorption studies. The percentages of colloid contents of the suspensions were determined by drying a known amount of each at 100°C to constant weights, and are given in Table 4.

For the purpose of desorption studies, 10 ml portions of the suspension were taken in a number of stoppered polypropylene bottles and varying amounts of different electrolytes were added. The total volumes were adjusted to 30 ml by quantitatively adding requisite amounts of distilled water. The bottles, with their contents, were shaken for four hours and kept overnight to equilibrate. Preliminary studies showed that this period was sufficient for the purpose. The mixtures were then centrifuged (100,000 r.p.m.) for 15 minutes or so and the dye content of the clear centrifugate was estimated spectrophotometrically as described earlier.

Table 4

Sample	Content
1. Na-montmorillonite-RG	0.112
2. Na-montmorillonite-RB	0.108
3. Na-Kaolinite-RG	0.132
4. Na-Kaolinite-RB	0.1281
5. Na-Laponite RG	0.08
6. Na-Laponite RB	0.114

The clay content is different from each sample. It is known however, that the difference does not affect the exchange reactions to a great extent (5)

Of the various electrolytes used in the desorption studies, LiCl, NaCl, KCl, NH₄Cl, RbCl and CsCl were of E. Merck quality : cetyl pyridium Bromide (CPBr), Cetyltrimethyl ammonium bromide (CTMABr), dodecylpyridinium bromide (DDPBr), dodecytrimethylammonium bromide (DDTMABr) were of BDH-AR quality. Standard solution of these electrolytes were prepared by direct weighing of vacuum dried salts. Tetramethyl ammonium Bromide (TMABr), tetraethyl ammonium Bromide (TEABr), tetrapropyl ammonium Bromide (TPABr), and tetrabutyl ammonium

Bromide (TBABr) were all of "Fluka" (Switzerland products). These were standardized by titration with AgNO_3 of E. Merck quality using potassium chromate as indicator.

MgCl_2 and CaCl_2 solutions were prepared with BDH. AR quality samples were standardized by EDTA titration, using Eriochrome Black T as indicator and the concentration of SrCl_2 and BaCl_2 prepared with A.R. quality samples were determined by precipitating as sulphates.

Spectrophotometric Study of Dye aggregation

On clay surface:

Varying amounts of increasing percentage of clays were added to a definite volume of a fixed concentration of dye. These were shaken and the spectra of the mixtures were recorded in Graphicord Model No. UV-240, double beam uv-vis Spectrophotometer (Shimadzu, Japan), using cell of 1 cm and 1 mm path in the visible region. The spectra were taken within 15-20 minutes after the preparation of the clay-dye suspensions to eliminate the effects of flucculations due to aging on the intensities of absorption bands (6).

X-ray measurements:

For preparing clay-dye complex at different percentage of saturation, appropriate amounts of selected dyes were added to Na-montmorillonite suspension, equilibrated and centrifuged

several times to wash off the excess dye. The samples were then allowed for drying in an air oven at 120°C , then gently grounded with a mortar and pestle and stored in a vacuum dessicator over silica gel. The X-ray diffraction study of the finely powdered samples containing different clay-dye complexes and Na-montmorillonite clay alone (dried as per above method) was carried out at the Department of Physics, College of Engineering, Anna University, Madras, using Philips, PW-1010, X-ray Diffractometer with $\text{CuK}\alpha$ radiation at 25 KV and 20 mA.

Infrared Analysis

The infrared analysis of different clays was carried out in our own laboratory with Beckman IR-20 Spectrophotometer using KBr pellete. Spectra of dyes and clay-dye complexes were recorded with KBr pellete at North Hill University, Shillong, Meghalay using instrument of Perkin Elmer, Model No. 297.

Effect of temperature on Adsorption

Adsorption experiments as described earlier were made in thermostatic shaker, at three different temperatures. The results are discussed in Chapter VII.

Measurement of concentration of the dyes

Quantity of adsorbed or exchanged dyes onto a clay from an aqueous solution was measured by determining with Graphicord, Model No. UV-240, double beam UV-VIS Spectrophotometer (Shimadzu, Japan) using cell of 1 cm path in the visible region, the amounts remaining in solution. In case of dimerisation of the dyes (Bergman and O'Konski, 1963) at higher concentration and salting out effect of the electrolytes at higher concentration, this measurement will be complicated. Beer's law was found through trial run to be applicable within 5% error at concentration below 8×10^{-6} (M) for RB, 9×10^{-6} (M) for RG and 6×10^{-6} (M) for BB. The measurements were made at wave lengths which showed maximum absorptions (λ -peaks) which were 525 nm for RG, 552 nm for RB, 640 nm for BB. Salt effects were noticed for electrolyte concentrations above 0.5(M). The absorption of these dyes by glass was another possible source of error. Hence the following measures were considered in carrying out adsorption and desorption studies of dyes.

(1) Polypropylene containers were used all along in carrying out the various experiments (3).

(2) The readings in Spectrophotometer were taken always after adequate dilution of the experimental solutions.