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COMPUTERIZED ANALYSES OF THE DIFFUSION PROCESSES IN COMPLEXING IONITES*

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SUMMARY

A theoretical and experimental study of the diffusion processes in complex-forming ion exchangers has been made. The theoretical study is based on diffusion-type mass balance equations for the counter ions and co-ion. These equations are solved by using computers. The influence of exchange selectivity and ion mobility on the kinetics of ion exchange in a complexing ionite is discussed. The theoretical deductions have been verified experimentally for exchange in a carboxylic cation exchanger and for exchange in a complex-forming vinylpyridine cation exchanger. The experimental data agree with the theoretical deductions.

INTRODUCTION

Complex-forming ionites are often used for effective chromatographic separations. The kinetic mechanism of ion exchange accompanied by the complexing of a counter ion with a fixed exchange group of an ion exchanger has been considered qualitatively¹. An approximate solution of this kinetic problem has been derived^{2,3} for the case of a "rectangular" isotherm and numerical solutions of the equations have been presented⁴⁻⁶ for arbitrary-shaped isotherms and certain combinations of individual ion diffusion coefficients.

This paper discusses the influence of exchange selectivity (expressed through dissociation constants) and ion mobility on the kinetics of ion exchange in complex-forming ionites.

THEORETICAL

The equation system describing the kinetics of such an ion-exchange process along with the law of mass balance:

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$$\frac{\bar{c}(a_i + C_i)}{\bar{c}t} = \text{div } I_i \quad (i = B, A, Y) \quad (1)$$

the condition for the absence of electric current:

$$\sum_i Z_i I_i = 0 \quad (i = A, B, Y) \quad (2)$$

and the condition for electroneutrality:

$$\sum_i Z_i (a_i + C_i) = a_0 \quad (i = B, A, Y) \quad (3)$$

includes an equation for the equilibrium between the bound (a_i) and free (C_i) ions in the ionite. In the ideal case, when the dissociation constants are independent of the degree of ion exchange, the equilibrium condition for the complexing reaction of singly charged ions can be written as⁷

$$K_{Ri} = \frac{C_i (a_0 - a_B - a_A)}{a_i} \quad (i = B, A) \quad (4)$$

where C_i are the concentrations of the free A^+ and B^+ ions, C_Y is the concentration of the co-ion Y^- , a_i are the concentrations of B^+ and A^+ ions associated with fixed groups R ($a_Y = 0$), a_0 is the concentration of the fixed exchange groups, Z_i are the charges, I_i are the ion fluxes and K_{Ri} are the dissociation constants of complexes RB and RA .

With the substitution the Nernst-Planck relations for ion fluxes:

$$I_i = D_i \left(\text{grad } C_i + Z_i C_i \cdot \frac{F}{RT} \cdot \text{grad } \phi \right) \quad (i = B, A, Y) \quad (5)$$

in eqn. 2, one obtains

$$\frac{F}{RT} \cdot \text{grad } \phi = \sum_i Z_i D_i \text{ grad } C_i / \left(\sum_i Z_i^2 D_i C_i \right) \quad (i = B, A, Y) \quad (6)$$

where D_i are the individual diffusion coefficients, F is the Faraday constant, R is the gas constant, T is the absolute temperature and ϕ is the electric potential.

From eqns. 5 and 6 we obtain equations for ion fluxes that contain concentration gradients only. One can easily obtain the relationship between $\text{grad } C_i$ and $\text{grad } a_i$ by differentiation of eqns. 3 and 4:

$$\begin{aligned} \sum_i Z_i \text{ grad } C_i &= -\text{grad } a_B - \text{grad } a_A \quad (i = B, A, Y) \\ \text{grad } a_i &= \text{grad} \left(\frac{a_0 K_{Ri} C_i}{K_{RA} K_{RB} + K_{RB} C_A + K_{RA} C_B} \right) \end{aligned} \quad (7)$$

Substitution of eqns. 5 and 6 in the mass balance eqn. 1 yields a system of two diffusion-type equations:

$$\frac{\partial(a_i + C_i)}{\partial t} = \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left[r^2 \left(D_{iA} \cdot \frac{\partial C_A}{\partial r} + D_{iB} \cdot \frac{\partial C_B}{\partial r} \right) \right] \quad (i = B, A)$$

$$D_{ij} = \frac{D_i}{D_0} \left\{ \delta_{ij} + \frac{C_i \left[D_Y \left(1 + \frac{a_0 f^2}{K_{Rj}} \right) - D_j \right]}{C_A(D_A + D_Y) + C_B(D_B + D_Y) + D_Y a_0 f} \right\} \quad (8)$$

where

$$f = \frac{K_{RA} K_{RB}}{K_{RA} K_{RB} + K_{RA} C_B + K_{RB} C_A} \quad \left(\delta_{ij} = \begin{cases} 1; & i = j \\ 0; & i \neq j \end{cases} \right)$$

where r and t are the radial space coordinate and time, respectively, D_0 is the unit used for measuring diffusion coefficients and D_{ij} are the effective diffusion coefficients. Concentration C_Y is eliminated from eqn. 8 by substituting eqns. 3 and 7.

