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## COMPUTER SIMULATION OF THE KINETICS OF ION EXCHANGE ACCOMPANIED BY COMPLEX FORMATION IN IONITES\*

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### SUMMARY

The kinetics of ion exchange accompanied by the formation of weakly dissociating compounds between counter ions and fixed ionite exchange groups has been studied by computer simulation of ion-exchange processes at different ratios of the individual diffusion coefficients and in the case of convex and concave exchange isotherms. The results show that exchange in ionites filled initially with less mobile ions is faster in the case of a convex than in the case of a concave isotherm. The distribution of counter ions and co-ions with particle radius is dependent on the relation between the equilibrium and kinetic parameters. The simulated ion distribution curves obtained for the exchange kinetics in carboxyl and vinylpyridinecarboxyl ionites are similar to the experimental ones.

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### INTRODUCTION

The formation of weakly dissociating compounds in an ionite or a solution phase is, in a number of cases, a necessary condition for effective chromatographic separation and controls both the equilibrium and kinetic separation parameters. The mechanism of the exchange when accompanied by the formation of a weakly dissociating compound of a counter ion with a fixed ionite exchange group has been discussed qualitatively by Helfferich<sup>1</sup>. An approximate solution of the exchange kinetics has been derived<sup>2,3</sup> for the complexing ion in the case of a rectangular isotherm, and equations together with a numerical solution have been presented<sup>4</sup> for an arbitrarily shaped isotherm with certain combinations of the individual ion diffusion coefficients.

The present paper discusses the kinetics of ion exchange in the presence of ion association in ionites for convex and concave isotherms, and considers various relations between the individual diffusion coefficients  $D_B$ ,  $D_A$ ,  $D_Y$  for the counter ions  $B^+$ ,  $A^+$  and co-ion  $Y^-$ .

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## THEORETICAL

The expression describing the kinetics of such a process<sup>2,3</sup>

$$\partial (a_i + c_i)/\partial t = -\operatorname{div} \bar{J}_i \quad (1)$$

where  $i = B, A$  or  $Y$ , the law of mass balance

$$\sum_{i=B,A,Y} z_i \bar{J}_i = 0 \quad (2)$$

in the absence of an electric current, where  $z_i$  are the charges, and the condition for electroneutrality

$$z_B c_B + z_A c_A + z_Y c_Y = a_0 - z_B a_B - z_A a_A \quad (3)$$

generate a condition for equilibrium between the bound and free ions in the ionite which for singly charged ions is

$$K_{RB} = c_B (a_0 - a_A - a_B)/a_B; K_{RA} = c_A (a_0 - a_A - a_B)/a_A \quad (4)$$

where  $c_B, c_A$  and  $a_B, a_A$  are the concentrations of the free ions and ion pairs formed by  $B^+, A^+$  and fixed ionite exchange groups, respectively,  $a_0$  is the concentration of the fixed exchange groups and  $K_{RB}, K_{RA}$  are the dissociation constants. The ion fluxes,  $J_i$ , are defined by Nernst-Planck relations

$$J_i = -D_i \left( \nabla c_i + \frac{F}{RT} z_i c_i \nabla \varphi \right) \quad (5)$$

where  $\varphi$  is the electric potential,  $F$  is the Faraday constant,  $R$  is the gas constant and  $T$  is the absolute temperature.

The system of eqns. 1-5 for the exchange kinetics of singly charged ions is computed at the initial and boundary conditions corresponding to the exchange between the ionite and continually renewed solution, when initially the ionite particle is filled with  $A^+$

$$c_B(r, 0) = 0; c_Y(r, 0) = 0; 0 \leq r \leq r_0 \quad (6)$$

$$c_B(r_0, t) = c_0; c_A(r_0, t) = 0; \left( r^2 \cdot \frac{\partial c_i}{\partial r} \right)_{r=0} = 0, t > 0 \quad (7)$$

where  $r$  is the radial space coordinate,  $r_0$  is the particle radius,  $t$  is the time and  $c_0$  is the concentration of the surrounding solution.

In ref. 4 a numerical solution has been obtained for the ratio between the individual counter ion diffusion coefficients,  $D_A/D_B = 0.1$ , and  $K'_{RB} = 0.001, K'_{RA} = 0.1$  where  $K'_i = K/c_0$ . This solution demonstrates that with time the well-defined boundary of the exchanging ion,  $B^+/A^+$ , shifts toward the particle centre, and ion

transfer toward and away from the exchange boundary involves the co-ion  $Y^-$  moving from the solution into the ionite particle.

