

CHAPTER V

DISCUSSION AND CONCLUDING REMARKS

5.1 Rate and order of the exchange reaction

One of the features of the results given in the previous chapter is the high exchange capacity of AMP (Table 4-12). It shows that the exchange cannot be a surface phenomena but that ions deep within the crystal structure is involved. It is therefore not surprising that the rate of the ion exchange process is determined by the rate of the film diffusion of the exchanging ions. The exchange reactions are generally much slower than reactions between electrolytes in the solution. The diffusion rates in the exchanger are usually some ten times smaller than in the free solution, mainly due to the rather tortuous paths taken by the pores through the matrix.⁽⁷⁾ Tables (4-3) - (4-11) show that exchange reactions begin at once, but a certain time elapse before the equilibrium state is reached. The rates of exchange vary very much from one system to another, Figure (4-4), shows the progress of exchange with a number of different cations exchanging with equal samples of AMP under the same conditions.

From the rate of exchange via the diffusion reaction, order of the exchange reaction was determined by the usual method and presented in Figure (5-1). Straight lines plot of $\log(a-x)$ vs. time indicated that the exchange reaction is the first order reaction with respect to cations in electrolyte solution. The slope of each straight line in

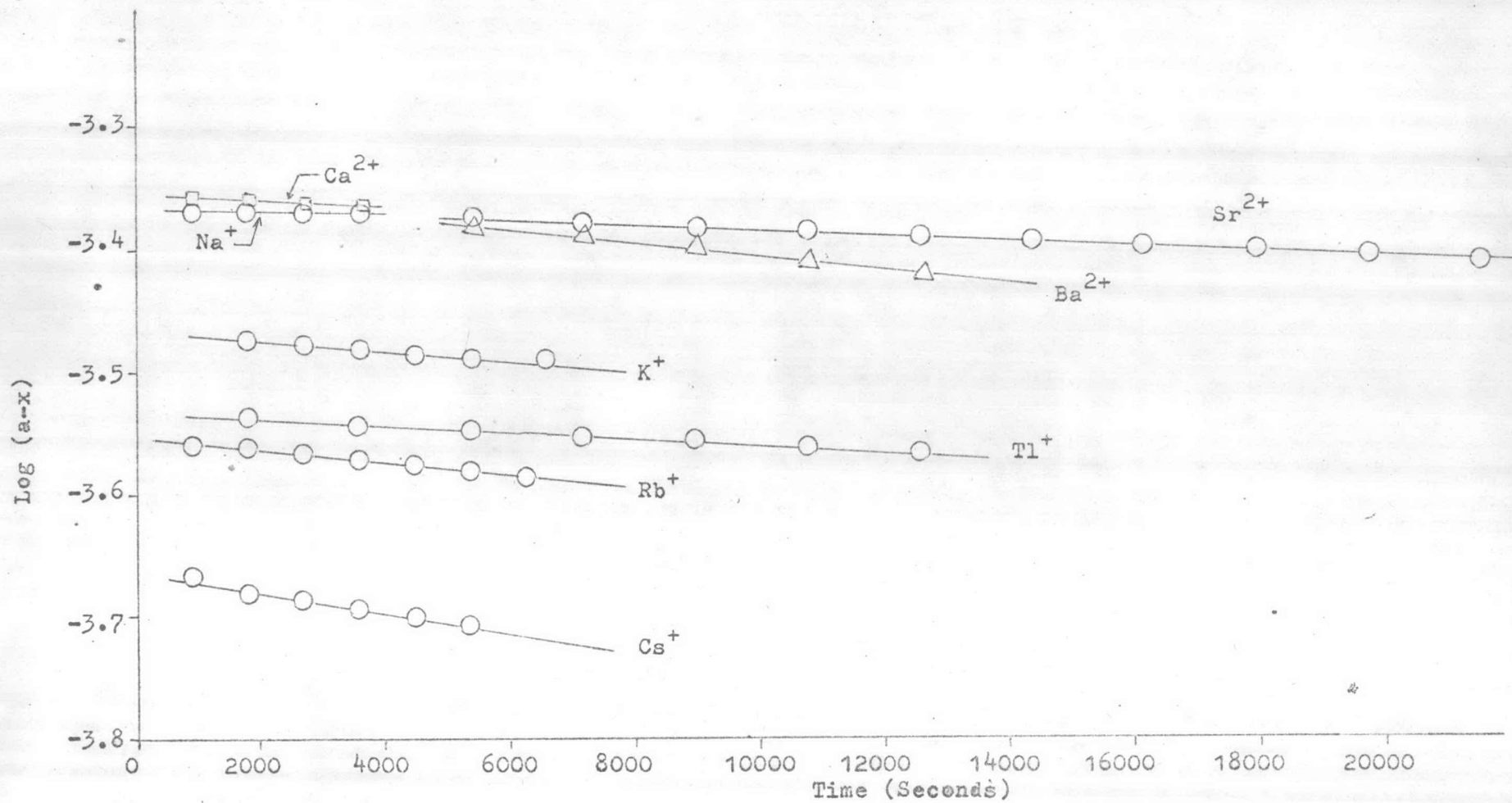


Fig. 5-1 First order reaction of the exchange reaction with respect to the cation in the electrolyte solution.

Table 5.1 Specific rate constant of the exchanging cations.

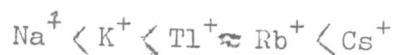
Exchanging cations	Specific rate constant (mins ⁻¹)
Na	6.71 X 10 ⁻⁵
K	3.20 X 10 ⁻⁴
Tl	2.46 X 10 ⁻⁴
Rb	5.53 X 10 ⁻⁴
Cs	8.26 X 10 ⁻⁴
Ca	3.30 X 10 ⁻⁵
Sr	3.32 X 10 ⁻⁵
Ba	3.44 X 10 ⁻⁵

Figure(5-1), yields the specific rate constant for the particular exchange reaction of each cation with AMP under a given condition. They are listed in Table (5-1).

