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Modeling of Ion-Exchange Column Operation.
II. Mass Transport Kinetics

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Abstract

A previously described method for modeling the operation of ion-exchange columns by numerical integration on a microcomputer is modified to include the effect on elution curves of the finite rate of mass transport of solute ions between the resin and the aqueous phase. This is done by means of a time constant approach. The time constant is estimated as the smallest nonzero eigenvalue of a suitably-chosen diffusion problem. Results are presented showing the effect of the size of the time constant and the salt concentration in the eluting liquid on the shapes of the elution curves.

INTRODUCTION

The use of ion exchangers in chemical technology and analytical chemistry has increased enormously since the first synthetic ion-exchange material was made by Harm and Rümpler in 1903 (*1*). This was greatly aided by the discovery that organic ion-exchange resins of quite high capacity could be made (*2*); these also could be precisely tailored for specific applications. Although ion exchangers have long been used in columns, it has been noted that the modeling of the operation of an ion-exchange column presents a formidable problem (*3*). Glueckauf has presented one of the more detailed and rigorous treatments of ion-exchange columns; he used a theoretical plate analysis (*4–6*). Helfferich (*3*) and Samuelson (*7*) have presented detailed discussions of the theoretical plate approach to modeling ion-exchange columns.

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In a recent paper we developed an extension of the theoretical plate approach which, by the use of so-called upwind asymmetrical algorithms for representing the advection term, greatly reduces the computer memory and time requirements of these calculations (*8*). This model assumed local equilibrium between the resin and the moving aqueous phase, and the cubic equations arising from the equilibrium condition for univalent–divalent ion exchange were solved exactly by Tartaglia's (Cardano's) method.

Here we remove the assumption of local equilibrium with respect to ion transport between the aqueous phase and the resin. We shall treat the mass transfer kinetics by a time constant method used earlier in the modeling of gas chromatography (*9*), activated carbon columns (*10*), and continuous-flow solvent sublation columns (*11*). This permits one to select Δt in the numerical integration of the differential equations only on the basis of the advection criterion $\Delta t \ll \Delta x/v$, where Δx is the thickness of one of the compartments into which the column is mathematically partitioned, and v is the linear velocity of the liquid. Use of differential equations to model the mass transfer of solutes between the aqueous phase and the ion-exchange resin requires that $\Delta t \ll$ the least of $\Delta x/v$ and τ, where τ is a time constant associated with the mass transfer. Since τ may be much less than $\Delta x/v$, one may find that the size of Δt required is so small that computation time becomes excessive.

We estimate the time constant τ as the reciprocal of the least positive eigenvalue of a suitably chosen diffusion problem.

In the following we first examine the diffusion of ions into and out of a resin bead in order to obtain an estimate for τ. Then we model the behavior of an ion-exchange column in which a divalent cation and a univalent cation are exchanging. Lastly, we examine numerical results showing how the displacement of a divalent cation by a high concentration of a univalent cation is affected by the time constant of the mass transport and by the salt concentration in the eluting liquid.

ANALYSIS

Estimation of the Mass Transport Time Constant

First we derive the diffusion equation appropriate for the diffusion of ions into (and out of) a spherical bead of ion-exchange resin. Then we solve this equation and obtain its least positive eigenvalue, the reciprocal of which we take as an estimate of the mass transfer time constant. Lastly, we include the effect of the quiescent aqueous boundary layer around the bead, and derive the equation for calculating the eigenvalues of this somewhat more realistic system.

We assume (with some trepidation) that the electrochemical potentials of the two ions in the resin are given by the ideal expressions

$$\mu_{Na} \equiv \mu_1 = \mu_1^0 + KT \log_e c_1 + e\psi \tag{1}$$

$$\mu_{Ca} \equiv \mu_2 = \mu_2^0 + KT \log_e c_2 + e\psi \tag{2}$$

where c_1 = Na^+ ions per cm^3 of resin
c_2 = Ca^{2+} ions per cm^3 of resin
e = $|$electronic charge$|$, esu
ψ = electric potential, statvolts

The diffusion equations for the ions in the resin are then

$$\frac{\partial c_i}{\partial t} = \frac{1}{6\pi\eta r_i} \nabla \cdot (c_i \nabla \mu), \qquad i = 1, 2 \tag{3}$$

where $(1/6\pi\eta r_i)$ is to be regarded more as just a diffusion scale factor than as a function of an admittedly ill-defined resin viscosity.

Poisson's equation is

$$\nabla^2\psi = \frac{-4\pi\rho}{D} = \frac{-4\pi}{D} e(c_1 + 2c_2 - S_0) \tag{4}$$

where ρ = charge density
D = effective dielectric constant
S_0 = number of (singly-charged) negative sites per cm^3 in the resin

Note that imposing the electrical neutrality requirement,

$$c_1 + 2c_2 = S_0 \tag{5}$$

gives the result that

$$\nabla^2\psi = 0 \tag{6}$$

a result which will be needed later.

