Single Particle Studies of Binary and Ternary Cation Exchange Kinetics

Extensive ternary ion-exchange rate data for cases where particle-diffusion is important are presented. Experimental rate data, using a single-particle radioactive-tracer technique, were obtained for the following systems in Dowex 50W-X8 resin: Mn-Cs-Na, Ba-Mn-Na, and Sr-Mn-Cs. Nernst-Planck equations have been used to describe the ternary ion-exchange kinetics. The Nernst-Planck model, when used for the correlation of binary and various types of ternary exchange data obtained under unfavorable equilibrium conditions, usually cannot afford to disregard liquid-film resistance. The model incorporating the film effects correlated satisfactorily most of the experimental data, and even in cases where the correlation was not good, it interpreted adequately the trend of the results.

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SCOPE

Practical applications of ion exchange often involve simultaneous exchange of more than two counter ionic species in packed beds of ion exchange resins. Despite the general understanding of the theory of ion-exchange processes, design methods for fixed bed units largely remain empirical because of mathematical complications inherent in the theory and a lack of comprehensive experimental data. It is possible to overcome mathematical complications with the help of numerical techniques and high speed computers. Thus, simplified rate equations and highly restrictive assumptions need not be used.

Much of the earlier fundamental work in the area of ion exchange was devoted to equilibria and thermodynamics although rate of ion exchange is also of equal importance. There is a growing interest now in the kinetic behavior of ion exchange. In the past, two major breakthroughs contributed to a greater understanding of ion-exchange kinetics. The first contribution was by Boyd and co-workers who in 1947 established the diffusional nature of ion-exchange rate processes. The current basis for quantitative theories of ion-exchange kinetics was given by Helfferich who showed the importance of electric field on the diffusion of dissimilar ions in ion-exchange resins.

Ion exchange in binary systems has been studied extensively. The Nernst-Planck equations describe adequately the ionic fluxes in a binary system. However, there exists today a very small body of published literature on multicomponent ion-exchange kinetics in part because of experimental difficulties. It is necessary to use an experimental technique that yields reliable rate data which does not contain superimposed effects of various variables. The object of the present study was to develop an adequate, theoretically-based model for ion-exchange processes in ternary systems and to obtain sufficient experimental data to test and refine the proposed rate model.

CONCLUSIONS AND SIGNIFICANCE

A rigorous quantitative treatment of particle-diffusion controlled ion-exchange kinetics in ternary systems has been presented. Equations for ionic fluxes in the resin phase were derived with the help of the Nernst-Planck model and were solved under various initial and boundary conditions by means of numerical techniques using a high-speed computer.

The single-particle radioactive-tracer technique developed earlier by Gopala Rao and David (1961, 1964) was adopted for ternary rate studies and was employed in obtaining comprehensive ion-exchange rate data for cases where particle diffusion is the rate controlling step. In this method, a single ion-exchange resin bead is placed in a small bed of similarly-sized glass beads, and a fluid of desired concentration is passed through the bed. The concentration change of the ion-exchanger bead is measured directly by radioactive tracer techniques. A great advantage of this method is that liquid concentration remains essentially constant throughout the bed as the amount of mass transfer to the particle is negligible. Another advantage of this method is that even with concentrated solutions the concentration history of the bead can be traced with rapidity and with reasonable accuracy.

Self, binary, and ternary exchange curves for the three systems were studied. For the ternary exchange, two types of studies were made: (1) ion A (tagged) initially present in the resin phase, exchanging with the other two ions B and C in the liquid phase, $\overline{A}^*$-(B-C); (2) in a resin bead containing initially a mixture of ions A and B, A being tagged, ion A exchanging with ion C in the liquid phase ($\overline{A}^*$-$\overline{B}$)-C. Depletion curves for various initial and boundary conditions were obtained.

It is known that film effects become important when

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the ion going into the resin must displace a more preferred ion (Helfferich, 1962a). Consequently, a correction for this effect was incorporated in the Nernst-Planck model despite its insignificance (in the present study) for self diffusion and exchanges under favorable equilibrium conditions. The modified model satisfactorily correlated a major part of the binary and ternary rate data in all directions of exchange.

Although ion exchange is a metathetical process, rates of ion exchange are determined by mass transfer steps, namely, ionic transport between the bulk fluid and the external surface of the resin, and the diffusion within the resin itself. Because of mathematical complications, simple rate models such as linear-driving force model for the fluid film and the Fick's law model for the internal diffusion, are employed in the design equations for the fixed-bed ion-exchange systems. Advent of faster computers and cheaper computer time would make it posible to use more realistic and theoretically-adequate mathematical models in the design of such systems.

