

CHAPTER IX

SUMMARY AND CONCLUSION

The structures of clay minerals, namely, vermiculite, bentonite, kaolinite, illite, silica gel and aluminium hydroxide are briefly described in the introductory chapter. Also, previous work on adsorption and desorption of cations on these minerals, ion-exchange, different theoretical ion-exchange formulations and thermodynamics involved in the processes have been discussed. The polarography of suspensions of insoluble substances have been reviewed in Section (D) of chapter I.

(PP 1-33)

The scope and object of the present investigation has been presented in chapter II. The investigation consists of two parts:

1. Determination of ion-exchange capacity and studies of interactions of thallium on H-bentonite, silica gel and aluminium hydroxide from solutions of $TlClO_4$ and $TlCl$ and thermodynamics thereof.

2. Polarographic studies of suspensions of vermiculite, bentonite, kaolinite, illite, silica gel and aluminium hydroxide which have been impregnated with an electro-active cation, namely, Tl or $Coen_3^3$, by a process of adsorption.

(PP 34-38)

The experimental details have been described in chapter III.

(PP 39-51)

Determination of cation exchange capacity of the exchangers have been described in chapter IV. Conventional methods in vogue, as well as the polarographic method have been discussed. The latter method has been found to be compatible with other methods. Results

have been interpreted in terms of the observed limiting currents, diffusion coefficients of electro-active ions and the viscosity of the suspension. The role of the supporting electrolyte has also been examined.

(PP 52-59)

The exchange-adsorption of thallium on H-bentonite, is presented in section (A), chapter V, while the desorption of thallium from Tl-H-bentonite is presented in section (B). Intake of thallium ions is found to be an endothermic process. Isotherms at different temperatures have been presented. The sorption and desorption data are found to fit excellently in the theoretical ion-exchange models of Hielland and Barrer. Results obtained by the abstract thermodynamic method are in harmony. The thermodynamic equilibrium constants K , and the free energy changes ΔG° have been calculated with help of these models, and from the variation of K with temperature, the heat of adsorption ΔH° and the entropy change have been determined separately for the three stages of adsorption. The activity coefficients in the solid phase of Tl^+ have been calculated with the help of Hielland's equation, and the interaction energy between adjacent ions on the surface of the exchanger have been calculated from Barrer's model. The ΔH° values for the sorption of Tl^+ on H-bentonite from solutions of $TlClO_4$ are found to lie between 1.9 and 11.7 K Cal/mole. The intake of Tl^+ from solutions of $TlClO_4$ is about three times the amount that is obtained when solutions of $TlCl$ are used. An interesting observation is that the stability constant of the ion-pair $TlCl$ and also the heat of formation of the $TlCl$ complex can be found from these data.

(PP 61-81)

The descriptions are carried out with monovalent inorganic and quaternary alkyl ammonium ions. For the inorganic ions, the efficiency of Pb^{2+} displacement has been found to be $\text{Li}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$, which conforms to the normal lyotropic series. For the three organic ions used the order is $(\text{CH}_3)_4\text{N}^+ < (\text{C}_2\text{H}_5)_4\text{N}^+ < \text{OTA}^+$. The desorption data are also examined in the light of the models of Kielland and Barrer. Using these models the thermodynamic equilibrium constants K , and the interaction energy of ions on the surface of the exchanger E_{ij} , the free energy change ΔG° and the activity coefficients of the desorbing ions in the exchanger-phase have been calculated. The desorption data are also found to fit in Pauli's model for ion-exchange. Plot of $\log K$ vs. $1/a^\circ$ (where a° is the Debye-Huckel parameter) is linear, whereas a plot of $\log K$ vs. the hydrated ionic radius is curved.

(PP 82-91)

The sorption of Pb^{2+} on silica gel from solutions of PbClO_4 and PbCl_2 and the thermodynamics involved therein have been presented in chapter VI. The results are similar in nature, to that obtained by sorption of Pb^{2+} on H-bentonite. Moreover, silica gel is found to behave as a tri-functional ion-exchanger. The sorption is shown to be endothermic. The thermodynamic parameters K , ΔG° , ΔH° , ΔS° , the solid phase activity coefficients, and the interaction energy E_{ij} between adjacent ions on the surface of the exchanger have been calculated. The data have been found to give the stability constant, ^{the} and heat of formation of PbCl_2 . The ΔH° values for the intake of Pb^{2+} from solutions of PbClO_4 are found to lie between 1.1 and 2.19 K Cal/mole.

(PP 92-108)

In chapter VII are presented the studies of Tl^+ -intake by aluminium hydroxide from solutions of $TlClO_4$ and $TlCl$. The different thermodynamic parameters have been calculated as in chapters V and VI with the help of the aforesaid theoretical ion-exchange models. The sorption is found to be endothermic, and the data have been utilised to evaluate the stability constant of $TlCl$ as also the heat of formation of $TlCl$. The aluminium hydroxide behaves as a bi-functional exchanger in relation to the exchange of Tl^+ by H^+ in it (pp 110-117). The ΔH^0 values for the exchange-adsorption of Tl from solutions of $TlClO_4$ are found to lie between 0.9 and 7.4 K Cals/mole.

(PP 100-122)

In section (C) of chapter VII are presented the titrations of aluminium hydroxide with dilute solutions of weak and strong bases. While the sample A (Cf. Table 3.1, pp 39-40) behaves as tri-basic, samples B and C (also used in the adsorption studies) behave as di-basic.