Substituting the expressions for the electrochemical potentials (Eqs. 1 and 2) into Eqs. (3) then yields

$$\frac{\partial c_1}{\partial t} = \frac{1}{6\pi\eta r_1} \nabla \cdot \left(c_1 \cdot \frac{kT}{c_1} \nabla c_1 + ec_1 \nabla\psi\right) \tag{7}$$

$$\frac{\partial c_2}{\partial t} = \frac{1}{6\pi\eta r_2} \nabla \cdot \left(c_2 \cdot \frac{kT}{c_2} \nabla c_2 + 2ec_2 \nabla\psi\right) \tag{8}$$

We define

$$\frac{kT}{6\pi\eta r_i} = D_i, \qquad i = 1, 2 \tag{9}$$

and rewrite Eqs. (7) and (8) as

$$\frac{\partial c_1}{\partial t} = D_1 \nabla^2 c_1 + \frac{eD_1}{kT} (\nabla c_1 \cdot \nabla\psi + c_1 \nabla^2 \psi) \tag{10}$$

$$\frac{\partial c_2}{\partial t} = D_2 \nabla^2 c_2 + \frac{2eD_2}{kT} (\nabla c_2 \cdot \nabla\psi + c_2 \nabla^2 \psi) \tag{11}$$

From the electrical neutrality requirement, Eq. (5), we obtain

$$\frac{\partial c_1}{\partial t} = -2 \frac{\partial c_2}{\partial t} \tag{12}$$

$$\nabla c_1 = -2 \nabla c_2 \tag{13}$$

and also note that, from Eq. (6), $\nabla^2\psi$ in Eqs. (10) and (11) can be dropped. So

$$\frac{\partial c_1}{\partial t} = D_1 \nabla^2 c_1 + \frac{eD_1}{kT} \nabla c_1 \cdot \nabla\psi \tag{14}$$

$$\frac{\partial c_2}{\partial t} = D_2 \nabla^2 c_2 + \frac{2eD_2}{kT} \nabla c_2 \cdot \nabla\psi \tag{15}$$

Substituting Eqs. (12) and (13) into Eq. (14) yields, on multiplying by −1/2,

$$\frac{\partial c_2}{\partial t} = D_1 \nabla^2 c_2 + \frac{eD_1}{kT} \nabla c_2 \cdot \nabla\psi \tag{16}$$

Equating Eqs. (15) and (16) then gives

$$\frac{(D_2 - D_1)}{D_1 - 2D_2} \nabla^2 c_2 = \frac{e}{kT} \nabla c_2 \cdot \nabla \psi \tag{17}$$

Substituting this result into Eq. (16) and rearranging slightly then yields

$$\frac{\partial c_2}{\partial t} = \frac{D_1 D_2}{2D_2 - D_1} \nabla^2 c_2 \tag{18}$$

Thus we see that the coupled diffusion of Na^+ and Ca^{2+} in the resin bead is equivalent to the diffusion of a single uncharged species.

We next calculate the mass transfer time constant for the case where the aqueous boundary layer can be neglected. For convenience we drop the subscripts used above, as they are no longer needed, and define

$$D_r = D_1 D_2/(2D_2 - D_1) \tag{19}$$

The diffusion equation for the spherical resin bead is

$$\frac{\partial c}{\partial t} = \frac{1}{r^2} D_r \frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right) \tag{20}$$

and our boundary conditions are

$$c(0,t) \text{ is finite} \tag{21}$$

$$c(a,t) = Kc_\infty \tag{22}$$

where a = bead radius
Kc_∞ = concentration of Ca^{2+} in the resin which is in equilibrium with a concentration c_∞ in the bulk solution

The differential equation is solved in the usual way by separating the variables. We set

$$c(r,t) = R(r) \cdot T(t) \tag{23}$$

which on substitution into Eq. (20) yields

$$T(t) = \exp(-\lambda t) \tag{24}$$

and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\lambda}{D_r}R=0 \tag{25}$$

The change of dependent variable

$$R = u/r \tag{26}$$

converts Eq. (25) into

$$\frac{d^2u}{dr^2}+\frac{\lambda}{D_r}u=0 \tag{27}$$

Solution of this equation then gives

$$u = A_0 + B_0 r, \qquad \lambda = 0 \tag{28}$$

$$u = A_\lambda \cos\sqrt{\frac{\lambda}{D_r}}\,r + B_\lambda \sin\sqrt{\frac{\lambda}{D_r}}\,r \tag{29}$$