The equation system 2 in the case of "rectangular" isotherm can be solved approximately by the method of integral relations. Under the physically justified assumption of constancy of the co-ion Y^- concentration at the B^+/A^+ moving boundary in an ion-exchanger particle, which has been supported experimentally⁸, the following equations can be obtained for a fractional conversion $F \leq 0.6^{2,3}$:

$$F(t) = 3 \sqrt{2D_{\text{eff}} \cdot \frac{c_0 t}{a_0 r_0^2}}$$

where

$$D_{\text{eff}} = \frac{(Z_B - Z_Y) D_A D_B}{Z_B D_B - Z_Y D_A} \quad (9)$$

where D_{eff} is the effective diffusion coefficient, C_0 is the solution concentration at the particle surface, r_0 is the particle radius and Z_B and Z_Y are the charges of B^+ and Y^- ions, respectively.

The system of equations 1–3 for the exchange of singly charged ions at the initial and boundary conditions corresponding to the exchange between the ionite and the continually renewed solution, when initially ionite particles are filled with A^+ ions, is calculated by using a computer.

Figs. 1–3 show the results of the numerical solution for different combinations of the individual diffusion coefficients D_B , D_A and D_Y and dissociation constants K_{RB} and K_{RA} which are given in Table I.

The values as used for the solution are $a_0 = 2.5 \text{ mmol/cm}^3$ and $C_0 = 0.1 \text{ mmol/cm}^3$. With a convex isotherm ($K_{RA}/K_{RB} = 5$) the exchange proceeds faster than with a concave isotherm ($K_{RA}/K_{RB} = 0.2$) (see Fig. 1).

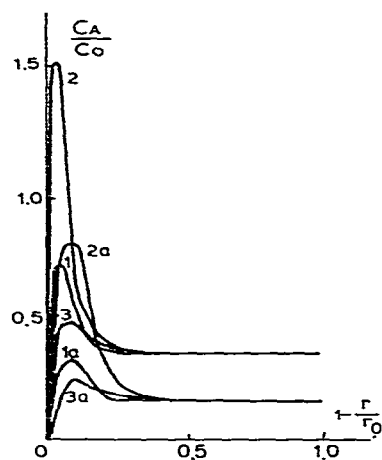
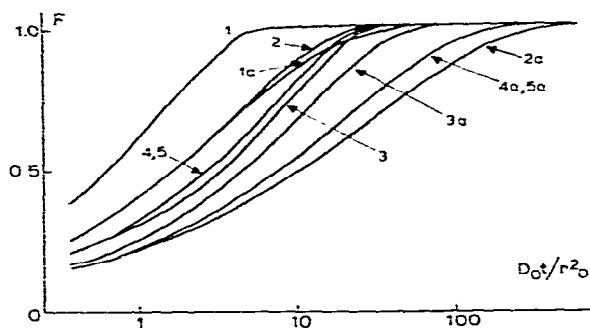


Fig. 1. Dependence of fractional conversion F on $D_0 t, r_0^2$. Curves numbered as in Table I.

Fig. 2. Distribution of concentration C_A at $F = 0.1$. Curves numbered as in Table I.

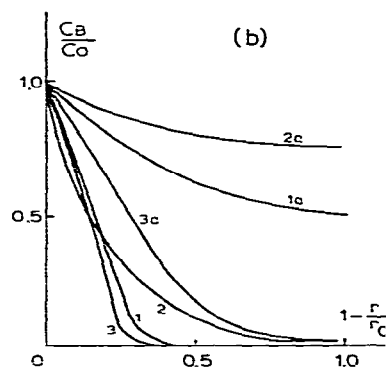
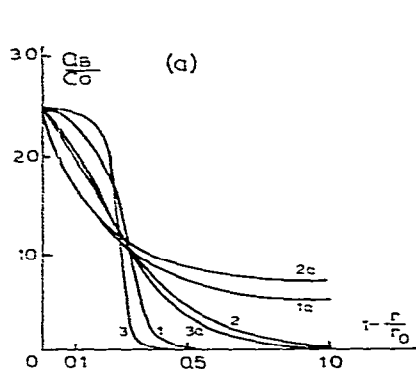


Fig. 3. (a) Distribution of concentration a_B at $F = 0.5$. Curves numbered as in Table I. (b) Distribution of concentration C_B at $F = 0.5$. Curves numbered as in Table I.

