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KINETICS OF DIFFERENTIAL ION-EXCHANGE PROCESSES IN A FINITE SOLUTION VOLUME

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SUMMARY

Rate equations are given for film diffusion-controlled, differentially small ion-exchange processes in a finite solution volume. Two possibilities of performing differential ion-exchange reactions were considered: (1) reactions in which, independent of the initial ionic composition of the sample, the same small amount of counter ions is added, and (2) reactions in which, depending on the initial ionic composition of the sample, the amount of counter ions added is adjusted so as always to yield the same differential conversion of the sample. The theory shows in which way the rate of a differential ion-exchange process, which may involve ions of arbitrary valency, depends on the diffusion coefficients of the ions in the film, on the selectivity of the ion exchanger, on the initial ionic composition of the sample and on the extent of each differential reaction. It is shown that at any given initial ionic composition of the sample, the ratio of the initial rate of the forward to that of the corresponding reverse differential ion-exchange process is independent of the diffusion coefficients of the ions.

INTRODUCTION

Investigations on the kinetics of ion-exchange processes are important not only for the economic employment of synthetic ion exchangers in industry, but also to give a better understanding of many of the ion-exchange processes that occur in nature, *e.g.*, in the soil or in biological membranes. Contrary to investigations on the rates of complete conversions of ion exchangers, which have been carried out over many years, determinations of the rates of differentially small ion-exchange reactions have been studied only recently. These studies, in which the ion exchanger is, independent of its initial ionic composition, converted only to a very small extent, offer several advantages: (1) information is obtained on the dependence of the rate of ion exchange as a function of the initial ionic composition of the ion exchanger; (2) quantities such as the separation factor, the diffusion coefficients or the water content of the sample, which, in general, depend on the ionic composition of the ion exchanger, can be considered to be constant within the small range of a differential ion-exchange process; and (3) a better understanding of many of the ion-exchange processes that

occur in nature, during which, in many instances, only very small amounts of ions are exchanged at a time, can be expected.

The kinetics of differential ion-exchange processes under infinite solution conditions were investigated first by Dickel and Körner[1] for particle diffusion-controlled and by Bunzl and Dickel[2-4] for film diffusion-controlled ion-exchange processes. For many substances with ion-exchange properties, e.g., soil constituents, however, the experimental procedures of simulating an infinite solution by a streaming solution are not applicable, as their particle size is too small to enclose them in a wire screen cage.

For this reason, it seemed appropiate to us to investigate differential ion-exchange reactions under the finite solution conditions of a batch procedure. For this purpose, ion exchanger particles of a given initial ionic composition are first suspended in well-stirred pure water in a thermostated reaction vessel. The differential ion-exchange process, the rate of which one wants to determine, is then started by adding only a very small amount of counter ions, B, to this mixture. When investigating the rates of differential ion-exchange processes according to this method as a function of the initial ionic composition of the ion exchanger, the following two possibilities controlling the extent of each reaction are conceivable. (1) The amount of ions B added in each experiment to the ion exchanger, which contains initially ions B and D, is always the same. In this case, the total concentration, c, of all counter ions B and D in the solution will be constant throughout every differential ion-exchange process, but the extent of each differential ion-exchange reaction decreases as the initial equivalent fraction of B in the sample increases. (2) The counter ions B are always added to the ion exchanger in such an amount that the extent of each differential ion-exchange reaction is constant, regardless of the initial ionic composition of the sample. In this case, increasing amounts of counter ions B have to be added to each experiment as the initial equivalent fraction of B in the sample increases.

In this paper, the theory describing the rates of differential ion-exchange processes under finite solution volume conditions is considered. As the concentration of the solution must always be very dilute in order to yield only differential ion-exchange processes, film diffusion was considered as the rate-determining step. Both possibilities for performing differential reactions as mentioned above are considered. In addition to calculating the rates of such reactions as a function of the initial ionic composition of the sample, of the selectivity coefficient and of the diffusion coefficients, the ratios of the rates for forward and reverse differential ion-exchange processes at a given initial composition were also investigated.

THEORY

Differential batch ion-exchange processes, initiated by adding small, but always constant, amounts of counter ions ($\Delta c = constant$)

Equilibria. The experimental procedure is as follows. The ion exchanger particles are loaded with counter ions B (subscript 1) and D (subscript 2) and suspended in well-stirred pure water in a thermostated reaction vessel. A small amount of B ions (dissolved in water) is added to this suspension at time $t = 0$. If this amount of B ions added is small compared to the total ion-exchange capacity of the sample, the ion-exchange reaction thus initiated will convert the sample towards the B form

only by a small differential amount (*e.g.*, a few percent). The rate of this differential reaction is measured by conventional procedures. In order to obtain the desired information on the rate of ion exchange as a function of the ionic composition, the above experiments are carried out with different initial equivalent fractions of B in the ion exchanger. This set of differential measurements can be carried out most conveniently if one starts with the pure D form of the resin and uses (after washing with water) the equilibrium ionic composition of the sample attained in the first experiment as the initial ionic composition of the next experiment, and so on. As the same amount of ions is added every time in this type of measurement, regardless of the initial ionic composition of the sample, the extent of each differential reaction will become smaller the higher is the initial equivalent fraction of B in the resin. The equilibrium values and hence the extent of each differential ion-exchange reaction as a function of the initial equivalent fraction and of the equivalent separation factor, α_2^1, can be derived for arbitrary valent ions from the equation