To avoid having $c(r,t)$ singular at $r = 0$, we must set A_0 and $A_\lambda = 0$, so that we obtain

$$c(r,t) = Kc_\infty + \sum_\lambda \frac{B_\lambda}{r}\sin\sqrt{\frac{\lambda}{D_r}}\,r\cdot\exp(-\lambda t) \tag{30}$$

as our general solution. The boundary condition at $r = a$, Eq. (22), requires that

$$\sin\sqrt{\frac{\lambda}{D_r}}\,a = 0 \tag{31}$$

from which we infer that

$$\lambda \equiv \lambda_n = D_r\left(\frac{n\pi}{a}\right)^2, \qquad n = 1, 2, \ldots \tag{32}$$

The least positive eigenvalue is

$$\lambda_1 = D_r\left(\frac{\pi}{a}\right)^2 \tag{33}$$

from which we have the desired time constant,

$$\tau = \frac{1}{\lambda} = \frac{a^2}{\pi^2 D_r} \tag{34}$$

We next turn to the case where the resin bead is surrounded by a quiescent aqueous boundary layer through which diffusion must take place. The diffusion equation is now

$$\frac{\partial c}{\partial t} = \frac{D_r}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right), \qquad r \leqslant a \text{ (Region I)} \tag{20}$$

$$\frac{\partial c}{\partial t} = \frac{D_l}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right), \qquad a < r \leqslant b \text{ (Region II)} \tag{35}$$

The boundary conditions are as follows.

$$c(0,t) \neq \infty \tag{36}$$

$$\lim_{\delta \to 0^+} c(a - \delta, t) = \lim_{\delta \to 0^+} Kc(a + \delta, t) \tag{37}$$

$$\lim_{\delta \to 0^+} D_r \frac{\partial c}{\partial r}(a - \delta, t) = \lim_{\delta \to 0^+} D_l \frac{\partial c}{\partial r}(a - \delta, t) \tag{38}$$

$$c(b,t) = c_\infty \tag{39}$$

In Region I (the resin), the solution to the differential equation is

$$c(r,t) = \sum_\lambda \frac{B_\lambda}{r} \sin \sqrt{\frac{\lambda}{D_r}}\, r \exp(-\lambda t) + Kc_\infty \tag{40}$$

where we have already used Eq. (36). In Region II (the aqueous boundary layer), the solution is

$$c(r,t) = \sum_\lambda \left[\frac{C_\lambda}{r} \cos \sqrt{\frac{\lambda}{D_l}}\, r + \frac{D_\lambda}{r} \sin \sqrt{\frac{\lambda}{D_l}}\, r\right] \exp(-\lambda t) + c_\infty \tag{41}$$

From Eq. (39) we obtain

$$C_\lambda \cos \sqrt{\frac{\lambda}{D_l}}\, b + D_\lambda \sin \sqrt{\frac{\lambda}{D_l}}\, b = 0 \tag{42}$$

From Eq. (37) we obtain

$$B_\lambda K^{-1} \sin \sqrt{\frac{\lambda}{D_l}}\,a - C_\lambda \cos \sqrt{\frac{\lambda}{D_l}}\,a - D_\lambda \sin \sqrt{\frac{\lambda}{D_l}}\,a = 0 \tag{43}$$

And from Eq. (38) we obtain, after some manipulation,

$$\begin{aligned} &B_\lambda \frac{D_r}{D_l}\left[\sin \sqrt{\frac{\lambda}{D_r}}\,a - a\sqrt{\frac{\lambda}{D_r}} \cos \sqrt{\frac{\lambda}{D_r}}\,a\right] \\ &\quad + C_\lambda\left[-\cos \sqrt{\frac{\lambda}{D_l}}\,a - a\sqrt{\frac{\lambda}{D_l}} \sin \sqrt{\frac{\lambda}{D_l}}\,a\right] \\ &\quad + D_\lambda\left[-\sin \sqrt{\frac{\lambda}{D_l}}\,a + a\sqrt{\frac{\lambda}{D_l}} \cos \sqrt{\frac{\lambda}{D_l}}\,a\right] = 0 \end{aligned} \tag{44}$$

Equations (42), (43), and (44) constitute three linear, homogeneous equations for the constants B_λ, C_λ, and D_λ. Since we want nonzero values for these, the determinant of the coefficients of the equations must vanish. This gives Eq. (45) (on page 999) as the eigenvalue equation for this system. It is readily seen that $\lambda = 0$ is a root of Eq. (45), and intuitively it is evident that Eq. (34) gives an upper bound to the least positive eigenvalue for this system, so that we have

$$\tau > \frac{a^2}{\pi^2 D_r} \tag{46}$$

for this case. Apparently Eq. (45) must be solved numerically.

