

Chapter III

EXPERIMENTAL

Silicate minerals, used as adsorbents, are described below in Table 1.

Table 1

Sample	Symbol	Description	Total Exchange capacity (me/100 gm of clay fraction*)	Source
1. Bentonite	B ₁	Light grey powder	92	Calcutta Mineral Supply Co.Ltd.
2. Bentonite	B ₂	Light pink powder	110	Do
3. Vermiculite	-	Pinkish yellow when powdered	120	Obtained through the courtesy of Prof. S.K. Mukherjee**, Calcutta.

The clay fractions having particle size $< 2.0 \mu$ were isolated and collected by the usual method of dispersion and sedimentation.

* Determined by BaCl₂ - Ba (OH)₂ method

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The fractions so collected were then treated several times with dilute HCl and after removal of acid with 6% H_2O_2 to remove traces of organic matter, if any. After boiling to decompose the organic matter and excess of H_2O_2 , the clay fractions were washed two or three times with distilled water to remove the soluble impurities. The clays were then converted into H-form by appropriate treatment with resin (Dowex 50W x 8 and Dowex 2 - X8). H-clays so formed were used for adsorption studies. The total exchange capacity values of the samples are of the expected order found in the literature.

10 ml portions of the suspensions, of known clay-content, were taken in different stoppered pyrex bottles and $Coen_3Cl_3$ and $Co(NH_3)_6Cl_3$ solutions, of known concentration, were added in increasing amounts. The total volumes were adjusted to 15 ml by adding requisite amounts of water. The bottles, with their contents, were shaken for one hour and kept overnight at known constant temperature in thermostat for equilibrium. Preliminary studies showed that this period was sufficient for the purpose. Next day the bottles were shaken for one hour at the same temperature. The mixtures were centrifuged (2000 r.p.m) for 15 minutes or so, and the supernatant liquids were analysed colorimetrically using the Zeiss photo electric grating colorimeter, 'Spekol'. From the difference between the initial concentration and that of the equilibrium concentration, measured above, the amount adsorbed was determined.

Exploratory experiments revealed that the adsorption of Coen_3Cl_3 and $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ on clays varies with pH.

The clay contents of the suspensions were determined by evaporating known volumes to dryness at $105 - 110^\circ\text{C}$ in air oven. The contents expressed in gms/100 ml vary slightly with the systems used and are given in Table 2.

Table 2

Sample	For Coen_3Cl_3 sorption	For $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ sorption
H-bentonite (B_1)	1.89	1.02
Na-bentonite (B_1)	1.80	1.81
H-vermiculite	1.62	1.62
Na-vermiculite	1.42	-

In order to study the dependence of adsorption on pH, the following procedure has been adopted. To mixtures of H-bentonite and Coen_3Cl_3 or $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ containing known amounts of each were added varying amounts of NaOH in order to bring them to different

pH values. The amounts of Coen_3Cl_3 or $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ adsorbed after equilibrium were then determined by absorbance measurements.

Desorption Studies.

For this purpose the mineral suspensions were mixed with Coen_3Cl_3 or $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ solution containing about three times the predetermined conc., at two different pH (one at the pH of the H-clay and the other at pH 9.5), shaken for two or three hours and allowed to equilibrate overnight as before in thermostat. The excess salt was washed out with distilled water by repeated centrifugation of the clay-complex till the leachate gave zero optical density. The resulting clay was then resuspended in distilled water and used for desorption studies. The percentage colloid content of the suspension was determined by drying a known amount of it at 105-110°C to constant weights, and are given in Table 3.

Table 3

Sample	H- Coen_3 -clay	Na- Coen_3 -clay	H- $\text{Co}(\text{NH}_3)_6$ - clay	Na- $\text{Co}(\text{NH}_3)_6$ - clay
Bentonite	1.94	1.534	1.72	1.35
Vermiculite	1.86	2.213	1.925	2.445

For the purpose of desorption studies 10 ml aliquots of the suspension were taken in pyrex bottles to which increasing amounts of different electrolytes were added. The total volume was adjusted with water to 15 ml in all the cases. The bottles with their contents were shaken for two hours and allowed to equilibrate overnight. Preliminary trials showed that these periods were sufficient to ensure equilibrium. The minerals were then centrifuged for 15 minutes or so and the Coen_3Cl_3 or $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ contents of the clear centrifugates were measured as described earlier.