$$\alpha_2^1 = \frac{C_{1,\infty} \cdot c_{2,\infty} \cdot r_{2c}}{C_{2,\infty} \cdot c_{1,\infty} \cdot r_{1c}} = \frac{\bar{\gamma}_{1,\infty} \cdot \gamma_{2,\infty}}{\bar{\gamma}_{2,\infty} \cdot \gamma_{1,\infty}} \tag{1}$$

where $C_{1,\infty}$ and $C_{2,\infty}$, and $c_{1,\infty}$ and $c_{2,\infty}$, are the concentrations of the counter ions B and D (in moles of ion per litre) in the ion exchanger phase after attainment of equilibrium (*i.e.*, $t = \infty$) and the concentrations of these ions (in moles of electrolyte per litre) in the solution at $t = \infty$, respectively; r_{1c} and r_{2c} are the stoichiometric coefficients for ionization of the two electrolytes $B_{r_{1c}}A_{r_{1a}}$ and $D_{r_{2c}}A_{r_{2a}}$ present in solution (A is the common co-ion); and $\bar{\gamma}_{l,\infty}$ and $\gamma_{l,\infty}$ are the equilibrium equivalent fractions of the counter ions in the ion exchanger and in the solution, respectively.

The initial equivalent fractions of the counter ions in the resin at $t = 0$ are given by

$$\bar{\gamma}_{l,0} = z_l \, C_{l,0}/C \tag{2}$$

($i = 1$ or 2), where z_l are the valencies of the counter ions and $C_{l,0}$ denotes C_l at $t = 0$. Eqn. 2 holds, of course, also at the equilibrium if one replaces the subscript 0 by ∞. C (mequiv./ml) is the total volume ion-exchange capacity of the water-swollen sample, given by

$$C = z_1 \, C_{1,t} + z_2 \, C_{2,t} \quad (0 \leqslant t \leqslant \infty) \tag{3}$$

As to V_0 ml of water, in which the ion exchanger particles are suspended by stirring, a small amount of B ions is added, the total equivalent concentration of counter ions in solution (in mequiv./ml) will increase from zero at $t = 0$ by a small amount Δc to an equivalent concentration, which is constant throughout the entire experiment and given by

$$\Delta c = z_1 r_{1c} \, c_{1,t} + z_2 r_{2c} \, c_{2,t} \quad (0 \leqslant t \leqslant \infty) \tag{4}$$

where $c_{l,t}$ are the concentrations (in moles of electrolyte per litre) of the ions B and D in solution at time t. According to the above experimental conditions, we have $c_{2,0} = 0$ and thus $\Delta c = r_{1c} z_1 c_{1,0}$. Note that for consistency with the diffusion coeffi-

cients introduced later according to the theory of irreversible thermodynamics[5], $c_i(t)$ has the unit moles of electrolyte per litre and c has the unit milliequivalents per litre. After addition of the small amount of the electrolyte solution containing B ions, the final solution volume is now given by V (ml). The boundary condition of the batch system under consideration is then given by

$$r_{2c}\, z_2\, c_2(t) = w\, z_1\, [C_1(t) - C_{1,0}] = w\, C\, [\bar{\gamma}_1(t) - \gamma_{1,0}] \tag{5}$$

where $w = \bar{V}/V$ ($\bar{V}$ ml = volume of the ion exchanger suspended in the reaction vessel in V ml of solution). Inserting eqns. 4 and 5, which also hold, of course, at $t = \infty$, into eqn. 1, we obtain for the equilibrium equivalent fraction, $\bar{\gamma}_{1,\infty}$, of a differential ion-exchange reaction, which started at $\bar{\gamma}_{1,0}$, the equation

$$\bar{\gamma}_{1,\infty} = [\sqrt{(b^2 + 4aH)} - b]/2a \tag{6}$$

where

$$a = w\,(1 - a_2^1);$$

$$H = a_2^1\,(w\,\bar{\gamma}_{1,0} + \Delta c/C);$$

and

$$b = w\,[a_2^1 - \bar{\gamma}_{1,0}\,(1 - a_2^1)] + a_2^1\,\Delta c/C$$

The extent of a differential ion-exchange reaction is then given by $\Delta\bar{\gamma}_1 = \bar{\gamma}_{1,\infty} - \bar{\gamma}_{1,0}$. The dependence of $\Delta\bar{\gamma}_1$ on the initial ionic composition and on the equivalent separation factor a_2^1, as calculated according to eqn. 6, is shown in Fig. 1. The constants
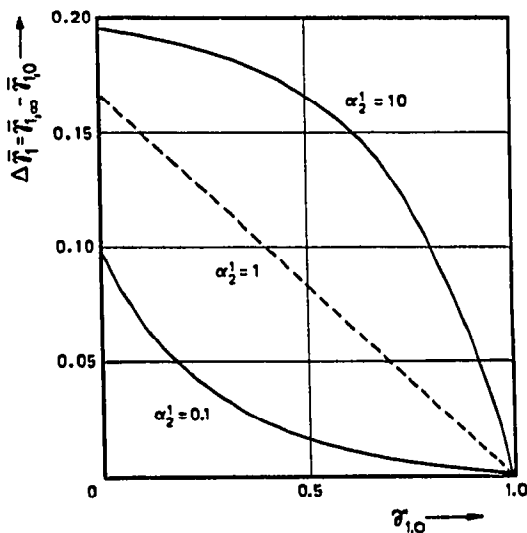