Modeling of Column Operation

We use here the model and notation employed in our earlier paper (*8*), modified as indicated below. Any one of several algorithms can be used to represent advective transport; four of these are

$$-v\frac{\partial c_n}{\partial t} = \frac{v}{V_w}(c_{n-1} - c_n) \tag{47}$$

$$= \frac{v}{V_w}\left(-\frac{1}{2}c_{n-2} + 2c_{n-1} - \frac{3}{2}c_n\right) \tag{48}$$

$$\begin{vmatrix} \dfrac{D_r}{D_l}\left[\sin\sqrt{\dfrac{\lambda}{D_r}}a - a\sqrt{\dfrac{\lambda}{D_r}}\cos\sqrt{\dfrac{\lambda}{D_r}}a\right] & -\cos\sqrt{\dfrac{\lambda}{D_l}}a - a\sqrt{\dfrac{\lambda}{D_l}}\sin\sqrt{\dfrac{\lambda}{D_l}}a & -\sin\sqrt{\dfrac{\lambda}{D_l}}a + a\sqrt{\dfrac{\lambda}{D_l}}\cos\sqrt{\dfrac{\lambda}{D_l}}a \\ K^{-1}\sin\sqrt{\dfrac{\lambda}{D_r}}a & -\cos\sqrt{\dfrac{\lambda}{D_l}}a & -\sin\sqrt{\dfrac{\lambda}{D_l}}a \\ 0 & \cos\sqrt{\dfrac{\lambda}{D_i}}b & \sin\sqrt{\dfrac{\lambda}{D_l}}b \end{vmatrix} \qquad (45)$$

$$= \frac{v}{V_w}\left(-\frac{1}{8}c_{n-2} + \frac{7}{8}c_{n-1} - \frac{3}{8}c_n - \frac{3}{8}c_{n+1}\right) \tag{49}$$

$$= \frac{v}{V_w}\left(-\frac{1}{6}c_{n-2} + c_{n-1} - \frac{1}{2}c_n - \frac{1}{3}c_{n+1}\right) \tag{50}$$

It was shown earlier (*8*) that Eqs. (49) and (50) are particularly effective in reducing numerical dispersion but have a tendency toward instability, while Eq. (47) gives a great deal of numerical dispersion but is also quite stable. It therefore proved advantageous to represent advection by a linear combination of Eq. (47) and either Eq. (49) or Eq. (50), as shown in

$$-v\frac{\partial c_n}{\partial t} = a \cdot (\text{Eq. } 47) + (1 - a) \cdot (\text{Eq. } 49 \text{ or } 50) \tag{51}$$

In the runs presented below, $a = 0.1$. We shall develop all the equations using Eq. (47) for advection for reasons of simplicity; then at the end we shall replace it by Eq. (51).

In our earlier paper it was shown that the requirements of electrical neutrality, mass balance, and local equilibrium give the following relationships in the *i*th compartment of the column:

$$c_{\text{Na},i} + 2c_{\text{Ca},i} = S_0 \tag{52}$$

$$m_{\text{Na},i} = V_w[\text{Na}^+]_i + V_s c_{\text{Na},i} \tag{53}$$

$$m_{\text{Ca},i} = V_w[\text{Ca}^{2+}]_i + V_s c_{\text{Ca},i} \tag{54}$$

$$K_i = \frac{[\text{Na}^+]_i^2 c_{\text{Ca},i}}{[\text{Ca}^{2+}]_i c_{\text{Na},i}^2} \tag{55}$$

where $c_{\text{Na},i}$ = Na^+ concentration in the resin, mol/L
$c_{\text{Ca},i}$ = Ca^{2+} concentration in the resin
S_0 = molar concentration of singly-charged anionic sites in the resin
$[\text{Na}^+]_i$ = Na^+ concentration in the aqueous phase
$[\text{Ca}^{2+}]_i$ = Ca^{2+} concentration in the aqueous phase
$m_{\text{Na},i}$ = total moles of Na^+ in the *i*th compartment
$m_{\text{Ca},i}$ = total moles of Ca^{2+} in the *i*th compartment
V_w = volume of liquid phase in the *i*th compartment
V_s = volume of resin phase in the *i*th compartment
K_i = effective equilibrium constant (here assumed constant throughout the column)

Successive elimination then yields a cubic equation for $c_{\mathrm{Ca},i}$ *at local equilibrium,*

$$a_3c^3_{\mathrm{Ca},i} + a_2c^2_{\mathrm{Ca},i} + a_1c_{\mathrm{Ca},i} + a_0 = 0 \tag{56}$$

where

$$a_0 = V_wK_im_{\mathrm{Ca},i}S_0^2 \tag{57}$$

$$a_1 = -V_wK_iS_0(4m_{\mathrm{Ca},i} + V_sS_0) - (m_{\mathrm{Na},i} - V_sS_0)^2 \tag{58}$$

$$a_2 = 4[V_wK_i(m_{\mathrm{Ca},i} + V_sS_0) - V_s(m_{\mathrm{Na},i} - V_sS_0)] \tag{59}$$

$$a_3 = -4(V_wK_i + V_s)V_s \tag{60}$$

The movements of Na^+ and Ca^{2+} in the column are described by the equations

$$\frac{dm}{dt}\mathrm{Na},i = v([\mathrm{Na}^+]_{i-1} - [\mathrm{Na}^+]_i) \tag{61}$$

$$\frac{dm}{dt}\mathrm{Ca},i = v([\mathrm{Ca}^{2+}]_{i-1} - [\mathrm{Ca}^{2+}]_i) \tag{62}$$

