

CHAPTER III

EXPERIMENTAL

Instruments, methods of operation and materials:

Polarograph: A recording polarograph (Radokis, Type OH : 102) has been used in all the polarographic work. The instrument is highly sensitive with a sensitivity upto 2×10^{-10} amp/div. The dropping mercury electrode with characteristics $n = 3.22$ mg/sec and $t = 3.56$ secs, measured open circuit, served as the cathode. The reference electrode is a saturated calomel electrode, specially constructed suitable for work in cells with a high resistance.

pH-meter: For all pH measurements and for the potentiometric titrations for aluminium hydroxide with bases, the Radokis Precision pH-meter of Type OR: 205 has been used. With a steady line voltage of 220 volts ac., the accuracy of the instrument is in the range of ± 0.005 . An extra sensitive combined glass and calomel electrode was used.

Spectrophotometer: For the measurement of the dye concentrations in the b.e.c. experiments the spectro-colorimeter 'Spectol' of Carl Zeiss was used.

Aluminium hydroxide, silica and the silicate minerals used in the investigation are described below in Table 3.1.

TABLE 3.1

Sample	Symbol	Description	Total exchange capacity (m.e. / 100 gm)	Source
1. Aluminium Hydroxide	A	White powder	6.15	C.S.I.R. chromatographic alumina (neutral)
2. Aluminium Hydroxide	B	"	6.06	Prepd. in the lab.

TABLE 3.1

Sample	Symbol	Description	Total exchange capacity (ml. eq./100 gm)	Source
3. Aluminium Hydroxide	G	White powder	6.61	Prepd. in the lab.
4. Silica Gel	S	"	16.4	D.D.H., L.R.
5. Bentonite*	B ₁	Light pink-grey powder	106.00	Dyan's Lab., (England)
6. Vermiculite*	V	Pinkish yellow	120.00	Obtained through the courtesy of Prof. S. K. Mukherjee**
7. Raja Bannohumpur* soil (pre-dominantly Illite)	I	Grey when powdered	19.6	Collected through P. Ray of this Department).
8. Kaolinite* (Rajmahal)	K	Pale white	12.3	Supplied by Calcutta Mineral Supply Ltd.

The fractions of minerals 1,4,5,6,7 and 8 having a particle of 2.0μ were isolated by the usual method of grinding, dispersion and fractionation by sedimentation. The fractions so collected were then

*,** Judged from X-ray examination samples 5-8 are pure montmorillonite, pure vermiculite, predominantly Illite with traces of Kaolin and pure Kaolinite respectively. Thanks are due to Prof. S.K. Mukherjee, Member, National Commission of Agriculture, New Delhi for the X-ray examined vermiculite sample (6), to the Director, C.G.C.R.I., Calcutta for the X-ray examination reports of samples (5) and (7) and to Dr. S.P. Bhattacharya of Calcutta University for the X-ray examination report of sample (8).

treated several times with dilute HCl and after removal of the acid, with 6% H_2O_2 for traces of organic impurities. It was then boiled to decompose the organic matter, if any, and to remove the excess H_2O_2 . The fractions were then washed with distilled water to remove soluble impurities. Next, the samples were subjected to appropriate ion-exchange treatment (Dowex 507 X-8 and Dowex 2-X6) to convert them to the H-form and also to remove traces of ionic impurities. The resulting exchangers in the H-forms were then used for adsorption, desorption and polarographic studies. The exchange capacities were found to be in order.

Samples (2) and (3) were prepared in the laboratory. (2) was prepared according to the standard method (139), by the hydrolysis of Al-ethoxide, the hydrolysis being carried out at 60° - 70° C in conductance water. The alcohol was removed by evaporation at low pressure and elevated temperature (60° - 70° C). (3) was prepared by the hydrolysis of Al-Hg amalgam in conductance water at 60° - 70° C. The former was prepared by the direct reaction of metallic aluminium (B.Merck) and triple distilled mercury (B.Merck). The resulting sol was a fine dispersion, being almost gel-like. The sols were rapidly aged by keeping around 60° - 70° C for a few hours.

All the above samples were used for polarographic studies, while B, C, B₁ and S were used for adsorption, desorption and polarographic studies as also for the determination of the base exchange capacity (b.e. c).