Fig. 1. Extent $\Delta\bar{\gamma}_1$ of differential ion-exchange processes as a function of the initial equivalent fraction $\bar{\gamma}_{1,0}$ of the ion exchanger, calculated according to eqn. 6. The values of the constants in this equation were taken as $w = 0.0001$, $V = 200$ ml, $c = 0.0001$ mequiv./ml and $C = 5$ mequiv./ml.

used for the system were: $w = \bar{V}/V = 0.0001$; $V = 200$ ml; $\Delta c = 0.0001$ mequiv./ml; and $C = 5$ mequiv./ml, which corresponds always to adding (independent of the initial ionic composition of the resin) 1 ml of a 0.02 N solution of B ions to 0.1 mequiv. of ion exchanger suspended in 199 ml of water. Fig. 1 shows how the extent of a differential ion-exchange reaction decreases the more the sample contains initially the ion to be taken up.

Rate equations. In order to obtain only differentially small ion-exchange reactions, the amount of counter ions added must be small (Δc will be about 0.0001 N, see above). For ordinary ion-exchange resins, the rate-determining step will thus be diffusion of the ions through the Nernst film surrounding the ion exchanger particles (film diffusion)[6].

The differential equation of a film diffusion-controlled ion-exchange process is given[7] for ions of arbitrary valency by

$$\frac{d\bar{\gamma}_1}{dt} = R' \cdot \frac{a_2^{\frac{1}{2}} r_{1c} c_1 z_1 (1 - \bar{\gamma}_1) - z_2 c_2 r_{2c} \bar{\gamma}_1}{a_2^{\frac{1}{2}} D_2 (1 - \bar{\gamma}_1) + D_1 \bar{\gamma}_1} \tag{7}$$

where

$\gamma_1 \quad = z_1 C_1/C$;

$R' \quad = \bar{F} D_1 D_2 / \bar{V} \delta C$;

$\bar{F}/\bar{V} \quad$ = surface to volume ratio of the ion exchanger, which for spherical particles = $3/r$ (r = particle radius);

D_1, D_2 = diffusion coefficients, which are functions of the four diffusion coefficients, D_{ij}, describing isothermal diffusion in the corresponding ternary electrolyte solution involving the counter ions 1 and 2 and the common co-ion 3. They can be determined by independent measurements, but as yet very few data are available;

$\delta \quad$ = film thickness.

Inserting the boundary and initial conditions (eqns. 4 and 5) of differential batch ion-exchange processes, we obtain

$$\frac{z_1 dC_1}{C dt} = R' \cdot \frac{a_2^{\frac{1}{2}} [\Delta c - w (z_1 C_1 - z_1 C_{1,0})] (C - z_1 C_1) - w z_1 (C_1 - C_{1,0}) z_1 C_1}{a_2^{\frac{1}{2}} D_2 (C - z_1 C_1) + D_1 z_1 C_1} \tag{8}$$

Eqn. 8 is the differential equation for the rate of uptake of B ions by the ion exchanger. It can be solved analytically, but as the solution is rather complicated for practical applications, it will not be reproduced here. As a more convenient characterization of the time dependence of the ion-exchange reaction we will use the initial rate, $(z_1 dC_1/dt)_{t=0}$, with which each differential ion-exchange process starts at a given $\bar{\gamma}_{1,0}$. This quantity is obtained from eqn. 8 as

$$\left(\frac{z_1 dC_1}{C dt}\right)_{t=0} = R' \cdot \frac{a_2^{\frac{1}{2}} \Delta c (C - z_1 C_{1,0})}{a_2^{\frac{1}{2}} D_2 (C - z_1 C_{1,0}) + D_1 z_1 C_{1,0}} \tag{9}$$

or, in terms of the equivalent fraction of the ions in the ion exchanger, as

$$\left(\frac{d\bar{\gamma}_1}{dt}\right)_{t=0} \cdot \frac{D_1}{R'\Delta c} = \left(\frac{dQ_1}{dt}\right)_{t=0} \cdot \frac{D_1}{Q_{tot}\, R'\, \Delta c} =$$

$$= \frac{a_2^1\,(1 - \bar{\gamma}_{1,0})}{\bar{\gamma}_{1,0}\,(1 - a_2^1\, D_2/D_1) + a_2^1\, D_2/D_1} \qquad (10)$$