TABLE I
CONDITIONS FOR NUMERICAL SOLUTION

No.*	$D_B D_0$	$D_A D_0$	$D_V D_0$	$K_{RB} C_0$	$K_{RA} C_0$
1	1.0	1.0	0.1	$1 \cdot 10^{-3}$	$5 \cdot 10^{-3}$
1a	1.0	1.0	0.1	$5 \cdot 10^{-3}$	$1 \cdot 10^{-3}$
2	1.0	0.1	0.1	$1 \cdot 10^{-3}$	$5 \cdot 10^{-3}$
2a	1.0	0.1	0.1	$5 \cdot 10^{-3}$	$1 \cdot 10^{-3}$
3	0.1	1.0	0.1	$1 \cdot 10^{-3}$	$5 \cdot 10^{-3}$
3a	0.1	1.0	0.1	$5 \cdot 10^{-3}$	$1 \cdot 10^{-3}$
4	0.2	0.2	0.1	$1 \cdot 10^{-3}$	$5 \cdot 10^{-3}$
4a	0.2	0.2	0.1	$5 \cdot 10^{-3}$	$1 \cdot 10^{-3}$
5	0.2	0.2	1.0	$1 \cdot 10^{-3}$	$5 \cdot 10^{-3}$
5a	0.2	0.2	1.0	$5 \cdot 10^{-3}$	$1 \cdot 10^{-3}$

* Curves in Figures.

The comparison of the $F(\tau)$ curves in Fig. 1 reveals that the variation of the exchange rate as D_B varies is considerably larger with the convex than with the corresponding concave isotherm.

In contrast, the value of D_A is more important with the concave isotherm. Therefore, the exchange rate depends greatly on the diffusion coefficient of the ion absorbed selectively. The ion-exchange rate does not depend on D_Y . Finally, the dependences $F(\tau)$ for the convex isotherm and $D_A \geq D_B$ are described by an equation of an in-sphere diffusion with a constant coefficient; in other cases this dependence features a formal correspondence to a model whose effective diffusion coefficient varies in the course of exchange. The distribution curves (a_i, C_i ; Figs. 2, 3a and 3b) characterize distinctly the features of the mass-transfer mechanism.

The results, shown in Fig. 3 (curves 1 and 3), demonstrate that with the convex isotherm and $D_A \geq D_B$ the ion-exchange process is accompanied by the formation of the welldefined boundary of the exchanging ions, B^+/A^+ . With a ratio $D_A/D_B = 0.1$ the low mobility of the A^+ ions leads to the accumulation of A^+ in the particle. Under these conditions, the concentration of C_A can strongly affect the front width of a_B (Figs. 2 and 3, curve 2). Further, the data in Fig. 4 indicate agreement between the results of the numerical solution and the approximate analytical solution (eqn. 9) for the exchange process accompanied by the formation of the well defined boundary B^+/A^+ , when $D_A \geq D_B$.

When $D_A < D_B$ the kinetic dependence is not described by eqn. 9 because the assumption of the constancy of the concentration of the ions Y^- and A^+ at the B^+/A^+ boundary is not verified, which can be seen from Fig. 5.

The validity of the approximate rate expression was verified by using eqn. 9 to calculate the effective interdiffusion coefficients for the experimental conditions corresponding to $D_A \geq D_B$ from kinetic curves of the exchange RNa-Ni, RNa-Zn, RNa-Sr, RZn-Ni, RSr-Ni, in vinylpyridinecarboxylic (VPC) ampholyte^{2,3,5}.

The results presented in Fig. 6 were obtained for experimental conditions corresponding to $D_A \ll D_B$ (RSr-H⁺) and $D_A > D_B$ (RNa-Sr²⁻).