When ions of dissimilar mobilities diffuse, an electric potential gradient is set up, which tends to slow down the faster ions and speed up the slower ones. The effect of electric potential gradient on binary ion-exchange kinetics was considered by Helfferich and co-workers (1957, 1958) who represented the ionic fluxes by the Nernst-Planck equations. There is a considerable experimental evidence to show the correctness of the Nernst-Planck model (hereafter referred as the *NP model*) for the description of binary ion-exchange processes (Dranoff and co-workers, 1963, 1964; Gopala Rao and David, 1964; Helfferich, 1963; Kataoka et al., 1971; Morig and Gopala Rao, 1965; Thibodeaux, 1968; Turner and Snowdon, 1968; Turner et al., 1966). The NP model has so far only rarely been extended to multicomponent ion exchange systems (Lupa, 1967; Clazie, 1967). Also, there is a general lack of experimental data on multicomponent ion exchange kinetics. The present study was undertaken to formulate a rigorous mathematical model to represent ion-exchange kinetics in ternary systems and to supply extensive particle-diffusion controlled rate data to verify the proposed model. Exchange rates of three ternary systems, Mn-Cs-Na, Ba-Mn-Na, and Sr-Mn-Cs, in a typical cation-exchange resin Dowex 50W-X8 were studied.

THEORY

Particle-diffusion controlled ternary ion exchange kinetics can be described by the Nernst-Planck equations. Rate equations have been derived under the following simplifying assumptions:

(i) The whole resin is treated as a quasi-homogeneous phase. Resin beads are assumed to be completely spherical in shape.

(ii) The effects of gradients of pressure and activity coefficients are neglected.

(iii) Co-ion concentration in the ion exchanger is negligible.

(iv) Individual ionic-diffusion coefficients in the resin phase remain constant.

The net flux of each counter ion is given by

$$J_i = -\bar{D}_i\left(\frac{\partial C_i}{\partial r} + \frac{C_i Z_i F}{RT}\frac{\partial \bar{\phi}}{\partial r}\right), \quad i = 1, 2, 3 \quad (1)$$

The principle of electroneutrality requires that the total concentration of counterions in equivalents is constant throughout the bead. Hence,

$$\sum_{i=1}^{3} Z_i \nabla C_i = 0 \quad (2)$$

The absence of electric current inside the ion exchanger gives the condition

$$\sum_{i=1}^{3} Z_i J_i = 0 \quad (3)$$

From a manipulation of Equations (1), (2), and (3), one obtains

$$\frac{F}{RT}\nabla\bar{\phi} = \frac{-(\bar{D}_1 - \bar{D}_3)Z_1\nabla C_1 - (\bar{D}_2 - \bar{D}_3)Z_2\nabla C_2}{\sum_{i=1}^{3} C_i Z_i^2 \bar{D}_i} \quad (4)$$

Substituting for $(F/RT)\nabla\bar{\phi}$ in Equation (1),

$$J_1 = -\bar{D}_1\left[1 - \frac{C_1 Z_1^2(\bar{D}_1 - \bar{D}_3)}{\sum_{i=1}^{3} C_i Z_i^2 \bar{D}_i}\right]\nabla C_1 - \frac{\bar{D}_1 C_1 Z_1 Z_2(\bar{D}_3 - \bar{D}_2)}{\sum_{i=1}^{3} C_i Z_i^2 \bar{D}_i}\nabla C_2 \quad (5)$$

$$J_2 = -\frac{\bar{D}_2 C_2 Z_1 Z_2(\bar{D}_3 - \bar{D}_1)}{\sum_{i=1}^{3} C_i Z_i^2 \bar{D}_i}\nabla C_1 - \bar{D}_2\left[1 - \frac{C_2 Z_2^2(\bar{D}_2 - \bar{D}_3)}{\sum_{i=1}^{3} C_i Z_i^2 \bar{D}_i}\right]\nabla C_2 \quad (6)$$

Flux equations can be considered with equations of continuity to calculate concentration profiles in the resin phase.

$$\frac{\partial C_1}{\partial t} = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 J_1) \quad (7)$$

$$\frac{\partial C_2}{\partial t} = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 J_2) \quad (8)$$

The initial and boundary conditions for the case of particle-diffusion controlled rates are given by

$$C_1 = C_{10},\ C_2 = C_{20} \quad \text{at} \quad t = 0,\ 0 \leqq r \leqq r_o \quad (9)$$

$$C_1 = C_{1s},\ C_2 = C_{2s} \quad \text{at} \quad t \geqq 0,\ r = r_o \quad (10)$$

While performing computations, equivalent fractions instead of molar concentrations were considered. Equivalent fraction of species i is defined as $\bar{C}_i = (C_i Z_i)/C_0$, where C_0 is the capacity in equivalents per unit volume of the resin $\left(\sum_{i=1}^{3} C_i Z_i\right)$. Equivalent ionic fraction of species i in the bead at time t can be obtained by the following expression:

$$q_{ti} = \frac{3}{r_0^3}\int_0^{r_0} \overline{C}_i(r, t)\, r^2\, dr \qquad (11)$$

The equations were solved by numerical methods using an IBM 7044 digital computer. A finite difference approximation with forward difference technique was employed.

Gopala Rao and co-workers (1969) derived rate equations for particle-diffusion controlled ternary ion-exchange kinetics from the principles of irreversible thermodynamics. However, with the dropping of cross-phenomenological coefficients and activity coefficients, the treatment reduces to the rate equations given in the present study.