where $Q_1 = z_1 C_1 \bar{V} =$ the total amount of ions, in milliequivalents, exchanged at time t by the sample and $Q_{tot} = C\bar{V}$ is the total amount of exchangeable ions in the sample. The value of $(dQ_1/dt)_{t=0}$ can be determined experimentally from the initial slope of a graph of Q_1 versus t.
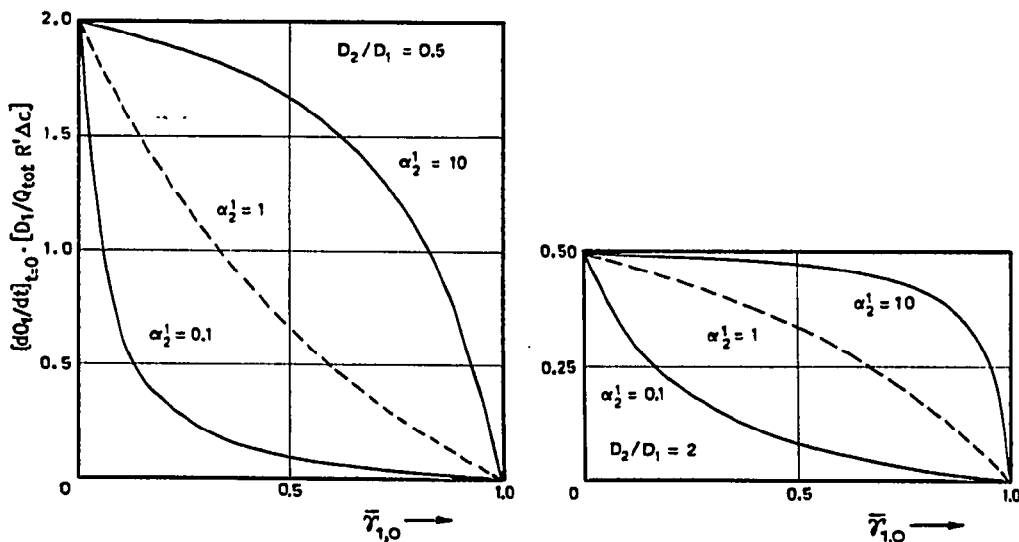

Fig. 2. Initial rates of differential ion-exchange processes plotted as the dimensionless quantity $(dQ_1/dt)_{t=0} \cdot (D_1/Q_{tot}R'\Delta c)$, according to eqn. 10, as a function of the initial equivalent fraction $\bar{\gamma}_{1,0}$ of the ions in the sample. Parameters are the separation factor a_2^1 and the diffusion coefficients D_2/D_1. $\Delta c = $ constant.

Several important characteristics of the initial rate of differential ion-exchange processes can be seen from eqn. 10 and from Fig. 2, where the dependence of the initial rate (plotted as the dimensionless quantity on the left-hand side of eqn. 10) on the initial composition $\bar{\gamma}_{1,0}$ of the ion exchanger is plotted as calculated according to eqn. 10; parameters in these plots are D_2/D_1 and a_2^1:

(1) The initial rate of each differential ion-exchange process is directly proportional to Δc (i.e., to the amount of B ions added) and to R' (i.e., to the surface to volume ratio of the ion exchanger). It is inversely proportional to the film thickness, δ, which is determined mainly by the rate of agitation in the reaction vessel.

(2) The initial rate of each differential ion-exchange reaction decreases if the ion exchanger contains initially more of the B ions to be taken up.

(3) At a given initial composition of the ion exchanger and for given ions B and D (which determine the value of D_1/D_2), the initial rate of a differential ion-

exchange process is faster if α_2^1 is high, *i.e.*, if the B ions are taken up preferentially compared with the D ions.

(4) Eqn. 10 and a comparison of the graphs in Fig. 2 show that the initial rate of each differential ion-exchange process increases as D_2/D_1 decreases.

Besides calculating, as above, the time dependence of the equivalent fraction of the ions in the ion exchanger during a differential reaction, it is even more revealing to calculate the time dependence of the fractional attainment, U, of the equilibrium of each process. U is defined as

$$U = \frac{C_1 - C_{1,0}}{C_{1,\infty} - C_{1,0}} = \frac{\bar{\gamma}_1 - \bar{\gamma}_{1,0}}{\bar{\gamma}_{1,\infty} - \bar{\gamma}_{1,0}} \tag{11}$$

Differentiation of eqn. 11 with respect to t yields

$$\frac{dU}{dt} = \frac{1}{\bar{\gamma}_{1,\infty} - \bar{\gamma}_{1,0}} \cdot \frac{d\bar{\gamma}_1}{dt} = \frac{1}{Q_{1,\infty} - Q_{1,0}} \cdot \frac{dQ_1}{dt} \tag{12}$$