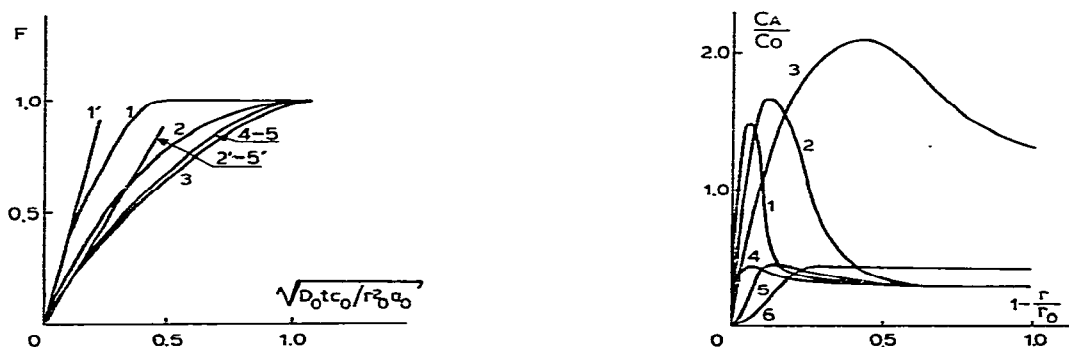


Fig. 4. Dependence of fractional conversion F on $\sqrt{D_0 t c_0 / r_0^2 a_0}$ for a convex isotherm. Curves are plotted on the basis of the numerical (curves 1-5) and approximate analytical (curves 1'-5') solutions.

Fig. 5. Distribution of concentration C_A in the case for a convex isotherm for $D_B/D_A = 10$ (curves 1-3) and $D_B/D_A = 0.1$ (curves 4-6) at $F = 0.1$ (1), $F = 0.19$ (2), $F = 0.43$ (3), $F = 0.08$ (4), $F = 0.19$ (5) and $F = 0.38$ (6).

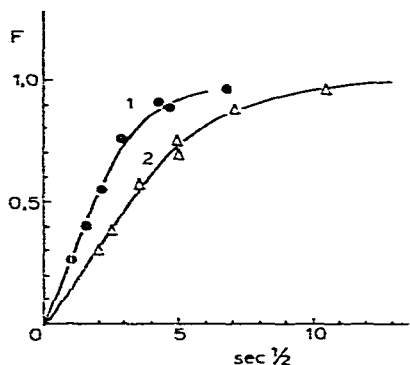


Fig. 6. Ion-exchange kinetic curves in ampholyte VPC: 1 = RSr-H^+ ; 2 = RNa-Sr^{2+} . $T = 298^\circ\text{K}$; $r^0 = 0.005\text{ cm}$; $C_{0(\text{H}^+)}$ = 0.05 mmol/cm^3 ; $C_{0(\text{Sr})}$ = 0.025 mmol/cm^3 .

The exchange rate was measured in a thin ionite layer^{2,3}. If, as in the exchange RSr-H , $D_A \ll D_B$, $Z_B = 1$, $Z_Y = -1$, then the effective interdiffusion coefficient is defined from eqn. 9 as

$$D_{\text{eff}(\text{Sr-H})} = \frac{(Z_{\text{H}} - Z_{\text{NO}_3}) D_{\text{Sr}} D_{\text{H}}}{Z_{\text{H}} D_{\text{H}} - Z_{\text{NO}_3} D_{\text{Sr}}} = 2 D_{\text{Sr}} \quad (10)$$

Further, it was generally assumed that $D_{\text{H}} > D_{\text{Na}} > D_{\text{Sr}}$. Thus:

$$2 D_{\text{Sr}} > D_{\text{eff}(\text{Sr-Na})} > D_{\text{Sr}} \quad (11)$$

The ratio between the effective interdiffusion coefficients, calculated from eqn. 9 on the basis of the experimental kinetic dependences 1 and 2 (Fig. 6), is equal to

$$\frac{D_{\text{eff}(\text{Sr-H})}}{D_{\text{eff}(\text{Sr-Na})}} = 3 \quad (12)$$

The evident disagreement between eqn. 12 and the conditions 10 and 11 is the experimental manifestation of the above-found boundaries of the application of eqn. 9.

The effect of the ratio between 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^{2,3,5,6,8}.

The theory has been developed for singly charged ions. However, in the complexing ionites the ion exchange of multiply charged ions mostly takes place. Therefore, it was of interest to consider, for example, the ion-exchange kinetics of Ni^{2+} and Zn^{2+} ions within ampholyte VPC. We have assumed that the results for multiply charged and singly charged ions are comparable as their exchange isotherms, having different analytical expressions, can be of a similar type.

Computer simulation of the kinetics for this system was carried out with the ratio $K_A/K_B = 12$ in the case of a convex isotherm (RZn-Ni^{2+}) and $K_A/K_B = 1/12$ in the case of a concave isotherm (RNi-Zn^{2+}).