EXPERIMENT

Particle-diffusion controlled rate data for the systems Mn-Cs-Na, Sr-Mn-Cs, and Ba-Mn-Na in Dowex 50W-X8 resin were obtained using the single-particle radioactive-tracer (SPRT) technique which was described earlier (Gopala Rao and David, 1961, 1964; Kuo and David, 1963). Radioactive isotopes ^{22}Na, ^{54}Mn, ^{85}Sr, and ^{137}Cs were used as tracers in the present study. All the isotopes were supplied carrier-free. Isotopes ^{22}Na, ^{137}Cs, ^{54}Mn, and ^{85}Sr were supplied by the International Chemical and Nuclear Corporation of the US. A part of ^{54}Mn was supplied by the Bhabha Atomic Research Centre, India.

A schematic diagram of the experimental setup is shown in Figure 1. Several resin beads with diameters of about 0.1 cm were used for obtaining the rate data. A pyrex glass column 1 cm in diam. and 12 cm long, and glass beads of a size similar to that of resin beads were used. Superficial liquid velocities of about 25 cm/s were employed to promote particle-diffusion controlled exchange. All the rate studies were made with a solution of 0.1N anion(chloride) concentration under down-flow conditions and at a room temperature of 28°C.

Rate data were obtained for the following cases in the above mentioned systems: self-exchange, binary exchange of all possible component binaries in the systems in both the directions (except for the $\overset{*}{\overline{\text{Ba}}}$-Mn exchange), and ternary exchange for the case of one ion initially inside the resin exchanging with two counterions in the liquid phase, and also for the case of two ions initially inside the resin phase exchanging with the third ion in the liquid phase.

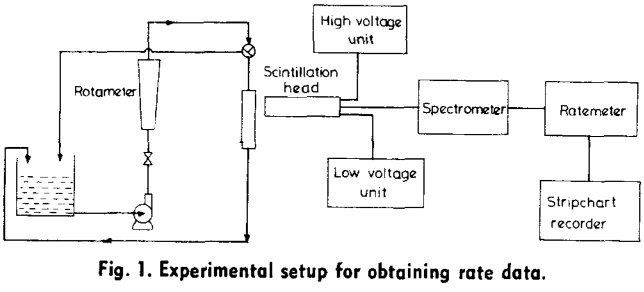

Fig. 1. Experimental setup for obtaining rate data.

RESULTS AND DISCUSSION

Experimental results for the self-exchange rate studies are given in the Supplement.* The Fick's law model works very well for the correlation of particle-diffusion controlled rates of isotopic exchange, and the equation for fractional attainment of equilibrium as a function of dimensionless group $\overline{D}t/r_0^2$ was available (Helfferich, 1962a). Self-diffusion coefficients obtained with an interpretation of the experimental data by the above model (except for Cs) are given below:

$\overline{D}_{Na} = 20.5 \times 10^{-7}$ cm^2/s (experimental)
$\overline{D}_{Mn} = 2.22 \times 10^{-7}$ cm^2/s (experimental)
$\overline{D}_{Sr} = 1.95 \times 10^{-7}$ cm^2/s (experimental)
$\overline{D}_{Ba} = 1.16 \times 10^{-7}$ cm^2/s (experimental Viswanathan 1968)
$\overline{D}_{Cs} = 30.0 \times 10^{-7}$ cm^2/s (estimated)

Equilibrium studies conducted separately showed that the selectivity of the resin phase for the systems under investigation was in the following order:

$$\text{Ba} > \text{Sr} > \text{Mn} > \text{Cs} > \text{Na}$$

In the present study, all the rate data (self, binary, and ternary exchanges) obtained by tagging of the resin bead with ^{137}Cs isotope were completely dissimilar to the rate behavior of the other ions and gave rise to a considerable amount of difficulties in the interpretation of the data. In the equilibrium studies, resin beads tagged with ^{137}Cs isotope did not present any problem except for the relative difficulty in the regeneration of the resin beads. The presence of nonradioactive cesium ions either in the liquid phase or in the resin phase for both the binary and the ternary exchanges created no problem in the interpretation of the data. Something must have been wrong with the purity of the cesium tracer used. Results obtained with the cesium tracer were not used in this report but were available in the Supplement.*

The self-diffusion coefficient of the cesium ion in the resin phase was estimated by an interpretation of the rate data of $\overset{*}{\overline{\text{Na}}}$-Cs exchange with the NP model. It has been well established that the NP model works very well in the correlation of binary ion exchange under favorable equilibrium conditions (Gopala Rao and David, 1964; Helfferich, 1962b, 1963; Morig and Gopala Rao, 1965; Turner et al., 1966). The ratio of sodium to cesium ionic self-diffusion coefficients in the present study is comparable to the values reported in literature (Boyd and Soldano, 1953; McHardy et al., 1969).

