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DETERMINATION OF THE OPTIMAL CONDITIONS FOR ION-EXCHANGE PROCESSES

R. N. RUBINSTEIN, M. M. SENYAVIN, E. V. VENITSIANOV, E. M. MAKHALOV, V. A. ALEKSEENKO and V. A. NIKASHINA

V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, U.S.S.R. Academy of Sciences, Moscow (U.S.S.R.)

SUMMARY

The theory of the use of the basic parameters of mathematical process models is discussed. In the calculations, it is assumed that the equilibrium is described by the law of mass action and the kinetics have a diffusional nature. Solutions of ion-exchange dynamics for film, particle and mixed diffusion in the case of linear and non-linear isotherms are given. As examples, theoretical curves and experimental results are compared graphically.

INTRODUCTION

Up to the present, an empirical approach has been mainly used to study the problem of the optimal conditions for ion-exchange processes. However, this approach does not enable the true optimal conditions for ion-exchange processes to be found, as a consequence of the many independent parameters that define real systems. In the calculations, it is assumed that the equilibrium is described sufficiently accurately by the law of mass action and the kinetics have a diffusional nature, so that in the description of any ion-exchange system it is possible to use as initial data the ion-exchange capacity, selectivity coefficients, film diffusion and particle diffusion coefficients. In this paper are discussed the principles and results of the creation of such models for single-component systems suitable for optimization purposes. It should be noted that the calculation of the sorption stage for some multicomponent systems may be reduced to the single-component dynamic problem (deionization until the break-through point of a component with the lowest selectivity coefficient, dynamics of ion-exchange of a micro-component with a macro-component[1]).

THEORETICAL

Ion-exchange dynamics are described by a system of three equations for each component in a mixture: balance, kinetics and isotherm. For the purpose of solving

these equations simply, they are written in dimensionless variables below:
balance equation:

$$\frac{\partial U}{\partial X} + \frac{\partial V}{\partial T} = A \cdot \frac{\partial^2 U}{\partial X^2} \tag{1}$$

kinetic equation:

$$\frac{\partial V}{\partial T} = F(U, V, V^{(s)}, U_{eq}) \tag{2}$$

isotherm equation:

$$V^{(s)}_{surface} = f(U_{eq}) \tag{3}$$

where

$U \equiv c/c_0$ = non-dimensional concentration of the exchanged ion in the liquid;

$V \equiv a/a_0$ = non-dimensional concentration of the exchanged ion in the resin, mean amount within the volume of the resin particle;

$V^{(s)} \equiv a^{(s)}/a_0$ = non-dimensional local concentration of the ion in the resin;

$U_{eq} \equiv c_{eq}/c_0$ = non-dimensional concentration of the ion in the liquid, being in equilibrium with $V^{(s)}$ on the particle surface of the resin;

c_0, a_0 = characteristic concentrations of the exchanged ion in the liquid and in the resin, respectively;

$X \equiv l/l_0$ = non-dimensional size;

$T \equiv t/t_0$ = non-dimensional time;

l_0, t_0 = characteristic values of size and time, connected with the peculiarities of each concrete problem;

D_l = longitudinal diffusion coefficient;

w = flow-rate, calculated for the pure section of the column;

$A \equiv D_l/wl_0$ = non-dimensional longitudinal diffusion coefficient.

In the calculations, it is assumed that the equilibrium is described accurately by the law of mass action, which has the following form under the conditions of an absence of any additional chemical interaction:

$$\frac{V}{(1-V)^\mu} = \bar{K} \cdot \frac{U}{(1-U)^\mu} \tag{4}$$

where

$\mu \equiv Z/Z_0$ = ratio of ionic charges;

$\bar{K}$ = non-dimensional selectivity coefficient.