## RESULTS AND DISCUSSION

Numerical solutions of the four combinations of the individual diffusion coefficients  $D_B$ ,  $D_A$  and dissociation constants  $K_{RB}$ ,  $K_{RA}$  are shown in Figs. 1–5. To compare the curves of ion distribution with particle radius, times were adopted cor-

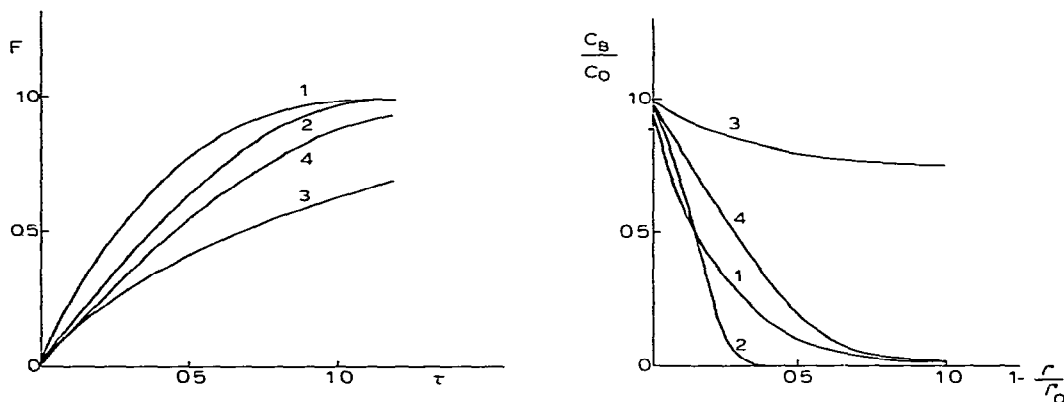


Fig. 1. Dependence of fractional conversion on the dimensionless time parameter  $\tau = \sqrt{\bar{D}} t c_0 / (r_0^2 a_0)$ , where  $\bar{D}$  is the unit used for measuring  $D_i$ . Curves: 1, 2,  $K'_{RB} = 0.001$ ,  $K'_{RA} = 0.005$ ; 3, 4,  $K'_{RB} = 0.005$ ,  $K'_{RA} = 0.001$ .  $D_B = 1$ ,  $D_A = 0.1$  for curves 1, 3;  $D_B = 0.1$ ,  $D_A = 1$  for curves 2, 4.

Fig. 2. Concentration distribution of the free  $B^+$  for the time corresponding to  $F = 0.58$ . Curves numbered as in Fig. 1.

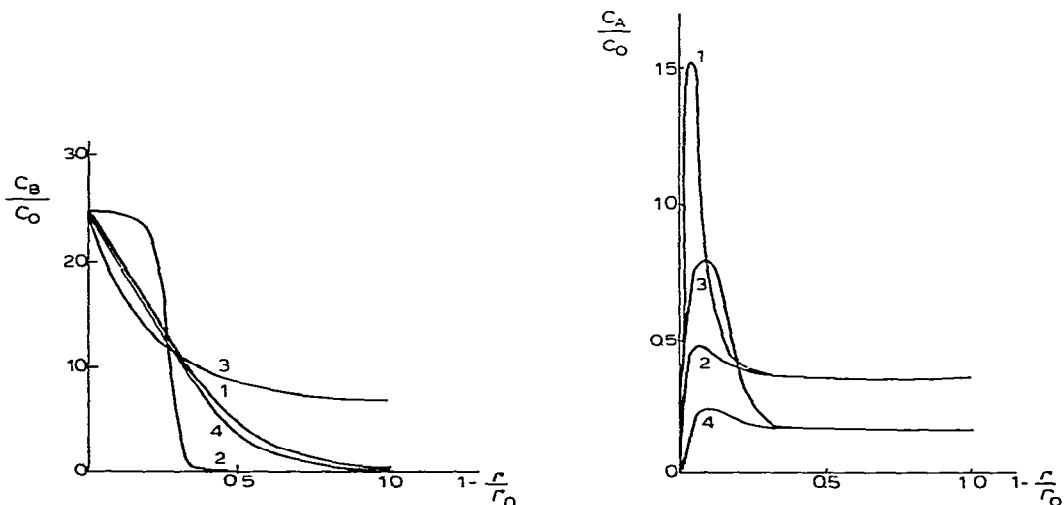


Fig. 3. Concentration distribution of the ion pairs  $RB$  at  $F = 0.58$ . Curves numbered as in Fig. 1.