We let $[\mathrm{Na}^+]_0$ and $[\mathrm{Ca}^{2+}]_0$ be the influent concentrations of these ions.

At this point we depart from our previous local equilibrium treatment to take into account the finite rate of mass transfer. Instead of integrating only Eqs. (61) and (62) forward in time and constantly imposing the equilibrium condition given by Eq. (55), we adjoin the following two sets of differential equations to Eqs. (61) and (62):

$$\frac{\delta[\mathrm{Na}^+]_i}{\delta t} = \frac{v}{V_w}([\mathrm{Na}^+]_{i-1} - [\mathrm{Na}^+]_i) \tag{63}$$

$$\frac{\delta[\mathrm{Ca}^{2+}]_i}{\delta t} = \frac{v}{V_w}([\mathrm{Ca}^{2+}]_{i-1} - [\mathrm{Ca}^{2+}]_i) \tag{64}$$

These equations describe how $[\mathrm{Na}^+]_i$ and $[\mathrm{Ca}^{2+}]_i$ would change if there were no mass transport between the solution and the resin.

Our procedure then is this. Given the conditions in the column at time t, we calculate new conditions at time $t + \Delta t$ as follows. (We illustrate with the simple Gauss formula for clarity—in actual fact a more complex predictor-corrector method was used.)

$$m_{\mathrm{Na},i}(t + \Delta t) = m_{\mathrm{Na},i}(t) + \frac{dm}{dt}\,\mathrm{Na},i(t) \cdot \Delta t \tag{65}$$

$$m_{\mathrm{Ca},i}(t + \Delta t) = m_{\mathrm{Ca},i}(t) + \frac{dm}{dt}\,\mathrm{Ca},i(t) \cdot \Delta t \tag{66}$$

$$[\mathrm{Na}^+]_i^0(t + \Delta t) = [\mathrm{Na}^+]_i(t) + \frac{\delta[\mathrm{Na}^+]_i}{\delta t}(t) \cdot \Delta t \tag{67}$$

$$[\mathrm{Ca}^{2+}]_i^0(t + \Delta t) = [\mathrm{Ca}^+]_i(t) + \frac{\delta[\mathrm{Ca}^{2+}]_i}{\delta t}(t) \cdot \Delta t \tag{68}$$

Equations (67) and (68) give the new aqueous concentrations $[\mathrm{Na}^+]_i^0(t + \Delta t)$ and $[\mathrm{Ca}^{2+}]_i^0(t + \Delta t)$ in the absence of mass transport between resin and solution. We then use $m_{\mathrm{Na},i}(t + \Delta t)$ and $m_{\mathrm{Ca},i}(t + \Delta t)$ along with Eqs. (52)–(54) and (56) to calculate what the aqueous concentrations would be if equilibrium were allowed to occur; call these concentrations $[\mathrm{Na}^+]_i^e(t + \Delta t)$ and $[\mathrm{Ca}^{2+}]_i^e(t + \Delta t)$.

We then assume that the decay from $[\mathrm{Na}^+]^0$ and $[\mathrm{Ca}^{2+}]^0$ toward $[\mathrm{Na}^+]^e$ and $[\mathrm{Ca}^{2+}]^e$ is exponential, with a time constant τ. This gives the following expressions for the actual aqueous concentrations at time $t + \Delta t$:

$$[\mathrm{Na}^+]_i^0(t + \Delta t) = [\mathrm{Na}^+]_i^0 + ([\mathrm{Na}^+]_i^e - [\mathrm{Na}^+]_i^0) \cdot [1 - \exp(-\Delta t/\tau)] \tag{69}$$

$$[\mathrm{Ca}^{2+}]_i^0(t + \Delta t) = [\mathrm{Ca}^{2+}]_i^0 + ([\mathrm{Ca}^{2+}]_i^e - [\mathrm{Ca}^{2+}]_i^0) \cdot [1 - \exp(-\Delta t/\tau)] \tag{70}$$

These concentrations are then used to calculate the concentrations of Na^+ and Ca^{2+} in the resin from

$$c_{\mathrm{Na},i} = (m_{\mathrm{Na},i} - V_w[\mathrm{Na}^+]_i)/V_s \tag{71}$$

$$c_{\mathrm{Ca},i} = (m_{\mathrm{Ca},i} - V_w[\mathrm{Ca}^{2+}]_i)/V_s \tag{72}$$

Use of an exponential decay toward equilibrium in Eqs. (69) and (70) permits one to use a value of Δt which is limited only by the advection criterion, $\Delta t \ll V_w/v$, independent of the speed of the mass transfer process.