The ion-exchange kinetics are determined by the mass transport in the liquid and in the resin. The film diffusion equation has the form

$$\frac{\partial V}{\partial T} = U - U_{eq} \tag{5}$$

and the scale factors are

$$l_0 = \frac{w}{\beta}; \ t_0 = \frac{a_0}{c_0 \cdot \beta} \tag{5a}$$

The kinetic coefficient, β, for aqueous solutions and resins with spherical particles at 20° can be calculated according to the equation (ref. 2, p. 68)

$$\beta = 7.5 \cdot 10^{-4} \left(\frac{z}{\lambda} + \frac{z_0}{\lambda_0}\right)^{-2/3} w^{0.47} (2R)^{1.53} \tag{6}$$

where
  R = radius of the resin particles;
  λ, λ_0 = equivalent conductivities of ions.
  It was shown (ref. 2, p. 84) that relative contributions of longitudinal diffusion and film diffusion to erosion of the front was determined by the factor Δ:

$$\Delta = \frac{D_l}{\beta R^2}$$

When $\Delta \gg 1$, the contribution of longitudinal diffusion is the most important, but when $\Delta \ll 1$, film diffusion predominates. It is further assumed that $\Delta \ll 1$ for the most commonly used conditions in practical ion-exchange and $D_l = 0$ in eqn. 1.
  Diffusion in particles is determined by Fick's laws, which have the following form for spherical particles:

$$\frac{\partial}{\partial T} (\varrho V^{(s)}) = \frac{\partial^2}{\partial \varrho^2} (\varrho V^{(s)}) \tag{7}$$

where
  $\varrho = r/R$ = non-dimensional variable radius in particle. In this case, characteristic scales of size and time are:

$$l_0 = \frac{w \, c_0}{a_0 \, D_l}; \ t_0 = \frac{R^2}{D_l} \tag{7a}$$

where
  D_l = particle diffusion coefficient.
  The particle diffusion is described by an equation similar to eqn. 5 for the final stages of sorption at the time when the greatest volume of the particle is removed:

$$\frac{\partial V}{\partial T} = V^{(s)} - V \tag{8}$$

The characteristic scales of size and time are:

$$l_0 = \frac{c_0 \, w}{a_0 \, \beta_l}; \ t_0 = \frac{1}{\beta_l} \tag{8a}$$

where

$$\beta_i = \frac{\gamma \, D_i}{R^2}$$

γ = constant.

The true kinetic process is the mixed diffusion process, and correlation of the contributions of film and particle diffusion is determined by the factor H:

$$H = \frac{\beta R^2 \, c_0}{a_0 \, D_i} \tag{9}$$

When $H \ll 1$, the kinetics are defined by film diffusion and it is possible to assume that redistribution of the concentration occurs instantly in the particle, *i.e.*, $V^{(s)} = V$.

The solutions stated below were obtained within the limitations indicated.

Linear isotherm

$$V^{(s)} = U \tag{3'}$$

(1) In the case of film diffusion ($H = 0$), tables of certain solutions[3] were obtained for a wide range of values of X and T by means of a computer and the solutions of sorption and desorption problems for chromatographic variants were also found[4].

(2) In the case of particle diffusion ($H = \infty$) (eqns. 1, 3' and 7), the particular solution[5] was supplemented with an asymptotic equation (ref. 2, p. 38). For comparison of the theory with experimental results, we investigated the sorption of copper(II) ions by oxidized coal[6]. The theoretical curve and experimental points are plotted logarithmically in Fig. 1.

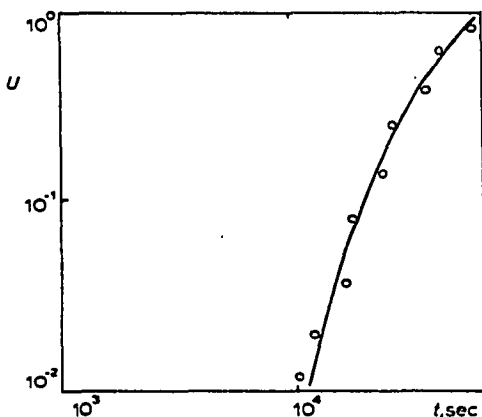The superposition of the non-dimensional theoretical curve on the experi-