Exchange capacity studies:

The exchange capacities of all the exchangers were determined first by the standard methods using half-saturated KCl, 1(N) BaCl₂.

(ii) Tetra-methyl ammonium chloride (TMA-Cl), the corresponding titrants being NaOH , $\text{Ba}(\text{OH})_2$ and tetra-methyl ammonium hydroxide (TMA-OH). The latter was prepared from TMA-Cl by treatment with anion exchange resin Amberlite IR 401 and was standardised. In the spectrophotometric method equal and definite volumes of suspension of known colloid concentration were taken in different stoppered pyrex bottles. Varying amounts of cationic dye viz., methylene blue, malachite green and crystal violet of known concentration were added, upto a concentration approximately equal to three times the b.e.c. These were then allowed to equilibrate with occasional shaking in a mechanical shaker and kept overnight. The samples were then centrifuged, and the dye concentrations in the centrifugate were determined with the help of the spectrophotometer "Spokol". From a difference of the concentrations of the amount of dye added and the amount in the centrifugate, the amount absorbed is determined. Adsorption isotherms are plotted, from the steady part of which the b.e.c is calculated.

Polarographic method for the determination of exchange capacity:

In the polarographic method, definite amounts of the suspension of known colloid concentration were taken in different stoppered pyrex bottles, and definite amounts of electroactive ions in the form of solutions of TiCl , TiClO_4 or Coon_2Cl_3 of known concentration, were added covering a concentration range from 10% to over 150% of the respective b.e.c.'s of the exchangers (as determined by the previous methods). The volume of the suspension in each bottle was made the same by the addition of requisite amount of water. The samples were equilibrated by shaking and were kept overnight. Next, 5 ml aliquots were drawn from each bottle and 5 ml of the supporting electrolyte viz., LiCl or LiClO_4 solution was added such that the concentration of the supporting

electrolyte is 0.075 (N) in the experimental suspension. The samples were once again equilibrated, and kept overnight. Concentrations of the electro-active species in the experimental suspension⁵ in the range 10^{-5} to 10^{-4} (N) and the colloid concentrations were : 0.02% for bentonite system; 0.16% for silica gel system; and 0.17% for the $Al(OH)_3$ system. Polarograms were recorded in degassed suspensions, using 0.0025% Triton K-100 as the maximum suppressor. It was found that a mild stirring of the suspension was necessary in order to obtain satisfactory results. This was achieved by passing a regulated stream of pure nitrogen gas through the suspension, at the rate of 80-100 bubbles per minute through a fine jet. Values of the current were taken corresponding to the mean oscillations of the recorder. The instrument was set at zero damping for the CoO_3^{3+} systems and a damping of 2 for the Tl^+ systems with a span voltage of -2.0 Volts and a running speed of 8 minutes. Corrections for the residual currents were done from the curves of the respective sol in H-form in supporting electrolyte of same concentration as in the above experiment. The measurement was done with the same colloid having identical consistency allowing it to equilibrate overnight with supporting electrolyte after shaking for 2-3 hours. The residual current is found to be very small. The currents thus obtained after residual corrections were plotted against the concentration of the electro-active ion in the experimental suspension. A curve is obtained with a point of inflexion. The amount of electrolyte in the suspension at the inflexion point is found to correspond to the exchange capacity of the respective sols.

After recording of the polarograms, the viscosity of the same suspensions was determined, using the Ostwald viscometer thermostated in water at a temperature of 28°C. The 'n' and 't' values for the

suspensions were also determined at potentials corresponding to the plateau of the Tl^+ and CeO_2^{3+} waves. The height of the mercury was maintained constant at 31 cm, throughout the experiment. The respective diffusion coefficients for the Tl were calculated from the experimental values of 'i', 'n' and 't', using the Ilkovic equation (140).

The same suspensions were next centrifuged and the polarograms of the centrifugates were recorded. Residual corrections were done by recording a polarogram of the centrifugate of the respective col in H-form of the same colloid concentration, and after being equilibrated with the same supporting electrolyte similarly as above. The pH of all the experimental suspensions was noted.