In the computations reported below we used a predictor-corrector method (*12*) instead of the simple Gauss formula used in Eqs. (65)–(68). The procedure is as follows.

Starter

$$y^*(\Delta t) = y(0) + \Delta t \cdot \frac{dy}{dt}(0) \tag{73}$$

Predictor

$$y^*(t + \Delta t) = y(t - \Delta t) + 2\Delta t \cdot \frac{dy}{dt}(t) \tag{74}$$

Corrector

$$y(t + \Delta t) = y(t) + \frac{\Delta t}{2}\left[\frac{dy}{dt}(t) + \frac{dy}{dt}^*(t + \Delta t)\right] \tag{75}$$

Also, the computer program was written such that any of the algorithms (Eqs. 47–51) could be selected to represent advection in Eqs. (61)–(64). The computer program was written in GW BASIC, and compiled and run on a Zenith 150 microcomputer with 320K of RAM and an 8088 microprocesser. The runs reported in the next section took about 30 min each—the difference in running time between this program and the program using the local equilibrium approximation was negligible.

RESULTS AND CONCLUSIONS

We next examine some results illustrating the effects of varying the mass transfer rate constant and the NaCl concentration in the eluting solution. In all cases we are considering the elution of a column nearly saturated with Ca^{2+} with relatively concentrated (3–7 *M*) NaCl solutions. The volume of the column was 40 L in all runs; 20 L of which was solid ion exchanger and 20 L of which was mobile aqueous phase. The ion-exchange resin contained 3.0 mol/L of univalent anionic sites. The column was assumed initially equilibrated with a very large volume of solution having $[Ca^{2+}] = 0.20\ M$, $[Na^+] = 0.05\ M$. The value of the distribution coefficient K was set equal to 4. In all cases the column was partitioned into 20 compartments, and the flow rate used was 1.0 L/min. Δt was set equal to 0.1 min, and a in Eq. (51) was set equal to 0.1. Using Eq. (49) in Eq. (51) produced results indistinguishable from those obtained using Eq. (50) in Eq. (51).

Plots of effluent Ca^{2+} and Na^+ concentrations versus time are shown in Figs. 1–4. In these runs the values of the mass transfer time constant τ are

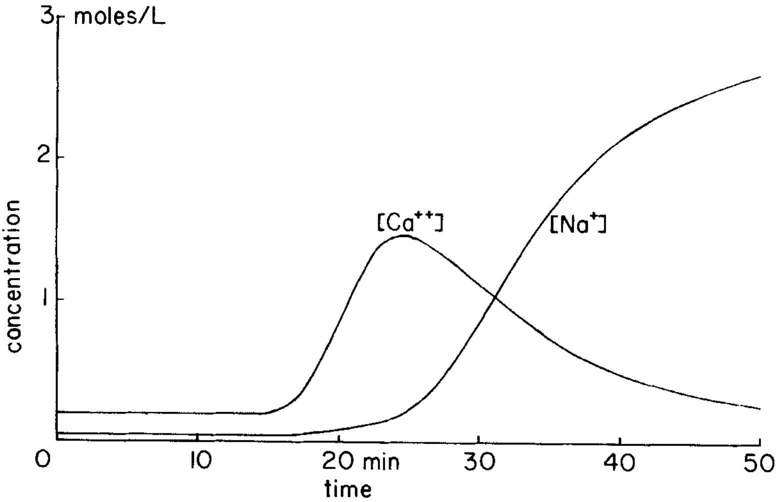

FIG. 1. Plots of effluent $[Ca^{2+}]$ and $[Na^{+}]$. $\tau = 0.1$ min, $[Na^{+}]$ in eluting solution = 3.0 *M*; other parameters as stated in the text.

