

CHAPTER II

SCOPE AND OBJECT OF THE WORK

The process of ion-exchange is one of the mechanisms considered to be operative in the uptake of ions by plant roots from clay minerals possessing ion-exchange properties. The plant tissues contain acid groups, capable of binding and exchanging cations and basic groups with a similar role towards anions. In the process of exchange between the plant and the soil, the clay fraction of the latter plays the most important part. Hence a study of the exchange behaviour of the clay fraction reveals, generally, the exchange characteristics of the soil as a whole.

Although literature records a large amount of work on the adsorption of trace element cations on different clay minerals, such studies with inorganic trivalent complex cations are rather meagre. Sorption and desorption studies with trivalent inorganic ions have been carried out by earlier workers. Not always could satisfactory results be obtained as the experiments were generally carried out either at low pH or at high pH.

At low pH of the medium, the interference of the H^+ in the exchange process can not be ignored, whereas high pH favours the existence of metal hydroxy ions rather than the simple metal ions. So, in most of the studies a proper knowledge

of the interaction of the adsorbate with the adsorbent was lacking. Unless this is known in reasonable details, an appreciation of the adsorption and desorption measurements may be difficult. It was therefore thought that for a systematic study adsorbents with well-defined surface characteristics and adsorbates which are stable over a wide range of pH would be most convenient. The inorganic ion-exchangers used in the present investigation consist of the clay minerals, bentonite, vermiculite and laponite (a synthetic hectorite), molecular sieve 13 X (powder form), and the organic exchanger is the resin Amberlite IRC-50. These provide more or less known features. The adsorbates

(a) Tris (1,2 propane diamine)cobalt(III) chloride
($\text{Co}(\text{pn})_3\text{Cl}_3$),

(b) Tris (1,3 propane diamine) cobalt (III) chloride
($\text{Co}(\text{tn})_3\text{Cl}_3$),

(c) Tris (ethylene diamine) cobalt (III) chloride
($\text{Co}(\text{en})_3\text{Cl}_3$)

and (d) Hexamine Cobalt (III) chloride $\left[\text{Co}(\text{NH}_3)_6\text{Cl}_3 \right]$
are trivalent complex compounds of known structure. From structural considerations, the stability of these complex compounds is also well known.

The interaction of the above exchangers and the trivalent complex cations was therefore investigated under

different conditions and from different angles in order to understand the mechanism of interaction and specificity of the ions. So the main objective of the present investigation is to study in fundamental details the physico-chemical aspects of ion-exchange equilibrium of the trivalent complex cations onto the exchangers mentioned above. For this purpose, adsorption isotherms of different trivalent complex cations on the above adsorbents were studied and the sorption data was analysed in the light of Langmuir equation. For a better understanding of the mechanism of sorption, the cation exchange process between tris (1, 2 propane diamine) cobalt (III) and Na^+ on bentonite was studied by x-ray diffraction, differential thermal analysis, and nitrogen sorption. In order to compare the results of exchange, natural and synthetic clays having different charge densities have also been chosen. The complex ions are suitable from another point of view. Very low concentrations of the ions are measurable spectrophotometrically. This is helpful to study desorption, in particular as well as sorption occurring at very low concentrations. To get a better insight into the nature of adsorbent - adsorbate interaction, relative binding strength, cation specificities etc., the desorption of the trivalent complex cations was studied with different monovalent, bivalent inorganic ions and also alkyl quaternary ammonium ions of varying sizes. Such studies also reveal the extent of extractibility of these ions from the

adsorbent surface from which we can have an idea of the affinity of the ions for the minerals, zeolites and resin surface as well as the relative desorbing abilities of the ions.

It may be mentioned in this connection that although the occurrence of the trivalent cobalt complex in soil is not reported in literature, the presence of cobalt²⁺ is well known and its function as soil nutrient is well established. Cobalt as Co^{3+} forms complex organic compounds. A considerable part of cobalt is dispersed through the soil in the crystal lattices of the aluminosilicates or fixed by the humus of the soil; another part is more loosely bound to the silicates as a result of base exchange. However, the main interest of the present work is restricted particularly to the study of the ion-exchange characteristics of the component of the soil using these complexes.

The studies of the adsorption and desorption onto clay minerals, resins and molecular sieves are useful from other points of view also. As for example, due to their characteristic structures and high exchange capacity, bentonite and vermiculite have recently been used for the decontamination of waste waters from nuclear pile plants. Another important application of these minerals is in the mining practice. The adsorption of gold and other precious metals on these clays especially for exploring the "lost or locked in" gold in barren land

sediments may be recalled. The properties of the synthetic hectorite, laponite XLG inorganic colloids make it suitable for use in a wide range of products viz. cosmetics, deodorants, food, shampoos, soap, suspensions, tablets, toothpaste, veterinary/pharmaceuticals etc., Dispersions of laponite, because of the large surface area and surface activity of the platelets, exhibit higher adsorptive powers. Laponite XLG, which is a synthetic hectorite, was also chosen because it forms stable colloid suspensions suitable for ion-exchange studies.

The study of the use of molecular sieves in adsorption and catalysis has deservedly received a great deal of interest in recent years. So with a view to obtaining insight into factors controlling the exchange, synthetic molecular sieve 13 X has been studied with regard to its cation exchange behaviour with the trivalent complex cations mentioned earlier. Also in view of the recent wide spread use of the clay, resin and molecular sieve complexes with these trivalent complex cations in gas chromatography as column packing material for the separation of light hydrocarbons and oxides of nitrogen and in Szilard Chalmers reaction for obtaining high yield and specific activity, a detailed investigation of the sorption and desorption behaviour of the amine, ethylene diamine and propylene diamine (1,2 and 1,3) complexes of Co(III) on bentonite, vermiculite, laponite and also on well defined ion exchangers

like a weak cation exchange resin, Amberlite IRC-50 and molecular sieve 13 X has been undertaken. Apart from various practical applications, the experimental data may also be used for testing and developing different existing theoretical models and equations for describing ion-exchange equilibria.