Another experiment was performed with H-bentonite suspension equilibrated with $TlClO_4$. Here, no supporting electrolyte is used for the polarographic work. To 5 ml. of the equilibrated suspension was added Triton X-100 so that its concentration in the suspension is 0.0025%, and polarograms were recorded. The limiting current vs concentration of $TlClO_4$ in the experimental suspension gives a point of inflexion. The amount of electro-active ions in the suspension corresponding to the inflexion point gives the h.s.c. of the exchanger.

Effect of supporting electrolyte:

The effect of the supporting electrolyte $LiClO_4$ on the nature of the polarograms, the reversibility of the reaction at the dropping mercury electrode (d.m.e) and its effect on the diffusion coefficient of Tl^+ in the suspension were studied by saturating the suspensions with the electro-active species in the manner as described above and recording the polarograms after equilibration with the supporting electrolyte of varying concentrations, viz. from 0.00037 (II) to 0.075 (II). The same

colloid concentration was maintained in each bottle by adding requisite amount of water. The limiting currents were noted and the 'm' and 't' values were determined at a potential corresponding to the plateau of the polarographic wave viz. at -0.65 Volt. The corresponding half wave potentials were noted. The diffusion current constants (I) and the diffusion coefficients (D) were calculated by use of the Ilkovic equation (136).

Adsorption studies:

Studies on adsorption were carried out on bentonite, silica gel and aluminium hydroxide (C). Aliquots of the suspension of known colloid content were taken in batches in different stoppered pyrex bottles and HClO_4 or HCl solution of known concentration were added in increasing amounts in a range from 10% to over 200% of the b.e.c. of the exchanger. The total volume in each bottle was adjusted to 40 ml by adding the requisite amount of water. The colloid content of the exchangers in the resulting suspensions were: 0.02% for bentonite, 0.16% for silica gel and 0.17% for aluminium hydroxide respectively. The concentration of the added electrolyte was of the order of 10^{-4} - 10^{-5} (M). The bottles with their contents were shaken for 4-6 hours and kept overnight at a known constant temperature in a thermostat to equilibrate. Next day the bottles were shaken for one hour at the same temperature and the contents were centrifuged (4000 r.p.m.) for about 5 minutes and the polarograms of the centrifugate were recorded using HCl as the supporting electrolyte and Triton X-100 as the maximum suppressor, in order to determine the concentration of the H^+ in the solution phase. From the difference between the concentration of added H^+ and that in the centrifugate, the amount adsorbed is calculated. The pH of the suspensions were noted before centrifugation. They were found to be in the range 6.15 to 6.54

for silica gel and bentonite, and 7.0 to 7.4 for aluminium hydroxide.

The colloid contents of the suspensions were determined by evaporating known volumes to dryness at 105° - 110° C in an air oven and subsequent drying at the same temperature for 24 hours.

In order to determine the extent of physical adsorption, the equilibrated suspensions containing $TlClO_4$ or $TlCl$ were centrifuged, the centrifugate decanted off and the residue was thoroughly leached with a known volume of conductance water and the polarograms of the leachates were recorded after centrifugation in order to determine the amount of Tl loosely bound to the solid. From the observed values it appears that physical adsorption is negligible.

Adsorption at different temperatures:

Exactly as above suspensions were saturated with $TlCl$ or $TlClO_4$ and the samples were thermostated at various temperatures in the range 2° - 32° C, and allowed to equilibrate overnight. During equilibration the suspensions were occasionally shaken at the same temperature. 10 ml portions were withdrawn and centrifuged at 4500-4800 r.p.m for 1-1½ minutes. 5 ml of the centrifugate was withdrawn and its polarogram was recorded to estimate the Tl^{+} using 0.075 (M) $LiCl$ as the supporting electrolyte and 0.0025% Triton X-100 as the maximum suppressor. From a difference of the amount of Tl initially added and that present in the centrifugate the amount adsorbed is determined and adsorption isotherms corresponding to different temperatures were plotted.

Preliminary studies showed that the above time of centrifugation was sufficient in order to obtain a clear centrifugate. For temperatures far below or above the room temperature precautions were taken so as to expose the suspension for a minimum time to the room temperature. The entire operation of withdrawal of the suspension till the

withdrawal of centrifugate after centrifugation was completed in about 4 minutes.