Fig. 4. Concentration distribution of the free  $A^+$  at  $F = 0.1$ . Curves numbered as in Fig. 1.

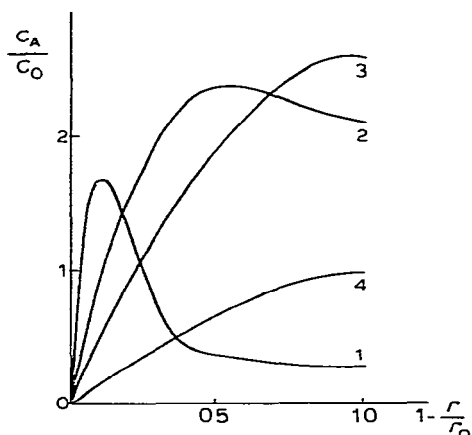


Fig. 5. Concentration distribution of the free  $A^+$  with radius for the system with  $K'_{RB} = 0.001$ ,  $K'_{RA} = 0.005$ ,  $D_B = 1$  and  $D_A = 0.1$  at different fractional conversions  $F$ : 1, 0.2; 2, 0.5; 3, 0.7; 4, 0.9.

responding to fractional conversions  $F = 0.58$  (Figs. 2 and 3) and  $F = 0.1$  (Fig. 4). At these values of  $F$  the distribution curves exhibit the characteristic features of each of the four groups. Fig. 5 illustrates how the distribution of  $A^+$  varies with radius during the process of exchange, for one of the combinations of the starting parameters.

Before discussing the results obtained it is necessary to note the difference between the kinetics of ion exchange accompanied by the formation of weakly dissociating compounds and that occurring in strong functional ionites. In the absence of ion association in the ionite phase, the rate of exchange from a continuously renewed solution is independent of its selectivity. It is governed by the value of and

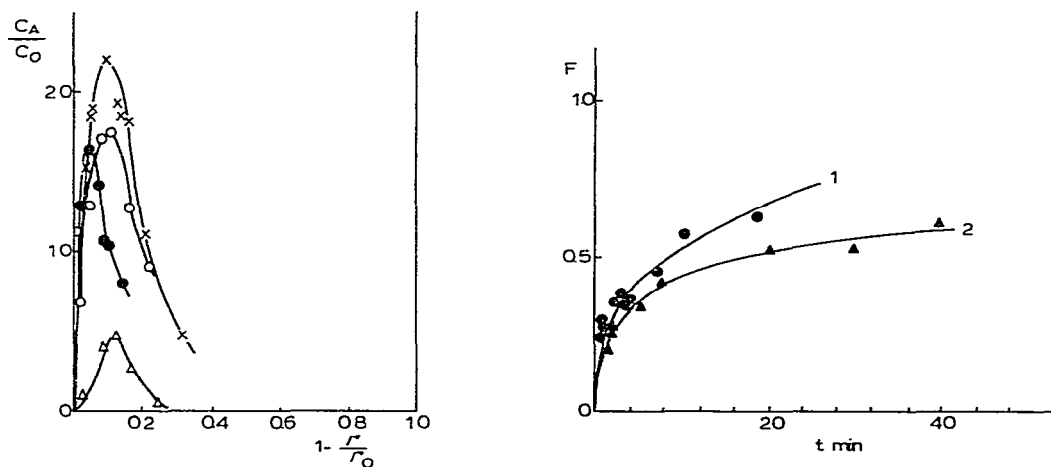


Fig. 6. Distribution of the free  $Ni^{2+}$ ,  $Na^+$  with radius as the  $Ni^{2+}$  are displaced from cationite KB-4 by  $H^+$  ( $\times$ ),  $Na^+$  from cationite KB-4 by  $H^+$  ( $O$ ,  $\bullet$ ) and  $Na^+$  from ampholyte VPC by  $Ni^{2+}$  ( $\Delta$ ). Fractional conversions: 0.16 ( $\times$ ); 0.22 ( $O$ ); 0.1 ( $\bullet$ ); 0.2 ( $\Delta$ ).