which also holds, of course, for the initial rates. As the initial rates $(d\bar{\gamma}_1/dt)_{t=0}$ are given by eqn. 10 and the extent $\Delta\bar{\gamma}_1$ as a function of $\bar{\gamma}_{1,0}$ by eqn. 6, the initial rate of U, *i.e.*, $(dU/dt)_{t=0}$, can be calculated for each differential ion-exchange process. According to eqn. 12, dU/dt is given by $(d\bar{\gamma}_1/dt)_{t=0}$ divided by the extent $\Delta\bar{\gamma}_1$ of each differential reaction. As both quantities decrease with increasing values of $\bar{\gamma}_{1,0}$ (see Figs. 1 and 2), one can expect $(dU/dt)_{t=0}$ to depend less on the initial composition of the ion exchanger than $(dQ_1/dt)_{t=0}$. That this is indeed the case can be seen from Fig. 3, in which $(dU/dt)_{t=0} \cdot D_1/R'\Delta c$ is plotted as a function of the initial composition of differential ion-exchange processes. The parameters are D_2/D_1 and α_2^1. The values of the constants are the same as used in Fig. 1. Again, the rates for the attainment of the fractional equilibrium U are higher if D_2/D_1 is small.
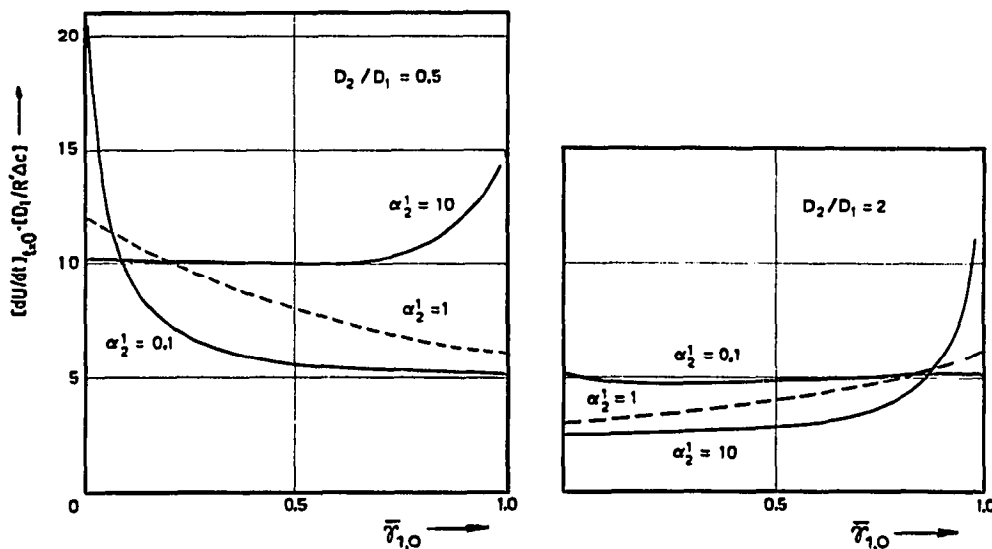

Fig. 3. Initial rates of the fractional attainment of equilibrium of differential ion-exchange processes plotted as the dimensionless quantity $(dU/dt)_{t=0}D_1/R'\Delta c$ according to eqn. 12 as a function of the initial equivalent fraction $\bar{\gamma}_{1,0}$ of the ions in the sample. Parameters are the separation factor α_2^1 and the diffusion coefficients D_2/D_1. Δc = constant.

Forward and reverse ion-exchange reactions. As yet we have only considered differential ion-exchange processes, in which counter ions B were added to the ion exchanger of a given initial ionic composition $\bar{\gamma}_{1,0}$. The sample thus absorbed B ions and released D ions. In order to obtain the rate for the reverse ion-exchange reaction, in which D ions are added and B ions released by the resin, we must calculate $(dQ_1/dt)_{t=0}$ at the same initial ionic composition $\bar{\gamma}_{1,0}$ as for the forward reaction. $\overleftarrow{(dQ_1/dt)}_{t=0}$ is given by eqn. 10. $\overleftarrow{(dQ_1/dt)}_{t=0}$ at $\bar{\gamma}_{1,0}$ is obtained by exchanging in eqn. 10 D_2 and D_1 and substituting $\alpha_1^2 = 1/\alpha_2^1$ for α_2^1, and $1 - \bar{\gamma}_{1,0}$ for $\bar{\gamma}_{1,0}$. We then obtain

$$\left| \overleftarrow{(dQ_1/dt)}_{t=0} \right| = \frac{Q_{tot}\,R'\,\Delta c}{D_2} \cdot \frac{\bar{\gamma}_{1,0}}{(1 - \bar{\gamma}_{1,0})\,(\alpha_2^1 - D_1/D_2) + D_1/D_2} \tag{13}$$

The ratio of the initial rate of a differential forward reaction to that of the corresponding reverse reaction at the same initial ionic composition $\bar{\gamma}_{1,0}$ is obtained from eqns. 10 and 13 as

$$\left| \frac{\overrightarrow{dQ_1/dt}}{\overleftarrow{dQ_1/dt}} \right|_{t=0} = \frac{\alpha_2^1\,(1 - \bar{\gamma}_{1,0})}{\bar{\gamma}_{1,0}} \tag{14}$$
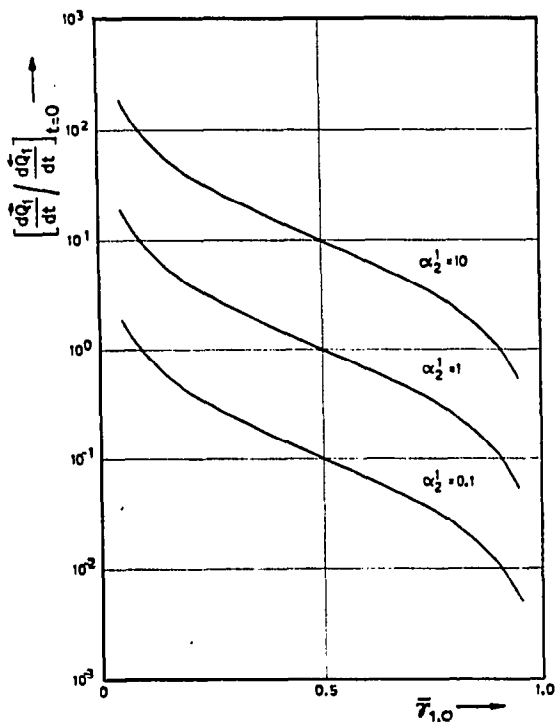