Binary Exchange

Binary rate data for Mn-Na and Ba-Na pairs in both the forward and the reverse directions are presented in Figures 2 and 3, respectively. Rate data for the Sr-Mn pair, and a consolidated plot of rate data of cesium ions

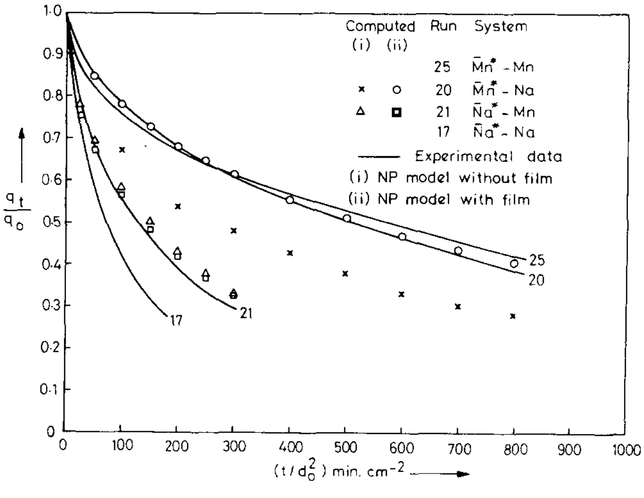

Fig. 2. Binary exchange curves for the system: Mn-Na-Dowex 50W-X8.

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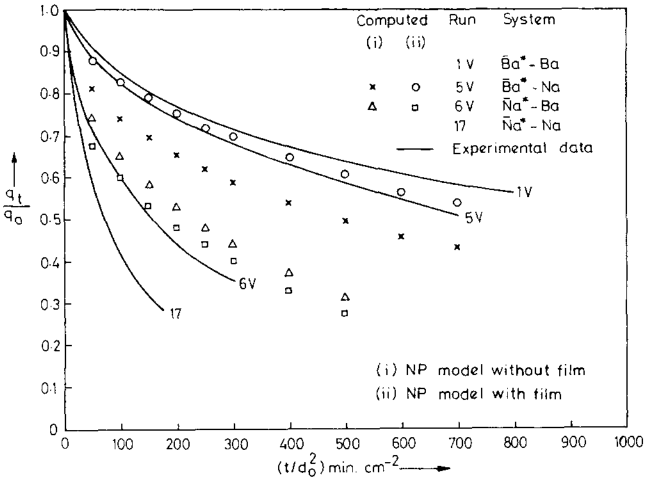

Fig. 3. Binary exchange curves for the system: Ba-Na-Dowex 50W-X8.

in the liquid phase replacing manganese, sodium, and strontium ions respectively in the resin phase, are given in the Supplement.

As pointed out earlier, the NP model works well in predicting the binary exchange under favorable equilibrium conditions. This was confirmed in the present study also (for example, see $\overline{\text{Na}}^*$-Mn, $\overline{\text{Na}}^*$-Ba curves). However, the NP model did not correlate satisfactorily the rate data for the unfavorable exchange; the experimental rates are very much slower than the computed ones. Morig and Gopala Rao (1965) and Viswanathan (1968) have reported similar observations. In the NP model for particle-diffusion controlled rates, the resin surface is assumed to be instantaneously saturated with the incoming ions at $t \geqq 0$. This is an unrealistic assumption for the case of unfavorable exchange. There is always a finite film thickness even at high liquid velocities, and the driving force for mass transfer through the film will be considerably smaller for unfavorable exchange, and thus film effects cannot be disregarded.

In the present study, the effect of film resistance to mass transfer was also considered in the computations of exchange rate data. The effect of electric field on the diffusion of ions in the film was also considered, but for the ease of computations, the change in co-ion concentration in the film was ignored. Equations for the ionic fluxes in the liquid film were given in the Supplement. Ionic diffusion coefficients in the liquid film were calculated from the data of limiting ionic mobilities (Parsons, 1959) by means of the Nernst-Einstein relationship. The film thickness δ at fluid velocities used in the present study (25 cm/s) was obtained from a correlation of the liquid-film controlled rate data of self exchange of sodium ions, using a solution of 0.00194N chloride concentration. The value of the film thickness was found to be 0.000354 cm. Similar hydrodynamic conditions were assumed to exist during all the experimental studies.

When the liquid-film resistance was also taken into account in the computations, the matching between the experimental and computed data for the unfavorable cases significantly improved (see $\overline{\text{Ba}}^*$-Na, $\overline{\text{Mn}}^*$-Na rate curves). Similarly, for the case of cesium ions in the solution phase exchanging with manganese or strontium ions in the resin phase, the matching of the rate curves was better when the liquid-film resistance was also considered. For the case of favorable exchange, there is no significant difference in the correlations with and without liquid-film resistance being considered.

Sharma et al. (1970), who studied the exchange of trace components, observed that film resistance should be considered in the correlation of particle-diffusion controlled exchange rates. In the present study also, the same conclusion is reached.

Ternary Exchange

Both the experimental and the computed ternary-ionic rate curves are shown in Figures 4 to 11. In the computations, both the NP model with film and the NP model without film were employed though only the computed data obtained with the NP model with film were plotted in the figures. For an explanation of the legend in the figures, the reader is referred to the section of Notation.

The equilibrium value of the resin surface composition, used in the computations, has been found to have a significant effect on mass transfer rates. A relatively small variation in these values tended to shift the computed exchange curves significantly. As one can expect, the effect is more significant for the unfavorable equilibrium cases. Van Brocklin (1968) has shown for such cases that good equilibrium data are necessary for adequate prediction of liquid-phase rates.