// Desorption studies from Ti-bentonite system:

// For desorption studies of Ti from Ti-bentonite systems the suspension was saturated to different extents with $TiClO_4$ exactly in the same manner as in the adsorption studies, and in a similar concentration range. For equilibrium, the samples were thermostated and shaken at the room temperature and kept overnight. 5 ml aliquots were withdrawn and thermostated at a definite temperature until equilibrium was attained. 5 ml of the desorbing electrolyte was thermostated at the same temperature and then was mixed with the suspension. The concentration of the desorbing ion bears a 1:1 symmetrical relationship to the b.e.c. of the bentonite solution. After equilibration overnight in the thermostat the suspension was centrifuged and the Ti^{+} in the centrifugate was estimated polarographically using 0.075 (M) LiCl as the supporting electrolyte and 0.0025% Triton X-100 as the maximum suppressor. From adsorption studies the amount of Ti^{+} initially present in the solution phase at the same temperature was known. Hence the amount of Ti^{+} desorbed is determined from the difference in concentrations.

// The desorbing species are the 1 : 1 electrolytes of the alkali metal series viz., Li^{+} , K^{+} , Rb^{+} and Cs^{+} while the organic 1 : 1 electrolyte species are $(CH_3)_4N^{+}$, $(C_2H_5)_4N^{+}$ and cetyl tri-methyl ammonium ions (CTA^{+}) .

// Desorption of Ti from Ti-B-bentonite at different temperatures:

// The temperature effect on the desorption of Ti^{+} from a suspension of 100% saturated Ti-bentonite system was studied. From the adsorption isotherms, the amount of $TiClO_4$ and LiCl necessary to fully saturate the bentonite gel was determined. The precise amounts were added and the systems equilibrated overnight. The $TiClO_4$ systems were centrifuged and

the centrifugate discarded. The residue was repeatedly leached with conductance water to remove the excess electrolyte; the suspension was again centrifuged and the residue resuspended in conductance water. The colloid content was determined by the usual method. For the TiCl_4 system, the desorptions were carried out in the presence of excess TiCl_4 . Next, 5 ml aliquots of the suspension was mixed with 5 ml. of various desorbing electrolyte solutions, viz., LiCl , KCl , RbCl , CsCl and $(\text{CH}_3)_4\text{NCl}$, $(\text{C}_2\text{H}_5)_4\text{NBr}$ and CTA-Br , so that the concentration of the desorbing ion was in a symmetry concentration of 1 : 1 to the b.c.c. of the bentonite sol. The system was thermostatted at temperatures 0° , 5° , 10° , 15° , 20° , 25° and 30° C, and kept overnight. The centrifugation was done with due care as in the adsorption studies, and the amount desorbed was calculated by estimating the Ti^+ in the centrifugate. The selectivity coefficients were calculated and plotted against the temperature.

pH-titrations of aluminium hydroxide:

Aluminium hydroxide suspensions A, B, C were subjected to pH titrations, using bases KOH , $\text{Ba}(\text{OH})_2$, TMA-OH , tri-methyl amine, ethyl amine, and n-hexyl amine. 10 ml. aliquots of the suspensions were taken in standard joint pyrex bottles and increasing amounts of a known concentration of base were added. The systems were equilibrated for 2-3 hours and the pH of the suspensions were noted. The colloid concentrations were for the three samples A, B, C, 0.27 g/100 ml., 0.22 g/100 ml., and 0.22 g/100 ml. respectively. The titrations were first performed with 10^{-3} (M) and next repeated with 10^{-5} (M) bases.

Polarograms of suspensions of ion-exchangers:

The exchangers C, S, B₁, V, K and L were treated with excess TiCl_4 , CaCl_2 at concentrations corresponding to 3-4 times the respective b.c.c.'s. They were then shaken for 3-4 hours and allowed to equilibrate

overnight and finally centrifuged. The centrifugate was discarded. The residue was leached with conductance water and again centrifuged. This process was repeated for all the exchangers separately until the centrifugate showed polarographically undetectable amounts of the electro-active species in solution. The residue was resuspended in conductance water and the colloid contents were determined by the usual method of evaporating and drying at 110° C of a known volume of suspension. The polarograms of the freshly prepared suspensions in the El- and Coen₃-forms were recorded first without supporting electrolyte. Separate curves were recorded for the suspension both in stirred and unstirred conditions. The effect of adding 0.0025% Triton X-100 as the maximum suppressor was also observed. From the curves thus obtained the positions of the polarographic maxima were located, the corresponding currents at the maxima, and the half-wave potentials were noted. The effect of ageing of the suspensions were studied by similar recordings at intervals of a few days, the last reading being obtained after 45 days of preparation of the respective sols.