Fig. 1. Comparison of the theoretical curve and experimental results for the sorption of copper ions from a solution containing $5 \cdot 10^{-4}$ mg-equiv./ml of Cu^{2+} and 1.25 mg-equiv./ml of $Na^{+}(NaNO_3)$ by oxidized coal ($w = 0.08$ cm/sec; $R = 0.02$ cm; $l = 11$ cm; $D_i = 9.6 \cdot 10^{-9}$ cm^2/sec; $a_0/c_0 = 300$; $X = 0.99$).
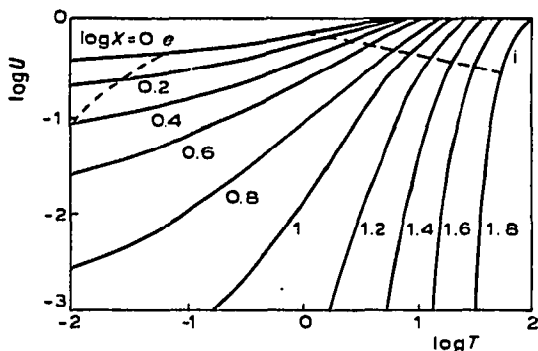
Fig. 2. Theoretical curves in the range of mixed diffusion and linear isotherm; $H = 10$.

mental results on a graph of log c/c_0 versus log t gives the possibility of finding the characteristic scales of size and time by the intercept on the abscissa equal to log t/T. It is then possible to calculate the parameters a_0/c_0, D_t or β, knowing the conditions of the experiment (w, R).

(3) In the case of mixed diffusion (eqns. 1, 3', 5 and 7), the exact solution for the dynamic sorption problem was found by means of a computer[7]. As it was found that the influence of film diffusion prevails in the initial stages of sorption, whereas particle diffusion prevails in the final stages, there must exist a stage of the process at which the rates of these two processes are equal and the duration of this stage depends on H and X. Graphs of $U(X, T)$ for $H = 10$ are given in non-dimensional logarithmic co-ordinates in Fig. 2. The ranges described by film or particle diffusion to within 10 % are shown by dotted lines. Fig. 3 gives a comparison of the theoretical curve and experimental results[8].

Non-linear isotherms

(1) *Film diffusion.* By means of a computer, the solution of the system of eqns. 1, 4, 5 and 5a for $U(X, T)$ was found[9] for selectivity constants, $\overline{K}$, changing over a wide
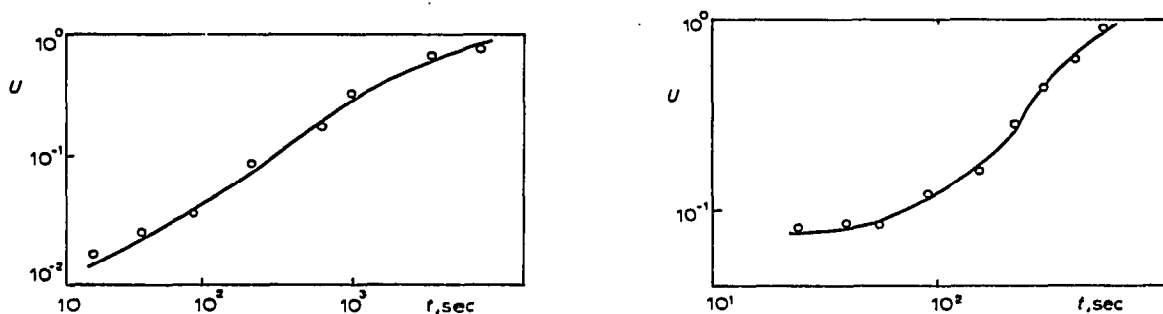

Fig. 3. Comparison of the theoretical curve and experimental results for the sorption of yttrium from a solution containing 0.1 mg-equiv./ml of Ca^{2+} and 10^{-5} mg-equiv./ml of Y^{3+} by oxidized coal in the Ca^{2+} form (pH = 3; $w = 0.35$ cm/sec; $R = 0.01$ cm; $l = 2.8$ cm; $D_t = 2.1 \cdot 10^{-9}$ cm^2/sec; $H = 68.5$; $a_0/c_0 = 500$; $X_\sigma = 5.76$).