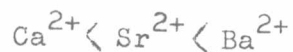
It should be noted that in all of this work, activity coefficients have been neglected. While an application of the Debye-Hückel equation for the activity coefficients would perhaps be applied to the solution, it is very difficult to know how activity coefficients vary in AMP. Therefore, there appears to be little to be gained here by attempting to introduce the activities in place of the concentrations of the ions concerned.

5.2 Selectivity of the exchanger for the counter ion

In dilute concentration (< 0.1 M.) of electrolyte,⁽⁸⁾ an ion exchanger will show a preference for one ion over another, i. e., the affinities are not equal. Such preferences can be determined for any given series of ions and if they are arranged in a relative order, selectivity sequences can be established for the group of ions. Selectivity sequences depend upon the nature of the functional group (i.e., the fixed ionic group) of the ion exchanger. Each ion of a given selectivity scale can be assigned a numerical value relative to a common ion contained in that series. These values are known as selectivity coefficients and the quantitative aspects of such determinations are discussed in which the law of mass action is applied to ion exchange reactions. The results show that the affinities of monovalent cations for a cation exchanger are in the increasing order:



and for divalent cations, the order is



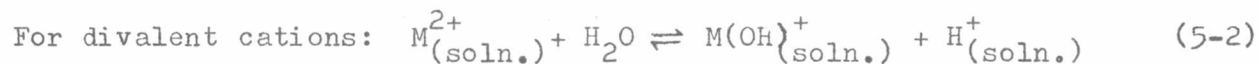
Since ion exchange involves electrostatic force, it was thought that selectivity should depend mainly on the relative charge and the ionic

radius of the (hydrated) ions competing for an exchange site.^(7, 8) Maximum exchange of univalent and divalent cations on AMP and selectivity coefficients of them are shown in Table (4-12). The results show that different ions of the same valence have maximum exchange proportional to their ionic radii, divalent ions have lower exchange than monovalent ions with approximate equal size.