Fig. 4. Ratio of the initial rates of forward and reverse ion-exchange reactions as a function of the initial ionic composition $\bar{\gamma}_{1,0}$ of the sample according to eqn. 14. Parameter is the separation factor α_2^1. Δc = constant.

As an illustration, this quantity is plotted in Fig. 4 for different values of α_2^1 as a function of $\bar{y}_{1,0}$.

It can be seen that if the ion exchanger shows no preference for either B or D ions ($\alpha_2^1 = 1$), the forward reaction is faster than the reverse reaction provided that the initial value of $\bar{y}_{1,0}$ is less than 0.5; if $\bar{y}_{1,0}$ is greater than 0.5, the opposite is true. If the ion exchanger prefers the counter ion B compared with the counter ion D ($\alpha_2^1 > 1$), the forward reaction, in which B ions are taken up by the resin, will be faster (except at high values of $\bar{y}_{1,0}$) than the reverse reaction. If the ion exchanger shows a selectivity for the counter ion D compared with the counter ion B ($\alpha_2^1 < 1$), the forward reaction, in which B ions are taken up, will be slower (except at low values of $\bar{y}_{1,0}$) than the reverse reaction. Note that the ratio of the initial rate of the forward reaction to that of the reverse reaction, as given by eqn. 14, does not depend on either the diffusion coefficients or the concentration Δc. As we kept the latter quantity constant for the forward and the reverse reactions, the extent of the forward reaction, $\overrightarrow{\Delta \bar{y}_1}$, will be different from that of the corresponding reverse reaction, $\overleftarrow{\Delta \bar{y}_1}$, starting at the same initial ionic composition $\bar{y}_{1,0}$. This can be taken into account by calculating the ratio of the initial rates for attainment of the fractional equilibrium U for the forward and the reverse reaction, which are given at $\bar{y}_{1,0}$ by

$$\left| \frac{\overrightarrow{dU}}{dt} \middle/ \frac{\overleftarrow{dU}}{dt} \right|_{t=0} = \left| \frac{\overrightarrow{dQ_1}}{dt} \middle/ \frac{\overleftarrow{dQ_1}}{dt} \right|_{t=0} \cdot \frac{|\overleftarrow{\Delta \bar{y}_1}|}{|\overrightarrow{\Delta \bar{y}_1}|} \tag{15}$$

As the values of $(\overrightarrow{dQ_1/dt})/(\overleftarrow{dQ_1/dt})_{t=0}$ are given by eqn. 14 and $\Delta \bar{y}_1$ by eqn. 6, $(\overrightarrow{dU_1/dt})/(\overleftarrow{dU_1/dt})_{t=0}$ was calculated for different values of α_2^1 using the values of $\Delta \bar{y}_1$ shown in
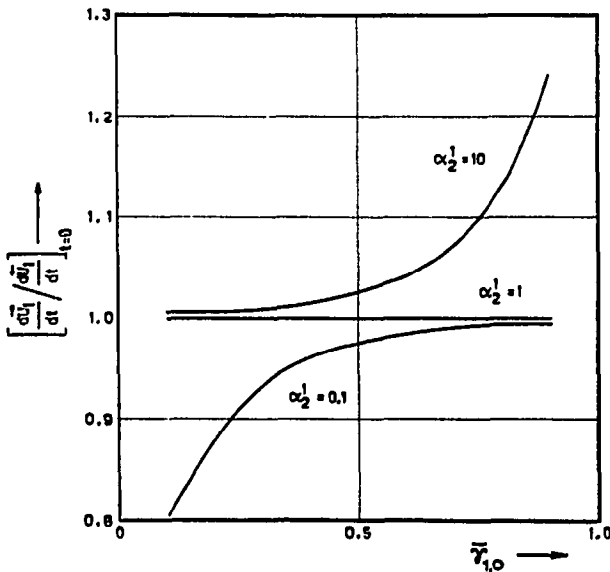

Fig. 5. Ratio of the initial rates for the fractional attainment of equilibrium of forward and reverse ion-exchange processes as a function of the initial ionic composition $\bar{y}_{1,0}$ of the sample according to eqn. 15. Parameter is the separation factor α_2^1. Δc = constant.