Fig. 7. Exchange rates for  $Ni^{2+}-H^+$  (convex isotherm) (1) and  $H^+-Ni^{2+}$  (concave isotherm) (2) on ampholyte VPC.

the ratio between the counter ion diffusion coefficients. The process is faster if initially the ionite contains more mobile ions<sup>5</sup>.

In the case of exchange accompanied by ion association in the ionite phase, the exchange rate and ion distribution in the particle depend on the adopted combination of the starting equilibrium and kinetic parameters. With a convex isotherm ( $K'_{RB} = 0.001$ ,  $K'_{RA} = 0.005$ ) the exchange is faster than with a concave one ( $K'_{RB} = 0.005$ ,  $K'_{RA} = 0.001$ ) (see Fig. 1). Filling the starting ionite with less mobile ions results in a higher exchange rate in the case of the convex isotherm (Fig. 1, curves 1 and 2) and a lower one in the case of the concave isotherm (Fig. 1, curves 3 and 4).

The different effect of the  $D_B/D_A$  ratio on the exchange rate for the convex and concave isotherms can be visualized as follows. The low mobility of  $A^+$  leads to its accumulation in the particle and lower relative free ion concentration,  $c_B/c_A$ . The relative variation of  $a_B$  as  $c_B/c_A$  varies is considerably smaller in the case of the convex exchange isotherm than with the concave isotherm, which, in the long run, may result in a variation of the exchange rate as suggested in Fig. 1.

Comparison of the  $F-\tau$  curves in Fig. 1 with the kinetic dependence for isotope exchange<sup>6</sup> reveals an interesting feature of exchange accompanied by ion association in the ionite particle. The dependence  $F-\tau$  for the convex isotherm and  $D_B/D_A = 10$  is described by an equation of an in-sphere diffusion with a constant coefficient; on the other hand, for the concave isotherm and  $D_B/D_A = 10$ , this dependence formally corresponds to a model whose effective diffusion coefficient decreases in the course of exchange.

The effect of the ratio of the individual diffusion coefficients, and of the exchange selectivity, on the kinetic dependences in real systems has been studied for ion exchange in carboxylic (KB-4) and vinylpyridinecarboxylic (VPC) ionites. The exchange rate was measured in a thin ionite layer<sup>3</sup>, and ion distribution was studied by using a spherical particle sector model<sup>7</sup>. The model comprised a cone made up of separate rings and filled with fine-ground swollen ionite. The cone, with a filter in its base, was immersed in a solution and after a period of ion exchange between the solution and the ionite in the cone it was removed from the solution, disassembled into separate layers and the concentration of the free and fixed group-bound ions in each layer was measured.

Fig. 6 compares the particle-radius distributions of the displaced ions not bound to the fixed exchange groups, for ion exchange with different  $D_B/D_A$  ratios. The exchange isotherms in all three cases are strongly convex since the hydrogen ions in the carboxylic cationite and the nickel ions in the vinylpyridinecarboxylic ionite yield weakly dissociating compounds ( $K_{RH} \approx 10^{-5}$ ,  $K_{RNi} \approx 10^{-7}$ ). It is seen that as the relative mobility of the displaced ions decreases ( $D_{Ni} < D_{Na} < D_H$ ) their maximum concentration increases, which is consistent with the results of the numerical solutions.

The experimental kinetic curves in Fig. 7 for the RH-Ni and RNi-H exchanges in VPC indicate a decrease in the exchange rate when passing from the convex to the concave isotherm and correspond to the calculated curves 2 and 3 of Fig. 1 where the exchange isotherm and ratio between the individual diffusion coefficients were used as starting parameters. It should be noted that the experimentally observed features of the kinetic exchange occur in the same sequence for ions having the same or different charges. This is not at variance with theory, since exchange isotherms of differently

charged ions and of singly charged ions, while having different analytical expressions, can be of a similar type. The value of qualitative comparison of experimental results and those from numerical solutions is thus demonstrated in all the present cases. Such a comparison is also valid for ion exchange processes in thin ionite layers and in the spherical particle sector model. The formation of the sharp boundary line of generations in the case of a square isotherm in ionite particles<sup>2</sup> and in the spherical particle sector model<sup>7</sup> shows that structural heterogeneity does not effect the formation of the profile  $a_i$ ,  $c_i$ .

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