5.3 Ion exchange equilibria on AMP.

The exchange reaction is reversible. Thus it makes no difference from which side equilibrium is approached, that is, whether A is exchanged for B, or B for A. The final equilibrium distribution of the counter ions is the same in either case, provided that the amounts of all the components in the system are the same. It was found that ammonium ions in AMP can be exchanged reversibly by alkaline metal ions.⁽⁹⁻¹³⁾ The reversibility of the process was checked for all ions concerned in this work. Results are shown in Table 4-13.

The proposed reversible reaction of AMP for monovalent ions and divalent ions are as follow:⁽¹⁴⁾



If divalent cation first undergoes hydrolysis and then exchanges with the NH_4^+ of the AMP as suggested in equations (5-2) and (5-3), it

might be expected that Ca^{2+} would be held more strongly than Ba^{2+} since the smaller Ca^{2+} would undergo hydrolysis more readily than the larger Ba^{2+} . The order of absorption of alkaline earth, would be the opposite to that of their size. However results obtained indicated that size seemed to be the most important factor in the exchanging process. It seems therefore that the primary requirement is that the cation entering the AMP must be sufficiently large regardless of its valency. Hence, the proposed mechanisms of divalent ions as suggested by equations (5-2) and (5-3) lead to the understanding that Ca^{2+} may hydrolyse more readily than Ba^{2+} but the size of the hydrated Ca^{2+} may be smaller than that of Ba^{2+} , therefore the affinities of Ca^{2+} are less than that of Ba^{2+} as can be seen from the order of affinities: $\text{Ca}^{2+} \zeta \text{Sr}^{2+} \zeta \text{Ba}^{2+}$. An alternative explanation of the exchange mechanisms with multivalent ions may be that hydrated protons H_3O^+ compete with the other ions presents. The implication of this proposal is that the higher the hydrogen ion concentration or the lower is the solution pH, the smaller degree of exchange of the cation concerned will be resulted. It is not possible however to justify this proposal since variation of pH of the solution has not been made. Nevertheless Roomaya⁽¹⁵⁾ found that on the addition of 0.02 M. lithium hydroxide solution to the equilibrated solution with AMP at original pH of 3.4, no significant pH changes were observed. In other words the pH of the solution initially remained at approximately 3.4 and did not appreciable increase until the AMP began to dissolved.

The specific rate constant given in Table (5-1) also increased with increasing the ionic size with the exception of Tl^+ and K^+ . This

should be understandable since other monovalent ions are alkalimetal ions, they are the so called d^0 cations while Tl^+ is the d^{10} cation: Different configuration may be accounted for the reverse order of rate of approaching equilibrium of Tl^+ and K^+ .

5.4 Concluding remarks and the future work

A knowledge of the rate of exchange is a prerequisite to the most effective use of ion exchangers. It must be mentioned however that the rate of exchange, the ion exchange equilibria all are subjected to the working conditions. By a series of controlled experiments in which one factor is varied at a time, it can readily be shown that other things being equal, a high rate of exchange is generally favoured by the following choice of conditions.

- (a) an exchanger of small particle size; ion is sufficiently large,
- (b) an efficient mixing of exchanger with the solution,
- (c) a high concentration of solution and a high working temperature,
- (d) an exchanger with low degree of cross linkage.

Hence the preparation method of the exchanger itself is important in yielding a satisfactory percent of uptake of the ions in the solution. In order to follow the exchange equilibria a batch method was chosen in this study because the behaviours of the individual cations under study are likely to be so similar that differences cannot be detected by the use of a packed bed or column method.

The choice of the analytical method of this work depends on individual cation to be analysed. Only the analysis for the concentration

of thallium ion in the solution that a radiochemical technique was introduced. Results show that it is a rapid and less troublesome technique but agreements with the iodometric technique is not so good. It is recommended that, the titration method should be used since radioactive materials should only be employed when there is no other equally suitable method available.

It should be interesting to investigate the dependence of an ion exchange process on temperature and pH of the solution for multivalent ions. Other ion-exchanger such as zirconium phosphate or clay minerals are of interest for similar studies as reported in this thesis. In Thailand there was some work concerning the investigation of the uptake of certain cations by local clay minerals⁽¹⁶⁾ but no report on kinetic studies have been found.