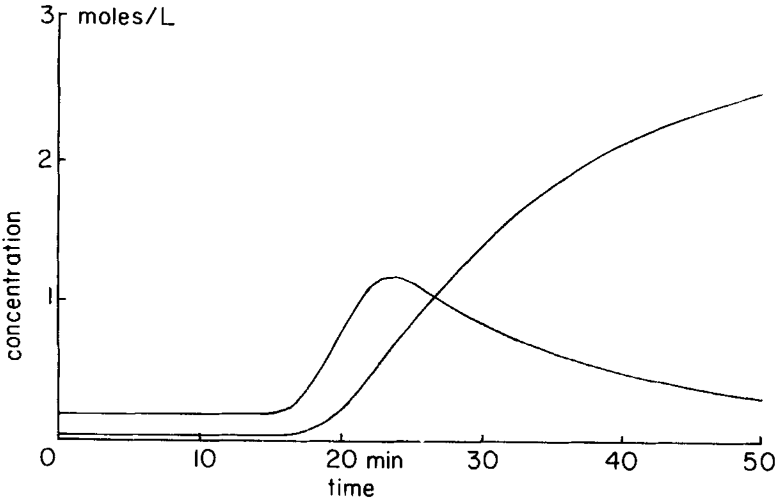

FIG. 2. Plots of effluent $[Ca^{2+}]$ and $[Na^{+}]$. $\tau = 2.0$ min, $[Na^{+}]$ in eluting solution = 3.0 *M*; other parameters given in the text.

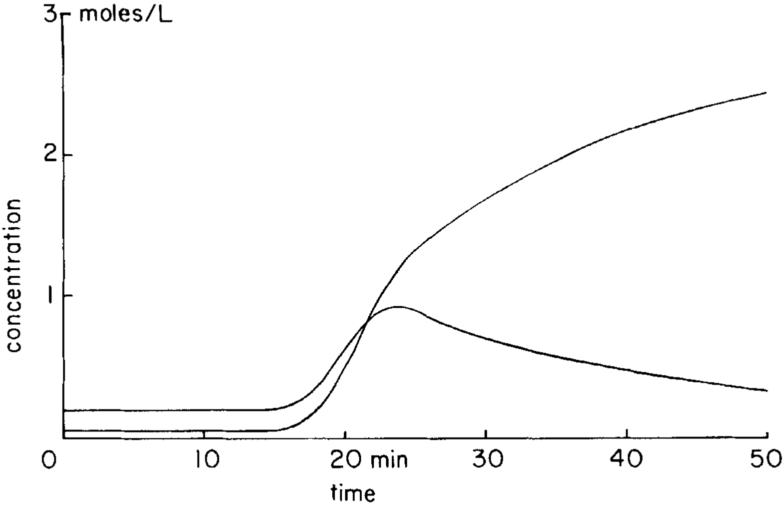

FIG. 3. Plots of effluent [Ca^{2+}] and [Na^+]. τ = 5.0 min, [Na^+] in eluting solution = 3.0 *M*; other parameters given in the text.

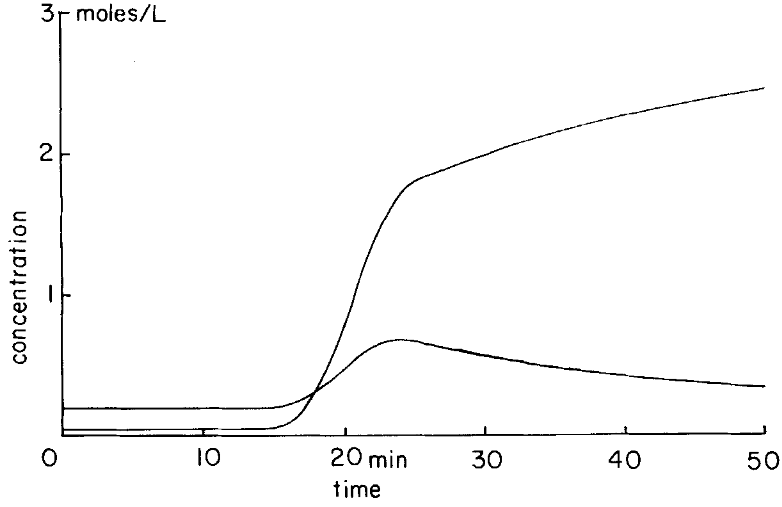

FIG. 4. Plots of effluent [Ca^{2+}] and [Na^+]. τ = 10.0 min, [Na^+] in eluting solution = 3.0 *M*; other parameters given in the text.

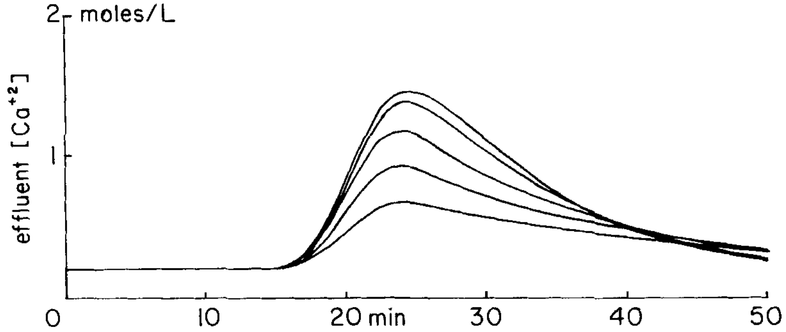

FIG. 5. Comparison of effluent [Ca^{2+}] curves for τ = 0.1, 1, 2.0, 5.0, and 10 min; [Na^+] in eluting solution = 3.0 *M*; other parameters given in the text.