In the computations, the following procedure was employed to obtain the equilibrium values of the liquid-phase composition at the interface from a knowledge of the resin-surface composition. A second-order polynomial equation was employed to fit the binary equilibrium data available with the authors (Bajpai et al., 1973). The equations were given in the Supplement.* Using these equations for the two binary pairs each containing the most favored ion of a ternary system and assuming that the ionic distribution (on a third-ion free basis) for a binary pair in a ternary system is the same as in the binary system itself, the authors predicted the ternary equilibria. A sample calculation was also given in the Supplement.

Two types of initial and boundary conditions were considered for ternary-exchange rate studies: (i) one ion ($\overline{\text{A}}^*$) initially present inside the resin exchanging with the other two ions (B and C) in the bulk solution, $\overline{\text{A}}^*$-(B-C); two ions ($\overline{\text{A}}^*$ and $\overline{\text{B}}$) initially present inside the resin phase, A being tagged, exchanging with ion C in the bulk solutions. ($\overline{\text{A}}^*$-$\overline{\text{B}}$)-C. In both the cases, the depletion

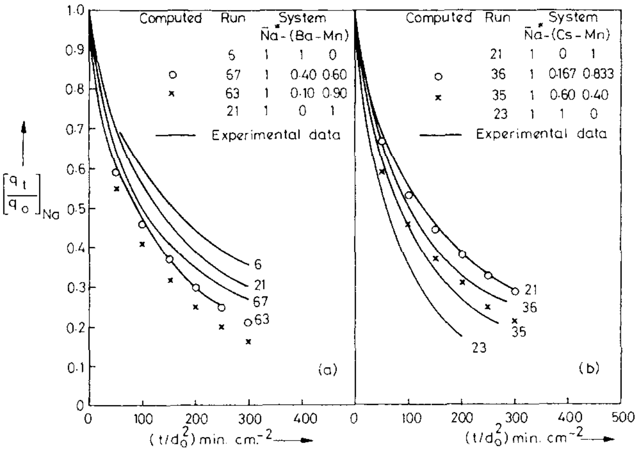

Fig. 4. Ternary exchange rate data for the systems (a) $\overline{\text{Na}}^*$-(Ba-Mn)-Dowex 50W-X8, (b) $\overline{\text{Na}}^*$-(Mn-Cs)-Dowex 50W-X8.

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* See footnote on page 991.

history of the tagged ion was measured and has been compared with the computed values.

Case $\overset{*}{\overline{\text{A}}}$ —(B — C)

In Figure 4, the depletion of sodium ions from the resin phase by exchanging with manganese and cesium ions in one case, and barium and manganese ions in the other case, is shown. In the case of $\overset{*}{\overline{\text{Na}}}$-(Mn-Cs) exchange, the experimental ternary data fall within an envelope composed by the two binaries, $\overset{*}{\overline{\text{Na}}}$-Cs and $\overset{*}{\overline{\text{Na}}}$-Mn. The NP model with film also predicts the same trend. In the $\overset{*}{\overline{\text{Na}}}$-(Ba-Mn) exchange, the experimental ternary curves fall outside the binary envelope and show higher rates of depletion than the two binaries $\overset{*}{\overline{\text{Na}}}$-Ba and $\overset{*}{\overline{\text{Na}}}$-Mn. It is interesting to note that the NP model with film shows the same result. If the NP model without film is used in the computations, the computed ternary curves fall within the binary envelope.

Ternary exchange curves for $\overset{*}{\overline{\text{Mn}}}$-(Na-Cs) and $\overset{*}{\overline{\text{Mn}}}$-(Ba-Na) were included in the Supplement, and the trend of the results were similar to the $\overset{*}{\overline{\text{Na}}}$-(Mn-Cs), and $\overset{*}{\overline{\text{Na}}}$-(Ba-Mn) systems, respectively. In qualitative terms, the following can be concluded. If in a ternary system A-B-C, the selectivity of the ions in the resin phase being in the order C > B > A, and C being very much more selective than A (such as Ba >> Na) for the case of $\overset{*}{\overline{\text{A}}}$ -(B-C) exchange, the diffusion of ion A is speeded up and the ternary depletion curves fall below the two binary curves ($\overset{*}{\overline{\text{A}}}$ -B, and $\overset{*}{\overline{\text{A}}}$ -C). If ion C is not predominantly more selective than ion A (such as Mn > Na), the ternary exchange curves for the case of $\overset{*}{\overline{\text{A}}}$ -(B-C) fall within the binary envelope.

In Figure 5, the depletion curves of $\overset{*}{\overline{\text{Sr}}}$-(Mn-Cs) exchange are presented, and the ternary curves fall within the binary envelope. It should be noted that the strontium ion is the most favored ion in the system, and the exchange took place under unfavorable equilibrium conditions. The NP model with film represents the data adequately. If the film resistance is not considered, the computed rate curves fall below the corresponding experimental curves.

