

CHAPTER II

SCOPE AND OBJECT OF THE PRESENT WORK

The present investigation may be broadly divided into two parts:

1. Equilibrium behaviour of exchange of Pb^{2+} in different exchange systems viz., H-bentonite, silica gel, hydrated alumina, etc.
2. Polagraphic behaviour of different exchangers in which electro-active ions are incorporated. Pure clay minerals, aluminium hydroxide and silica gel are the exchangers; Pb^{2+} and Co^{3+} are the electro-reducible ions.

Equilibria on the distribution of competing counter ions species between an ion-exchanger and a solution has been the subject matter of investigation for-a long time. In these studies both inorganic and organic exchangers have been taken into consideration. Theories and models have been developed for the interpretation of the results. Notwithstanding considerable amount of work done in this field, uncertainties are often met with in the proper understanding of the experimental data in terms of these theories, principles and models. For example, it is of common experience that the values of the equilibrium constants, affinity or other thermodynamic quantities in an exchange reaction involving Zn, Cu, Fe, Be, Mg and other multi-valent cations are not consistent while the solutions contain different anions. The results are best explained on the basis of association of the anions with these cations either in the solution and/or in the exchanger phase. Pb^{2+} , a heavy metal ion, is known to undergo anomalous association in solution with hydroxyls, halides etc., even in very dilute solutions. The ion is capable of forming positive, negative and neutral complexes with anions. In view of these anomalous tendencies Pb^{2+} is expected to show interesting

features with regard to its behaviour towards different exchangers. Except a small amount of work with resins, no systematic work has so far been reported with other ion-exchangers where El^+ is used as the counter ion species. In the present investigation therefore, an attempt is made to, study extensively the equilibrium behaviour of exchange of El^+ on different clay minerals, silica gel, and aluminium hydroxide. The latter are selected for the study as they are the important components of the vast majority of natural soils. A knowledge of the equilibria on the distribution of counter ions having anomalous tendencies of association between such exchangers and solutions may be of interest to the physical, analytical and agricultural chemists and to the plant physiologists. In addition, it is also of interest to record that the existence of thallium ions is not very widespread on the surface of the earth. It is mostly localised to parts of Central Asia, and occurs generally along with the ores of other metals, most commonly zinc. The thallium ion is toxic to both plants and animals. Plant roots are capable of taking up cationic and anionic substances from the soil by a process of ion-exchange. Hence it is desirable that a proper understanding of sorption-desorption characteristics of the thallium (I) ion be undertaken. The studies when carried out at different temperatures enable one to interpret the results in terms of several thermodynamic parameters. The applicability of several theoretical models of ion-exchange may also be tested for the above systems. Moreover, the poly-functional behaviour of these exchangers, under consideration, has been a subject matter of continued scientific research by different workers. The conclusions arrived at as to the causes of this characteristic behaviour do not seem to be consistent. Some work in this line may be informative and useful. Results

obtained in the investigations are presented in Chapters IV, V, VI and VII.

Polarography has long been considered as a very successful analytical technique for characterising different substances. The technique is applied for both qualitative and quantitative purposes. The polarographic investigations of different electro-reducible substances are usually carried out in clear solutions. It is also recognised that even an organic compound which does not contain an electro-active group may be studied by the introduction of a polarographically active group in it. Thus the technique was found to be useful for both inorganic and organic compounds. As stated earlier this versatile technique was also extended for studies in the domain of macro-molecules (223), (136a), (179).

As pointed out earlier (pp 30-33), Kalveda, Zageraki, Miska (123), (250), (179) and others, applied the instrument for studies of precipitates and suspensions. Chakravarti (59) noticed a shift of the half-wave potential in the reduction wave of Coen_3^{3+} when a small amount of bentonite or illite is added to the experimental solution. Similar shifts of half-wave potential have been observed in complex forming reactions also (251), (136). Thus the shift of half-wave potential may be considered as an index of complexation.

Although considerable amount of work has been done on the equilibrium behaviour of different ions in the exchange process involving the use of monovalent and di-valent ions; tri- and other multi-valent complex ions were only occasionally used for the purpose. Among the latter, hexamine, and tri- \rightarrow ethyleno diamine cobaltic ions were found to furnish valuable information of great theoretical and practical interest, as shown by Manungo, Chakravarti and Mukherjee (52). These complex ions were also found to be of considerable polarographic interest by Iaitinen and

others (136). The importance of these complex ions were also felt by nuclear scientists (154). A continuous extraction of recoil products from the Saillard - Chalmers reaction on hexamine cobaltic ion and tri-ethylene diamine cobaltic ion adsorbed on an ion-exchange resin has been proposed for obtaining a high yield and specific activity. The latter ions were found to be suitable as they give rise to the bi-valent cobaltous ion upon neutron irradiation, which is separated from the parent by some chemical procedure by use of an eluant. Keeping these in mind, a polarographic investigation has also been proposed on the behaviour of Coen_3^{3+} towards the aforesaid inorganic ion-exchangers.

It appears from what has been discussed above that the polarographic method may also be successfully employed for solving problems associated with colloidal suspensions which are fairly stable. The experimental conditions should be established in such a way that the undesirable factors are eliminated. The use of electro-reducible ions, which may produce prejudicial effects on the system or on the final results should be avoided.

In order to test the suitability of the approach Zn^{2+} and Coen_3^{3+} ions are used as the electro-reducible ions while the suspensions of pure clay minerals, silica gel and aluminium hydroxide are the colloids. The electro-reducible ions are incorporated in the matrix of the exchangers by adsorption under appropriate conditions. One may expect to get useful information about the exchangers as well as the reducible ions if the following are examined critically:

- (i) Electro-capillary curves
- (ii) Polarographic maxima
- (iii) Limiting currents

(i) (iv) Diffusion coefficients

(v) Rate of attainment of exchange equilibrium.

The technique may also be applied to ascertain some of the physico-chemical properties associated with a heterogeneous reaction. The work in this connection is reported in Chapters IV and VIII.