The electro-capillary curves were obtained by use of a separate lot of the freshly prepared suspensions. A $\frac{1}{10}$ aliquot of suspension was taken in the polarographic cell, and the time for 50 drops was determined using a stop-watch. This was done at different potentials from 0 to -1.6 volts. The individual drop time was determined and plotted against the applied potential.

In another experiment the suspensions either in El- or Coen₃-form were mixed with a supporting electrolyte eg., LiClO_4 . The polarograms were recorded in deaerated solution within 5 minutes of mixing, using 0.0025% Triton X-100 as the maximum suppressor. Rapid recording of the polarogram is necessary because prolonged contact with the supporting electrolyte causes desorption of the electro-active ion from the exchanger

matrix. In order to see whether appreciable desorption takes place or not, the same suspension was immediately centrifuged as soon as the recording was over, and the centrifugate was examined polarographically. Results show that desorption of Coen_3^{3+} is negligible while, the desorption of Tl^+ is considerable. The E_p of the suspensions were also noted.

Determination of the rate and time of attainment of exchange equilibrium

in the desorption of Tl^+ and Coen_3^{3+} by Li :

The exchangers C, S and B were saturated by adding a known excess of electro-active species viz., TlClO_4 or Coen_3Cl_3 in a concentration 3-4 times the respective b.e.c.'s. The systems were shaken for 3-4 hours and equilibrated overnight. They were then centrifuged, and the centrifugate was discarded and the residue were repeatedly leached with conductance water and the suspensions were again centrifuged. This process was repeated until the centrifugate showed negligible amounts of Tl^+ or Coen_3^{3+} in the solution phase. The residues were resuspended in conductance water and the colloid contents were determined by evaporating definite volumes of suspensions in an air-oven and subsequently drying for 48 hours at $100^\circ - 110^\circ \text{C}$. 5 ml. aliquots of the suspensions were taken in polarographic cells and 5 ml. of LiCl , (where Li is the desorbing ion) was added, such that the concentration of the LiCl in the suspension was 0.075 (M). 0.0025% Briton K-100 was used as the maximum suppressor. Both the suspension and the LiCl solution were deaerated before mixing, by bubbling pure nitrogen gas through them separately. The time of mixing of the two was noted, and polarograms of the system were recorded at definite intervals of time. From the resulting curves the E_p and limiting currents were noted. The limiting currents were plotted against time. A final flat region indicates the attainment of equilibrium.

Reagents:

The reagents employed in the adsorption and desorption studies and polarographic studies and pH titration of aluminium hydroxide were of the following grade: TiCl_3 , TiClO_4 , LaClO_4 , LiCl , KCl , BaCl_2 , KOH , $\text{Ba}(\text{OH})_2$, CaCl_2 , RbCl , were of E. Merck grade, while $(\text{CH}_3)_4\text{NCl}$, $(\text{C}_2\text{H}_5)_4\text{NBr}$, cetyl trimethyl ammonium bromide (CTA-Br), trimethyl amine, ethyl amine and n-hexyl amine were of Fluka, and were 'polarographic pure' reagents. The cationic dyes malachite green and crystal violet were of E. Merck while methylene blue (Gurr's, England) was purified from the products of its degradation (18) by solvent extraction (18) and its purity was checked spectrophotometrically ($\lambda_{\text{max}} = 6670\text{\AA}$). The Cs_2CO_3 was prepared in the laboratory by Jorgensen's method (62), and was doubly recrystallised from alcohol - water medium. The tetra methyl ammonium hydroxide (TMA-OH) was obtained by repeatedly passing a solution of tetra methyl ammonium chloride through an anion exchange column (Dowex 1-N3) in OH-form.

Standard solutions of the adsorbing electrolytes viz., LiCl , KCl , RbCl , CsCl were obtained by weighing definite amounts of the vacuum dried sample. The tetra methyl salts were standardised in solution by titration with standard AgNO_3 using potassium chromate as the indicator. The amines and the TMA-OH were standardised potentiometrically by titration with a standard solution of potassium bi-phthalate.