Fig. 4. Comparison of the theoretical curve and experimental results for the sorption of calcium by cationite KU-2 (H$^+$) ($\overline{K} = 2$; $w = 5.3$ cm/sec; $R = 0.024$ cm; $l = 8$ cm; $\beta = 2.3$ sec^{-1}; $X = 3.5$).

range (from 0.1 to ∞). As an example, the theoretical curve and the experimental results are given in Fig .4.

(2) *Particle diffusion, described by eqns. 1, 4, 8 and 8a.* In this case, the solution can be expressed by the solution of the film diffusion problem by means of the following calculations. Let us designate the solution of the film diffusion problem (see section (1), above) with a selectivity coefficient $\overline{K}_e$ and a ratio of charges μ_e by $U(X, T, \overline{K}_e, \mu_e)$ and $V(X, T, \overline{K}_e, \mu_e)$. Then, the solution for the sorption problem in the case of particle diffusion $U^{(i)}$ and $V^{(i)}$ with a selectivity coefficient $\overline{K}_i$ and a ratio of charges μ_i is expressed by the equations

$$U^{(i)}(X_i, T_i, \overline{K}_i, \mu_i) = 1 - V\left(T_i, X_i, \overline{K}_i^{\mu_i}, \frac{1}{\mu_i}\right)$$

$$\tag{10}$$

$$V^{(i)}(X_i, T_i, \overline{K}_i, \mu_i) = 1 - U\left(T_i, X_i, \overline{K}_i^{\mu_i}, \frac{1}{\mu_i}\right)$$

By means of eqn. 10, it is possible to plot easily the solutions of the problems in section (1) in the case of particle diffusion. Fig. 5 shows a comparison of the theoretical curve and experimental results.
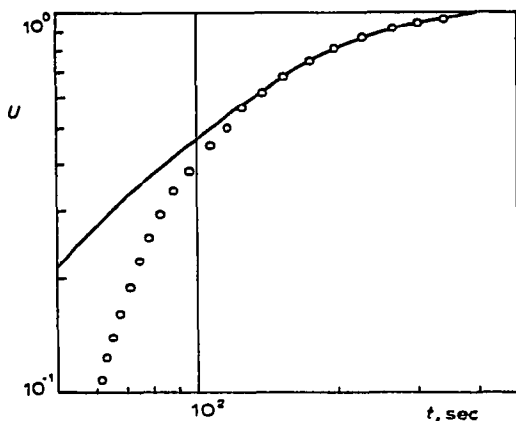

Fig. 5. Comparison of the theoretical curve and experimental results for hydrogen in the regeneration of KU-2 (Na$^+$) by 1 N acid ($w = 0.25$ cm/sec. $R = 0.03$ cm; $l = 15.8$–17.5 cm (H$^+$ form); $\overline{K} = 0.8$; $a_0 = 1.5$ mg-equiv./ml; $X = 5$).

(3) We found the approximate solution[10] for the case of S-shaped isotherms, to which the ion-exchange dynamics may be reduced, for example, when complex formation occurs or in the case of resin mixtures. The isotherm is divided into two parts by drawing a tangent at the point (c_0, a_0) (Fig. 6). The initial part is approximated by the isotherm in eqn. 4 with $\mu = 1$ and the selectivity coefficient

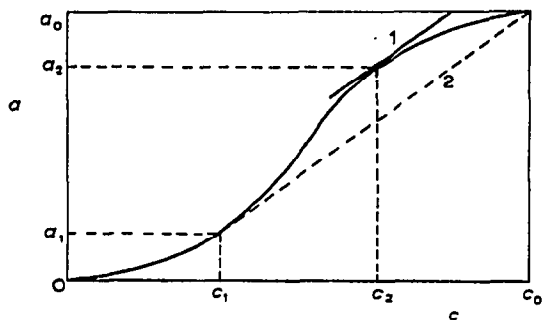$$\overline{K}_1 = \frac{c_1}{a_1}\left(\frac{da}{dc}\right)_{c=0} < 1$$

Fig. 6. Method of division of S-shaped isotherm into two parts (straight line 2 is parallel to tangent 1).