Fig. 1. Note that if $\overrightarrow{\Delta \bar{\gamma}_1}$ for the forward reaction is taken at $\bar{\gamma}_{1,0}$ from the curve of a given value of α_2^1, the value of $\overleftarrow{\Delta \bar{\gamma}_1}$ of the reverse reaction has to be taken from the curve of $1/\alpha_2^1$ at $1 - \bar{\gamma}_{1,0}$. The ratio of the rates of the forward and reverse reactions for the attainment of the fractional attainment U are shown in Fig. 5. It can be seen that if the ion exchanger shows no selectivity for the two counter ions ($\alpha_2^1 = 1$), the forward and reverse rates for the attainment of fractional equilibrium U are identical. If the resin prefers the counter ions B compared with the counter ions D ($\alpha_2^1 > 1$), the rate of the forward reaction will always be higher than that of the corresponding reverse reaction. If the ion exchanger prefers the counter ions D compared with the counter ions B ($\alpha_2^1 < 1$), the opposite will be true.

Differential batch ion-exchange reactions, initiated by adding counter ions always in such amounts that the extent of each ion-exchange process remains constant ($\Delta \bar{\gamma}_1 = constant$)

Equilibria. The ion exchanger particles of a given initial ionic composition $\bar{\gamma}_{1,0}$ are again stirred in pure water in a reaction vessel at time $t = 0$ as in the first section *Equilibria*. The amount of counter ions B added to this mixture however, is now, depending on the initial ionic composition of the resin, selected in such a way that the extent $\Delta \bar{\gamma}_1$ of each differential ion-exchange reaction is always the same. This means, in general, addition of increasing amounts of counter ions B as long as $\bar{\gamma}_{1,0}$ increases. The exact amount of B ions to be added, *i.e.*, the value of Δc as a function of the initial ionic composition $\bar{\gamma}_{1,0}$ in order to achieve a given $\Delta \bar{\gamma}_1$, can be calculated from eqn. 6.

Rate equations. If we again use the initial and boundary conditions used in the first section *Equilibria* but now express the rate as a function of $\Delta \bar{\gamma}_1$, we obtain for the initial rate of the uptake of B ions the equation

$$\left(\frac{dU}{dt}\right)_{t=0} \cdot \frac{D_1}{R'wC} = \left(\frac{dQ_1}{dt}\right)_{t=0} \cdot \frac{D_1}{Q_{tot} \, \Delta \bar{\gamma}_1 \, R'wC} =$$

$$= \frac{[\alpha_2^1 - (\alpha_2^1 - 1)(\Delta \bar{\gamma}_1 + \bar{\gamma}_{1,0})] \cdot (1 - \bar{\gamma}_{1,0})}{(1 - \bar{\gamma}_{1,0} - \Delta \bar{\gamma}_1)[\alpha_2^1 (D_2/D_1)(1 - \bar{\gamma}_{1,0}) + \bar{\gamma}_{1,0}]} \qquad (16)$$

As dU/dt and dQ/dt differ in this case only by a constant factor, it is sufficient to show in Fig. 6 only the dependence of dU/dt as a function of $\bar{\gamma}_{1,0}$ for different values of α_2^1 and D_2/D_1, as calculated according to eqn. 16. As one can see from these figures (calculated for differential ion-exchange reactions of $\Delta \bar{\gamma}_1 = 0.05$), the rates at low values of $\bar{\gamma}_{1,0}$ can, depending on the values of α_2^1 and D_2/D_1, either increase or decrease with increasing values of $\bar{\gamma}_{1,0}$. All curves converge, however, asymptotically to infinitely high rates at $\bar{\gamma}_{1,0} = 0.95$, because at this point the addition of an infinite amount of counter ions B to the solution would be required in order to convert the sample by a further step of $\Delta \bar{\gamma}_1 = 0.05$ completely into the B form ($\bar{\gamma}_{1,\infty} = 1$). This is, however, an unrealistic case, because at such high concentrations, film diffusion would no longer be the rate-determining step.

Forward and reverse ion-exchange reactions. The ratio of the rates of the forward and reverse reactions at the initial ionic composition $\bar{\gamma}_{1,0}$ is obtained in the same way as in the first section *Forward and reverse ion-exchange reactions*, and one obtains
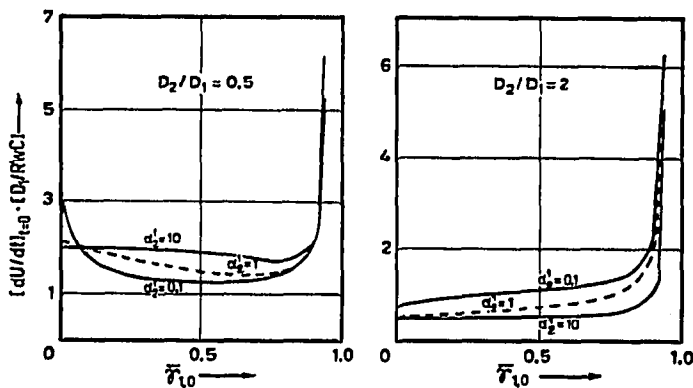
Fig. 6. Initial rates for the fractional attainment of equilibrium of differential ion-exchange processes plotted as the dimensionless quantity $(dU/dt)_{t=0} \cdot D_1/R'wC$ as a function of the initial equivalent fraction $\bar{\gamma}_{1,0}$ of the ions in the sample (eqn. 16). Parameters are the separation factor α_2^1 and the diffusion coefficients D_1/D_2. $\Delta\bar{\gamma}_1$ = constant = 0.05.