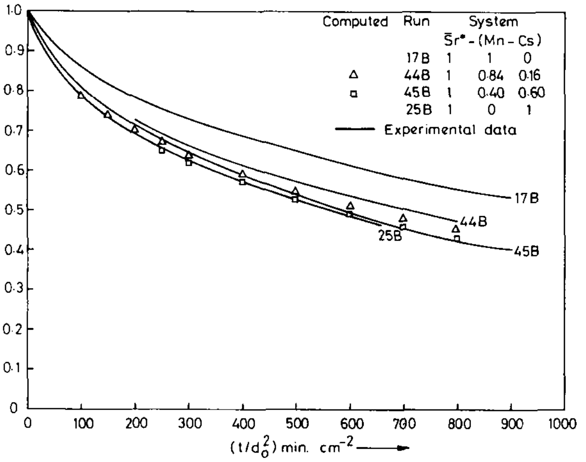

Fig. 5. Ternary exchange rate data for the system: $\overset{*}{\overline{\text{Sr}}}$-(Mn-Cs)-Dowex 50W-X8.

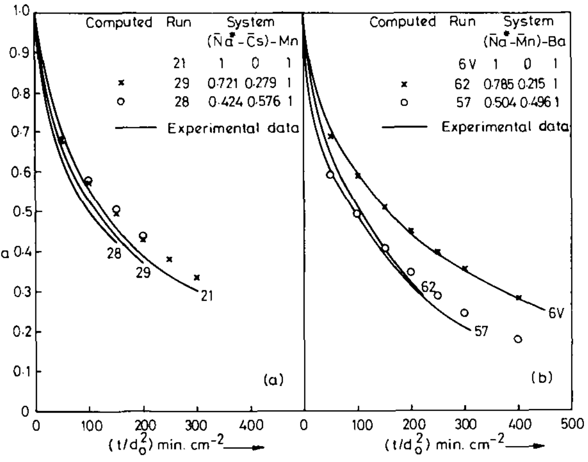

Fig. 6. Ternary exchange rate data for the systems: (a) $(\overset{*}{\overline{\text{Na}}}\text{-}\overline{\text{Cs}})$-Mn-Dowex 50W-X8, (b) $(\overset{*}{\overline{\text{Na}}}\text{-}\overline{\text{Mn}})$-Ba-Dowex 50W-X8.

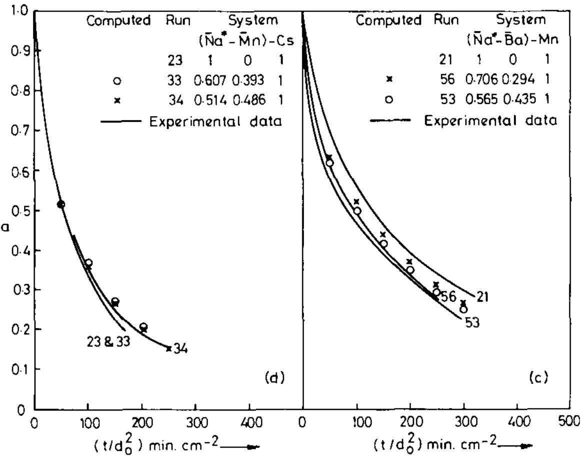

Fig. 7. Ternary exchange rate data for the systems: (c) $(\overset{*}{\overline{\text{Na}}}\text{-}\overline{\text{Ba}})$-Mn-Dowex 50W-X8, (d) $(\overset{*}{\overline{\text{Na}}}\text{-}\overline{\text{Mn}})$-Cs-Dowex 50W-X8.

Case $(\overset{*}{\overline{\text{A}}} — \overline{\text{B}})$ — C

Ternary depletion curves for $(\overset{*}{\overline{\text{Na}}}\text{-}\overline{\text{Mn}})$-Ba and $(\overset{*}{\overline{\text{Na}}}\text{-}\overline{\text{Cs}})$-Mn systems are shown in Figure 6. In both the cases, the most favored ion of the system is in bulk fluid phase. The present model interprets the trend of the data satisfactorily. In the case of $(\overset{*}{\overline{\text{Na}}}\text{-}\overline{\text{Mn}})$-Ba exchange, the data obtained at two different equivalent fractions of manganese ions yielded nearly the same experimental curve whereas the model predicted two different curves. Rate curves for $(\overset{*}{\overline{\text{Na}}}\text{-}\overline{\text{Ba}})$-Mn and $(\overset{*}{\overline{\text{Na}}}\text{-}\overline{\text{Mn}})$-Cs exchanges are shown in Figure 7. In both the cases, the most favored ion of the system is the other counter ion initially present in the resin phase. The model represents the ternary exchange behavior adequately. In the above cases, an increase in the initial equivalent fraction of the more favorable and the slower ion (Ba or Mn) has resulted in an increase in the depletion rate of the sodium ion.