The second convex part of the isotherm is also approximated by the isotherm in eqn. 4 with $\mu = 1$ and the selectivity coefficient

$$\bar{K}_2 = \left(\frac{a_2 - a_1}{a_0 - a_2}\right)^2$$

The method of finding a_2 is shown in Fig. 6.

For the first part, the solution could be found from the equation

$$\frac{c}{c_1} = U(X, T, \bar{K}_1, 1)$$

and for the second part, it could be found from the equation

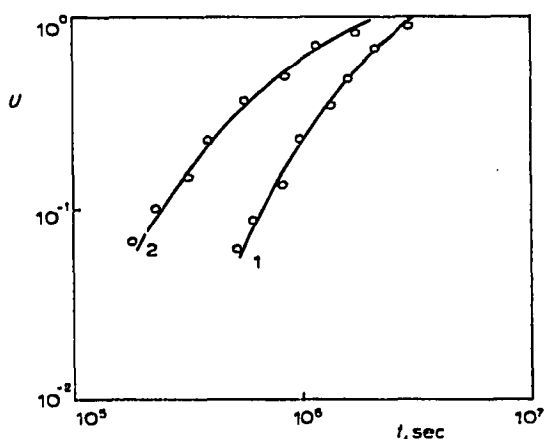$$\frac{c - c_2}{c_0 - c_2} = U(X, T, \bar{K}_2, 1) \tag{11}$$

Fig. 7. Comparison of the theoretical curves and experimental results for the sorption of calcium from natural carbonated water by cationite Kb-4p-2 (1: $w = 0.03$ cm/sec; $l = 14.6$ cm; $\bar{K}_2 = 2$; $X = 0.07$. 2: $w = 0.04$ cm/sec; $l = 29.2$ cm; $\bar{K}_2 = 2$; $X = 0.1$).

where $U(X, T, \overline{K}, 1)$ is the solution for the cases in section (1) or (2) depending on the kind of kinetics. Fig. 7 shows a comparison of the data obtained by eqn. 11 and the theoretical curves corresponding to them.

The solutions given above are used for the calculation of the sorption dynamics and the regeneration dynamics of different true single-component and multicomponent systems. These models are also the basis for the calculation of the optimal conditions for ion-exchange processes. It is appropriate to mention here that information on the systems studied (selectivity coefficients; coefficients of film diffusion and particle diffusion) could be obtained for use in calculations in ion-exchange processes by superimposing the theoretical curves and experimental results.

REFERENCES

1 N. K. Galkina and M. M. Senyavin, *Zh. Fiz. Khim.*, 43 (1969) 1783.
2 M. M. Senyavin, R. N. Rubinstein, E. V. Venitsianov, N. K. Galkina, I. V. Komarova and V. A. Nikashina, *Essentials of Calculation and Optimization of Ionexchange Processes*, Nauka, Moscow, 1972.
3 A. A. Zhukhovitsky, I. L. Zabezhinsky, and A. N. Tikhonov, *Zh. Fiz. Khim.*, 19 (1945) 253.
4 E. V. Venitsianov, B. A. Volkov, V. P. Ioffe, G. M. Kolosova and R. N. Rubinstein, *Zavod. Lab.*, 37 (1971) 513.
5 I. A. Myasnikov and K. A. Golbert, *Zh. Fiz. Khim.*, 26 (1953) 1311.
6 V. A. Alekseenko, V. A. Nikashina, M. M. Senyavin, I. A. Tarkovskaya, L. N. Grashchenkova and V. E. Goba, *Adsorption and Adsorbents*, Vol. 2, Naukova Dumka, Kiev, 1974.
7 E. V. Venitsianov, E. M. Makhalov and R. N. Rubinstein, *Zh. Fiz., Khim.*, 47 (1973) 665.
8 V. A. Alekseenko, V. A. Nikashina and E. V. Venitsianov, *Zh. Fiz. Khim.*, 47 (1973) 1033.
9 V. A. Nikashina, B. A. Volkov, R. N. Rubinstein and M. M. Senyavin, *Zh. Fiz. Khim.*, 46 (1972) 686.
10 R. N. Rubinstein, A. M. Sorochan, V. A. Alekseenko and A. K. Kunbazarov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 7 (1973) 1461.