The value of K_A/K_B is identical with the relationship of the distribution coef-

ficients of Ni^{2+} and Zn^{2+} ions between the solution and the ionite under the conditions $K_{A,B} \ll 1$ and $C_0 \ll a_0$. This relationship was obtained from the experimental isotherm of the Ni^{2+} - Zn^{2+} exchange⁹. The values of K_A and K_B can be chosen arbitrarily, because their effect (when $K_{A,B} \ll 1$) on the numerical results is remarkably small.

As shown earlier⁵, the individual diffusion coefficients can be characterized by the experimental kinetic curves for the systems $\text{RNa}^+ - \text{Ni}^{2+}$ and $\text{RNa}^+ - \text{Zn}^{2+}$: $D_{\text{Ni}} \approx D_{\text{Zn}} \approx 2 \cdot 10^{-7} \text{ cm}^2/\text{sec}$. The modelling of the spherical particle for the ion distribution study has been described previously¹⁰. The ion distribution curves calculated for the exchange kinetics of Ni^{2+} and Zn^{2+} ions are similar to the experimental ones (Figs. 7 and 8).

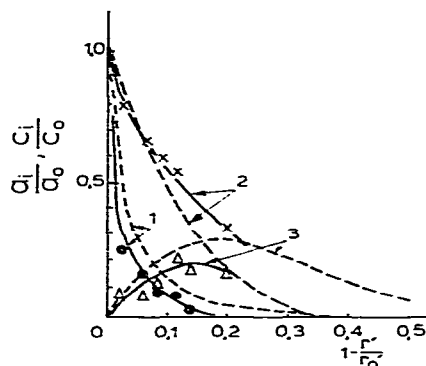
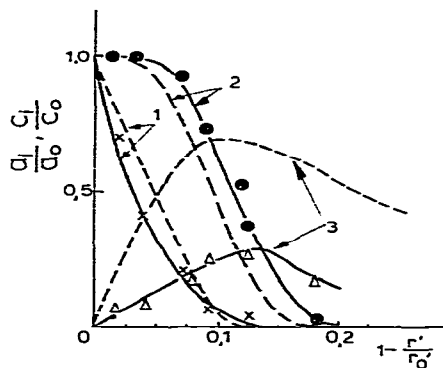


Fig. 7. Distribution of $a_{\text{Ni}}(2)$, $C_{\text{Ni}}(1)$ and $C_{\text{Zn}}(3)$ concentrations in the spherical particle sector model (r'_0 is the spherical radius) at the convex isotherm of the displacement of Zn^{2+} ions by Ni^{2+} ions from the vinylpyridine ampholyte VPC. $T = 298^\circ\text{K}$; $C_{0(\text{Ni})} = 0.25 \text{ mmol}/\text{cm}^3$; time of contact of the solution with the ampholyte, 66 h; $F_{\text{exp}} \approx 0.25$; $F_{\text{calc.}} = 0.247$. Solid lines, experimental; broken lines, calculated.

Fig. 8. Distribution of $a_{\text{Zn}}(1)$, $C_{\text{Zn}}(2)$ and $C_{\text{Ni}}(3)$ concentrations at the concave isotherm $\text{RNi}-\text{Zn}$. $C_{0(\text{Zn})} = 0.25 \text{ mmol}/\text{cm}^3$; time of contact, 264 h; $F_{\text{exp.}} = 0.18$; $F_{\text{calc.}} = 0.176$. Solid lines, experimental; broken lines, calculated.

Some disagreement between the theoretical and experimental results can be explained mainly by the variability of the activity coefficients of ions and the dissociation constants. However, it is difficult and sometimes inadvisable to take account of these factors, because the disagreements in the distribution curves lead to only small differences in the exchange rates. For example, satisfactory agreement between the experimental and calculated values was observed on comparison of the rates of the $\text{RZn}-\text{Ni}^{2+}$ and $\text{RNi}-\text{Zn}^{2+}$ exchanges. The rate of exchange can be characterized by the value $\tau_{0.5}$, which is the time corresponding to a fractional conversion $F = 0.5$. The $\frac{(\tau_{0.5})_{\text{concave}}}{(\tau_{0.5})_{\text{convex}}}$ ratios are 7.8 and 6.5 for the experimental and calculated values, respectively.

Hence the results of computer simulation can be used for the analyses of ion-exchange kinetics accompanied by complex formation in real systems.

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