Extensive ternary data were obtained by tagging manganese ions in the resin phase. $(\overset{*}{\overline{\text{Mn}}}\text{-}\overline{\text{Na}})$-Cs, $(\overset{*}{\overline{\text{Mn}}}\text{-}\overline{\text{Cs}})$-Na and $(\overset{*}{\overline{\text{Mn}}}\text{-}\overline{\text{Ba}})$-Na changes are presented in the present report (Figures 8, 9, and 10, respectively) and $(\overset{*}{\overline{\text{Mn}}}\text{-}\overline{\text{Na}})$-Ba, $(\overset{*}{\overline{\text{Mn}}}\text{-}\overline{\text{Cs}})$-Sr, and $(\overset{*}{\overline{\text{Mn}}}\text{-}\overline{\text{Sr}})$-Cs were included

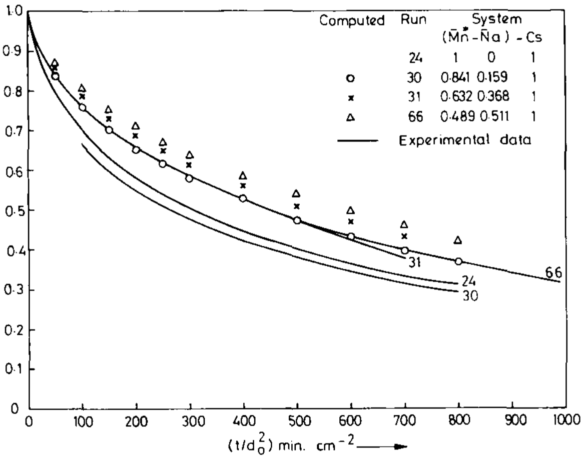

Fig. 8. Ternary exchange rate data for the system: $(\overset{\bullet}{\overline{\text{Mn}}}\text{-}\overline{\text{Na}})$-Cs-Dowex 50W-X8.

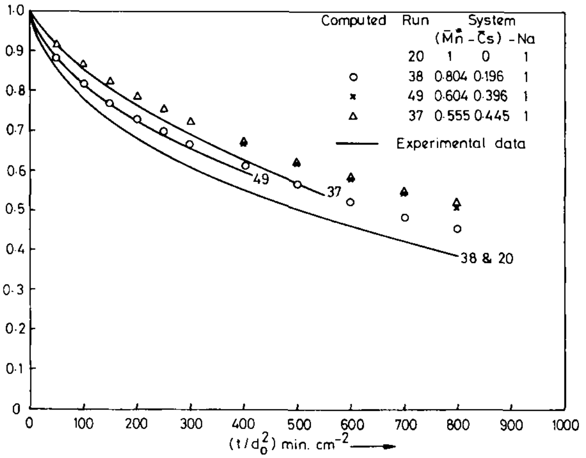

Fig. 9. Ternary exchange rate data for the system: $(\overset{\bullet}{\overline{\text{Mn}}}\text{-}\overline{\text{Cs}})$-Na-Dowex 50W-X8.

in the Supplement. When Mn and Na ions are initially present in the resin phase, exchanging either with Cs or Ba ions in liquid phase, the depletion behavior of Mn ion with respect to the change in the initial values of Na ionic fraction is similar. As the initial Na ionic fraction in the resin phase is increased, the rate of Mn ionic depletion is decreased, and the experimental depletion curves fall above the binary ($\overset{*}{\overline{\text{Mn}}}$-Cs or $\overset{*}{\overline{\text{Mn}}}$-Ba) except for one case (see run 30 in Figure 8). The proposed model predicted the same trend, but the matching of the curves was not satisfactory. It is useful to recall that Mn ion is slower and more preferred ion in comparison with Na ion. When a faster ion is present initially in the resin phase, the depletion rate of the other ion in the resin phase is decreased as the initial fraction of the faster ion is increased. The same general conclusions can be drawn from $(\overset{*}{\overline{\text{Mn}}}\text{-}\overline{\text{Cs}})$-Na and $(\overset{*}{\overline{\text{Mn}}}\text{-}\overline{\text{Cs}})$-Sr exchanges. An interesting case is the exchange of the $(\overset{\bullet}{\overline{\text{Mn}}}\text{-}\overline{\text{Ba}})$-Na system. Here, barium is the slower and more favored ion. From the previous discussion, one would expect the depletion rate of Mn ion from the resin phase to increase as the initial ionic fraction of Ba in the resin phase is increased. Results of the $(\overset{*}{\overline{\text{Mn}}}\text{-}\overline{\text{Ba}})$-Na system presented in Figure 10 confirm the above expectation. Both the experimental and the predicted Mn (ternary) depletion curves are below the $\overset{\bullet}{\overline{\text{Mn}}}$-Na binary curve.

Ternary exchange data for the $(\overset{\bullet}{\overline{\text{Sr}}}\text{-}\overline{\text{Cs}})$-Na system are presented in Figure 11. The strontium ion is the most favored and the slowest ion in the system. From the previous discussion, one would expect that an increase in the initial ionic fraction of cesium (faster) ion in the resin phase would decrease the depletion rate of strontium ions from the resin phase. The results confirm the above observation. For this case, the correlation between the computed and the experimental rate data is good.