(PP 123-126)

The polarographic studies on suspensions of the minerals vermiculite, bentonite, kaolinite, illite, silica gel and aluminium hydroxide impregnated with Tl^+ or $Coen_3^{3+}$, are presented in chapter VII. The electro-capillary curves, C-V curves, polarographic maxima, half-wave potentials and the effect of supporting electrolyte, maximum suppressor and stirring of the suspensions during polarographic recordings have been described. The time for the attainment of equilibrium in the desorptions of Tl^+ from the systems Tl -bentonite, Tl -silica gel and Tl -aluminium hydroxide and $Coen_3$ -bentonite, $Coen_3$ -silica gel and $Coen_3$ -aluminium hydroxide have been studied. The desorbing agent is

0.075 (M) LiCl. Equilibrium is found to be rapidly attained in Cl- systems. For Coen₃-bentonite, the time of equilibrium is 10 hours, 3 hours for Coen₃-silica gel and 1½ hours for Coen₃-aluminium hydroxide systems.

(PP 127-150)

The exchange studies have also revealed that all three exchangers behave as poly-functional exchangers and that the extent of adsorption is always a function of the degree of dissociation of the adsorbate electrolyte. The tri-basic nature in bentonite is due to presence of exchangeable hydrogens at two different affinity levels on the surface, and the third type being due to those at the inter-lamellar region. On the surface of H-bentonite, the hydrogens are attached to two types of groups viz., Si-O- and Al-O-, where the acidity function of the former is greater than that of the latter. The heat of adsorption ΔH° , and entropy change ΔS° for the first two types of adsorption are small while for the third stage it is large. A positive ΔG° value shows that the third type of adsorption is a process of unstable equilibrium. This is also supported by the calculated data of the solid phase activity coefficients. That the cationic bonding energies are in the order: first stage > second stage > third stage, has also been suggested. The first two stages account for about 50% of the total exchange.

For the desorption of Cl from Cl-H-bentonite, the curve does not show distinct stages in the process, but the slope of the curve (cf. Fig. 75) shows that desorption is relatively difficult upto an ionic fraction of 0.5 of Cl⁺ on the exchanger. This fraction corresponds to the external surface of the bentonite sample. The cationic bonding

energies of the desorbing ions as evident from the values of the solid phase activity coefficients are in the order $\text{Li}^+ \succ \text{K}^+ \succ \text{Rb}^+ \succ \text{Cs}^+$ for the inorganic ions and $(\text{CH}_3)_4\text{N}^+ \succ (\text{C}_2\text{H}_5)_4\text{N}^+ \succ \text{CFA}^+$ for the organics.

For the silica gel and aluminium hydroxide samples the observed poly-functional nature is due to the presence of 'free' and 'paired' i.e., inter-hydroxyl hydrogen bonded exchange sites on the external surface and also due to exchange sites present in the 'pores' of the solid matrix. Thus in silica gel the 'free' hydroxyls on the external surface account for about 24% and 'paired' hydroxyls for about 51% of the total number of exchange sites, while the sites in the 'pores' account for the remaining 25%. For aluminium hydroxide the 'free' and 'paired' hydroxyls on the surface account for about 50% of the total number of exchanger sites while the remaining sites correspond to those present in the 'pores'. The high values of entropy change for second and third stages in silica gel and second stage of aluminium hydroxide suggest weaker interaction forces for the process due to the probable presence of hydrogen bonding. The solid phase activity coefficient values show clearly that the cationic bonding energies are in the order: first stage \succ second stage \succ third stage for silica gel; first stage \succ second stage for aluminium hydroxide. The heat of adsorption, as expected, is just in the reverse order.

Comparing the three exchangers, it is found that the affinity for Li^+ is in the order: H-bentonite \succ aluminium hydroxide \succ silica gel. The theoretical models as applied are found to be quite adequate to explain the equilibrium behaviour of mono-valent cations to H-bentonite, silica gel, and aluminium hydroxide in relation to the

desorption-desorption phenomena.

An important conclusion which can be drawn from the data of polarographic work on the exchangers is that the reductions of the electro-active ions from surfaces of solid particles do take place directly at the d.m.e. The shifts of the electro-capillary zero to positive potentials confirm that the colloidal particles in the Ti- and $\text{Coen}_3\text{-}$ forms are specifically adsorbed at the d.m.e. The $\text{Coen}_3\text{-}$ systems are more strongly adsorbed at the d.m.e. than the Ti- systems.

Characteristic polarographic maxima and the half-wave potential for each of the exchangers are the unique features of this work. These are reproducible under rigid experimental conditions. Thus, it appears that by use of this technique a distinction between clay-minerals in suspensions may be made. For this, a consideration of (i) the b.o.e. results, (ii) the characteristic maximum (iii) the half-wave potential and (iv) the nature of the electro-capillary curve is necessary. Thus, combined with one or more of the following: X-ray, D.T.A., electro-chemical, viscometric and optical methods the polarographic technique may be successfully employed for identification of clay-minerals. The advantage of this technique over others is that the polarograph is less expensive and available in almost all standard laboratories and also that very small amount of the substance is required for the purpose.

From the above discussions, it may be inferred that polarographic work on suspensions may be conveniently utilized in the solution of problems in relation to different physico-chemical aspects associated with heterogeneous reactions. Numerous points of

interest made their appearance during the course of the present study, all of which cannot be accommodated in the present thesis. It is also desirable to state here that there is considerable scope to improve the technique discussed so far. A-C or oscillo-polarographs when used for similar work may provide more useful information.