0.1, 2, 5, and 10 min, respectively. Increasing the time constant (by, perhaps, increasing the resin bead size) is seen to have little effect upon the position of the Ca^{2+} elution peak maximum, but to increase the extent of tailing of this peak greatly. The increased breadth of the elution is also shown by the increased width of the Na^+ front. The effects on the Ca^{2+} elution curve of increasing τ are more readily compared in Fig. 5, in which Ca^{2+} elution curves for τ = 0.1, 1, 2, 5, and 10 min are plotted.

The effects of increasing the NaCl concentration in the eluting solution are shown in Figs. 6 (local equilibrium and τ = 0.002 min, indistinguishable) and 7 (τ = 5 min). In both cases it is seen that narrower elution peaks result when the concentration of the displacing ion in the eluting solution is increased.

In conclusion, we note the following points. First, the effects of the finite rate of mass transport between the resin and the moving solution are readily modeled by the time constant method described here. Second, the use of asymmetrical upwind algorithms giving low numerical dispersion is effective in this model; these reduce the number of compartments into which the column must be partitioned and correspondingly increase the maximum size of Δt which can be used in the numerical integration. Third, the model is readily adapted for use with microcomputers running compiled BASIC.

A diskette for MS-DOS computers with the BASICA source program and the compiled program is available for \$3.00 to cover the costs of mailing and the diskette.

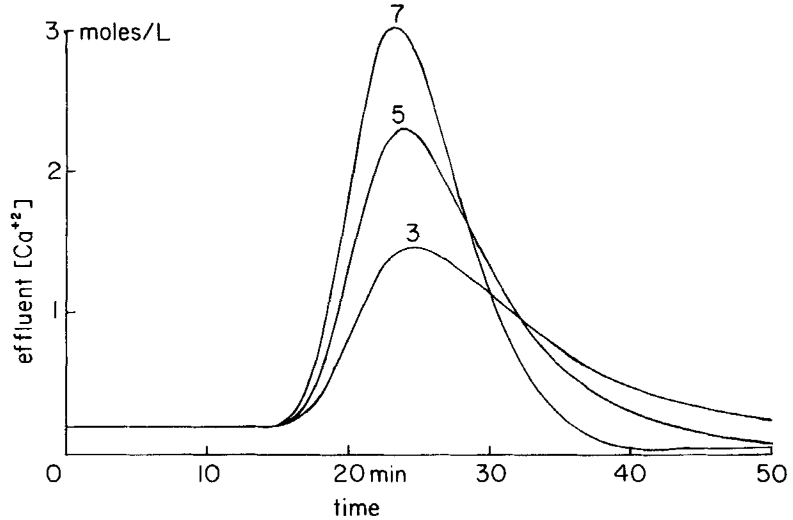

FIG. 6. Effluent curves for [Ca^{2+}]. $\tau = 0.002$ min; [Na^+] in eluting solution = 3.0, 5.0, and 7.0 *M* as indicated. Other parameters as stated in the text. These curves are superposed on curves made with the assumption of local equilibrium with a different computer program.

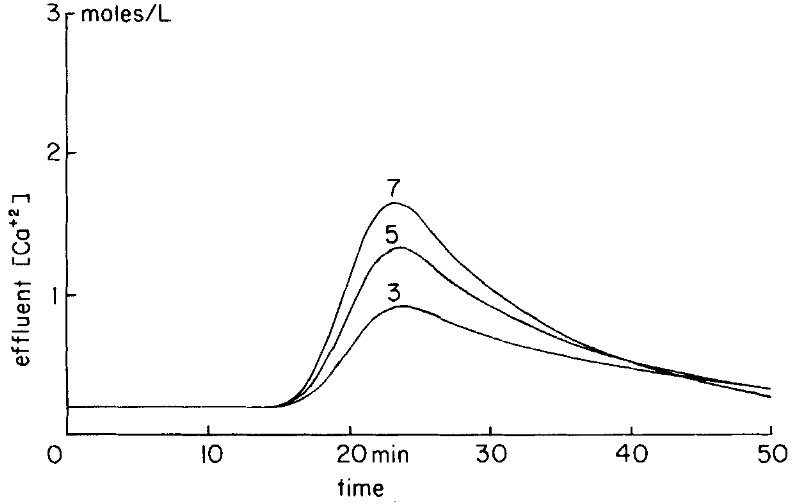

FIG. 7. Effluent curves for [Ca^{2+}]. $\tau = 5.0$ min; [Na^+] in eluting solution = 3.0, 5.0, and 7.0 *M* as indicated. Other parameters given in the text.

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