On the whole, the NP model with film correlated the experimental ternary exchange curves satisfactorily. Even in cases where the matching between experimental and computed data was not very good, the model interpreted the trend of the results satisfactorily. One need not expect better matching between the experimental and the computed ternary exchange curves because of certain limiting assumptions in the formulation of the model, possible errors in the estimation of parameters used in the computations, and also experimental errors. Variation of self-diffusion coefficients with ionic composition of the resin has not been taken into account in the formulation of the model. Earlier works of Boyd and Soldano (1953), Barrer et al. (1963), and the recent reports of Sharma et al. (1970) and Lutze et al. (1971) point out that self-diffusion coefficients vary with ionic composition in hetero-ionic systems. Also, cross-phenomenological coefficients and activity coefficients in

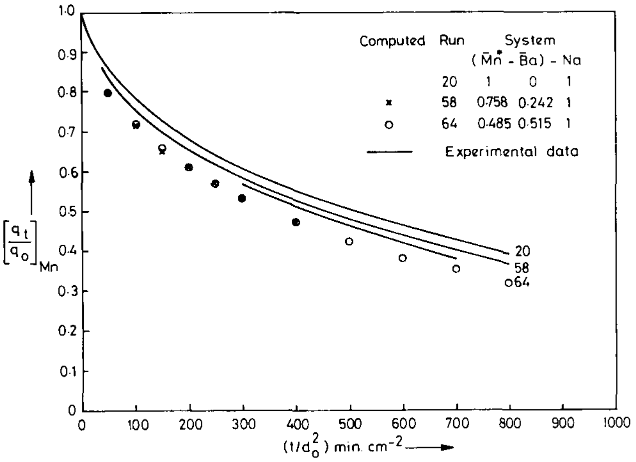

Fig. 10. Ternary exchange rate data for the system: $(\overset{\bullet}{\overline{\text{Mn}}}\text{-}\overline{\text{Ba}})$-Na-Dowex 50W-X8.

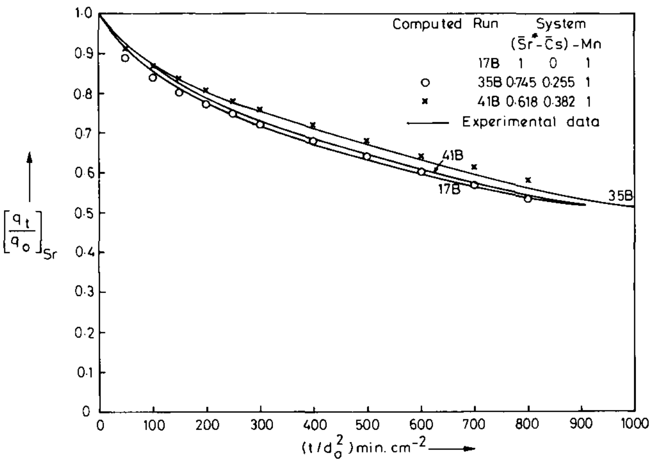

Fig. 11. Ternary exchange rate data for the system: $(\overset{\bullet}{\overline{\text{Sr}}}\text{-}\overline{\text{Cs}})$-Mn-Dowex 50W-X8.

the resin phase were neglected in the development of the NP model. Interfacial ternary equilibrium data were predicted from the component binary equilibrium data. An error of ± 10% (worst cases) is expected in the estimation method. As pointed out by Van Brocklin (1968) very good equilibrium data were necessary for adequate prediction of liquid-phase mass transfer rates, which becomes particularly important for unfavorable equilibrium cases.

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NOTATION

C = concentration, moles/cm^3
C_0 = total concentration in the resin phase, equivalents/cm^3
$\overline{C}$ = equivalent fraction
$\overline{D}$ = self-diffusion coefficient of an ion in the resin phase, cm^2/s
d_0 = diameter of ion exchange resin bead, cm
F = Faraday constant, C/equivalent
J = ionic flux, moles/cm$^2 \cdot$ s
q_t = equivalent fraction of any ionic species at time, t
R = gas law constant
r = radial coordinate
r_0 = radius of ion exchange resin bead, cm
T = temperature, °K
t = time, s
Z = valency, equivalents/mole
δ = film thickness, cm
$\overline{\phi}$ = electric potential

Subscripts

i,j,k = different ionic species

Superscripts

$\overline{}$ = ion initially present in the resin phase
$*$ = ion in the resin phase tagged with radioactive isotope

$\overset{*}{\overline{A}}$-(B-C) = ion A, tagged with its radioactive isotope, initially present in the resin phase, exchanging with ions B and C present in the bulk-liquid phase.

$(\overset{*}{\overline{A}}$-$\overline{B})$-C = two ions A and B, initially present in the resin phase-A being tagged, exchanging with ion C present in the bulk-liquid phase

Explanations for Figure Legends

$\overset{*}{\overline{A}}$-(B-C) This is a ternary exchange, ion A(tagged),
1 .4 .6 initially in the resin phase, exchanging with a solution containing a mixture of ions B and C, the equivalent fractions of which are 0.4 and 0.6 respectively.

$\overset{*}{\overline{A}}$-(B-C) This is a binary exchange, ion A(tagged)
1 0 1 initially in the resin phase, exchanging with ion C in the solution phase.

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