$$\left| \frac{\overrightarrow{dU}}{dt} \middle/ \frac{\overleftarrow{dU}}{dt} \right|_{t=0} = \frac{(1 - \bar{\gamma}_{1,0})\,(\bar{\gamma}_{1,0} - \Delta\bar{\gamma}_1)}{\bar{\gamma}_{1,0}\,(1 - \bar{\gamma}_{1,0} - \Delta\bar{\gamma}_1)} \times$$

$$\times \frac{\Delta\bar{\gamma}_1\,(1 - \alpha_2^1) + \alpha_2^1\,(1 - \bar{\gamma}_{1,0}) + \bar{\gamma}_{1,0}}{\Delta\bar{\gamma}_1\,(\alpha_2^1 - 1) + \alpha_2^1\,(1 - \bar{\gamma}_{1,0}) + \bar{\gamma}_{1,0}} \qquad (17)$$

i.e., a quantity that again is independent of the diffusion coefficients.

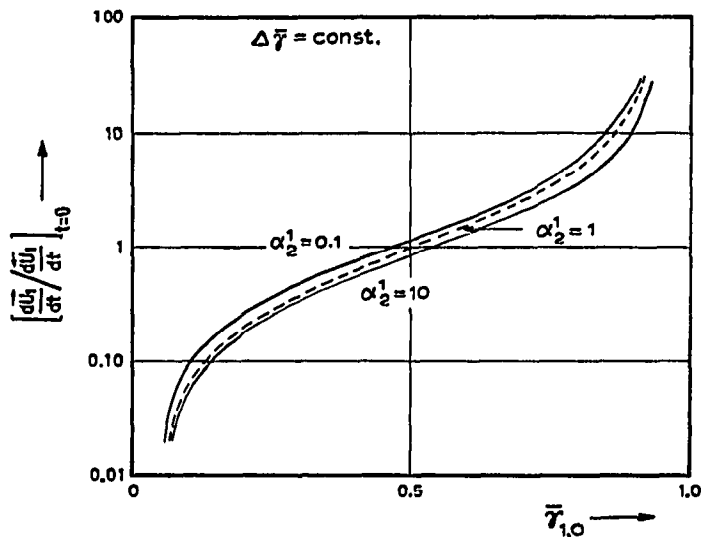The ratio of the rates of the forward and reverse reactions, as calculated ac-

Fig. 7. Ratio of the initial rates for the fractional attainment of equilibrium of forward and reverse ion-exchange reactions as a function of the initial equivalent fraction $\bar{\gamma}_{1,0}$ of the ions in the sample (eqn. 17). Parameter is the separation factor α_2^1. $\Delta\bar{\gamma}_1$ = constant = 0.05.

cording to eqn. 17 for a value of $\Delta\bar{\gamma}_1 = 0.05$, is shown in Fig. 7 as a function of $\gamma_{1,0}$ for different values of α_2^1.

As expected, the rate of the forward reaction is higher than that of the reverse reaction if $\bar{\gamma}_{1,0}$ is larger than about 0.5, because in order to convert the ion exchanger further towards the B form, a higher concentration of these ions in solution is necessary compared with the ion-exchange reaction in which the resin is converted by the same amount towards the D form. If $\bar{\gamma}_{1,0}$ is less than about 0.5, the opposite behaviour is found. The selectivity of the ion exchanger, *i.e.*, the value of α_2^1, in this case has a comparatively small influence on the shape of the curves. At $\bar{\gamma}_{1,0} = 0.95$ and 0.05, the rate of the forward reaction compared with that of the reverse reaction becomes infinite and zero, respectively, for reasons which were explained in the previous section. If $\Delta\gamma_1$ approaches zero, $|(\overrightarrow{dU/dt})/(\overleftarrow{dU/dt})|_{t=0}$ approaches unity.

DISCUSSION

In all of the above figures, in which the dependence of the rates of differential ion-exchange processes on the initial ionic composition $\bar{\gamma}_{1,0}$ of the sample is shown, the equivalent separation factor α_2^1 was, for simplicity, always assumed to be independent of $\bar{\gamma}_{1,0}$. In many experiments, more complicated behaviour will be observed, however. In this case one can, nevertheless, apply all of the above rate equations because, and this is the advantage of considering only differential ion-exchange processes, within the small range $\Delta\bar{\gamma}$ of each reaction, α_2^1 can still be considered to be constant, although different for different values of $\bar{\gamma}_{1,0}$.

A similar situation arises for the diffusion coefficients D_1 and D_2. As the four diffusion coefficients D_{ij} in the ternary solution of the film, which determine the values of D_1 and D_2 (eqn. 18 in ref. 7), depend to some extent on the equivalent fraction[5], D_1 and D_2 are not strictly constant. This effect, however, probably need be considered only if the counter ions involve H^+ ions.

Finally, if one compares experimental results for forward and reverse reactions with the above theoretical predictions, one should first check if both reactions are actually film diffusion-controlled. As pointed out by Helfferich[8], the rate-determining step of forward and reverse reactions need not necessarily always be the same.

Preliminary experimental results obtained in our laboratory are in satisfactory accordance with the above theory.

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