For identification of the pure clays and clay-complexes, x-ray diffraction studies of some of the samples were done and the results are given in the Table (4) below. X-ray diffraction patterns* were taken in a Nonius Guinier Camera provided with a quartz crystal monochromator. Philips PW - 1010 X-ray crystallographic unit fitted with a copper target was used. Tube was run at 30 K.V. and 20 M.A.. The time of exposure was 15 hours and 30 minutes. Intensity $\frac{I}{I_1}$ was estimated visually with respect to the strongest line of pattern taken as 10.

* Obtained through the courtesy of the Director, Glass and Ceramics Research Institute, Calcutta-32.

Table 4

H-bentonite (B ₁)		H-Coen ₃ -bentonite(B ₁)		Na-Coen ₃ -bentonite(B ₁)		H-vermiculite	
d in A°	I/I ₁	d in A°	I/I ₁	d in A°	I/I ₁	d in A°	I/I ₁
13.33	WB	13.065	10	13.29	6VVB	14.49	10
4.485	10	4.48	10	4.50	10	4.61	4
4.04	7	4.03	7	4.05	5	2.64	5
3.35	6	3.345	4	3.35	2	2.59	4
						2.55	4
						2.39	3B

V = Very;

W = Weak;

B = Broad.

Few words must be said with regard to the data presented in table above.

It has already been pointed out (PB 3,4 Chapter I) that the c-axis dimension of montmorillonite is not fixed but varies from about 9.6\AA , when no polar molecules are between the unit layers, to substantially complete separation of the individual layers in some cases. From the data presented in Table 4 it is apparent that the spacings in H-bentonite, Na-Coen₃-bentonite, H-Coen₃-bentonite are almost similar. This identity in the values suggests that the replacement of H⁺ or Na⁺ by [Coen₃]³⁺ does not change the thickness of water layers between the silicate layers. Remembering that under ordinary conditions a montmorillonite with Na as the exchange ion has one molecular water layer and a c-axis spacing of about 12.5\AA , the presence of single water layer is highly probable in H-Coen₃-bentonite and Na-Coen₃-bentonite also. The intensity (I/I_1) of H-Coen₃-bentonite is 10, while that of H-bentonite is weak and broad. On the same scale the intensity of Na-Coen₃-bentonite is 6 but it is too broad. The results, therefore, seem to be of considerable importance for identification of montmorillonite. In this context it may also be mentioned that the role of the size as well as the structure of the [Coen₃]³⁺ as the exchange ion cannot be completely ruled out in interpreting the x-ray data. The presence of very little water or no water at all in between the unit silica layers may be the reason for its higher intensity. However, for a better understanding, more data are necessary. It may be noted in this

connection that Martin and Glaeser (31) observed that the characteristic spacing of 14\AA of $\text{Co}(\text{NH}_3)_6$ -montmorillonite complex does not vary with humidity. From this observation these authors concluded that the adsorption of $[\text{Co}(\text{NH}_3)_6]^{3+}$ in montmorillonite suppresses the effect of swelling or expansion in moisture. Referring to the data of H-vermiculite, it is seen that the strong reflection at 14.49\AA with I/I_1 value as 10 and the subsequent weaker basal reflections are characteristic of vermiculite and the sample appears to be fairly pure.

Trisethylenediamine cobaltic chloride (Coen_3Cl_3) was prepared by the method of Jørgenson (93) from ethylenediamine and cobalt chloride by aerial oxidation and crystallised three times from alcohol-water medium.

Similarly, hexammine cobaltic chloride ($\text{Co}(\text{NH}_3)_6\text{Cl}_3$) was prepared by the method of Fernelius (94) by vigorous aerial oxidation from ammonium chloride, ammonia and cobalt chloride in the presence of activated carbon. It was also crystallised 2-3 times from water before use.

NaCl , KCl , NH_4Cl , RbCl , CsCl , cetylpyridinium chloride (CPCl) were of E. Merck quality, cetyltrimethylammonium bromide (CTABr) was of BDH-AR quality. Standard solutions of these

electrolytes were prepared by direct weighing of vacuum dried salts. LiCl was of BDH-AR quality and $(\text{CH}_3)_4\text{NCl}$, $(\text{CH}_3)_4\text{NBr}$, $(\text{CH}_3)_4\text{NI}$, $(\text{C}_2\text{H}_5)_4\text{NCl}$, $(\text{C}_2\text{H}_5)_4\text{NBr}$, $(\text{C}_2\text{H}_5)_4\text{NI}$ were 'Fluka' products. These were standardised by titration with AgNO_3 of E. Merck quality using potassium chromate as indicator. MgCl_2 and CaCl_2 solutions, prepared with reagent quality samples, were standardised by EDTA titration, using Eriochrome Black T as indicator and BaCl_2 , also of the same quality, was analysed by precipitation as BaSO_4 .