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Modeling of Ion-Exchange Column Operation. I. Equilibrium Model for Univalent-Divalent Exchange

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Abstract

A mathematical model is presented for the operation of an ion-exchange column exchanging divalent cations for univalent cations. Local equilibrium is assumed to be maintained between the ion-exchange resin and the aqueous phase. The cubic equations arising from the assumption of local equilibrium are solved by Tartaglia's method. The two partial differential equations describing the advective motion of the ions are approximated by two sets of coupled ordinary differential equations. The advective terms in these are represented by an asymmetrical "upwind" algorithm which greatly reduces spurious numerical dispersion.

INTRODUCTION

One of the most useful, powerful, and selective separation techniques provided to the analytical chemist and the chemical engineer is that of ion exchange. Helfferich argues that the roots of the technique go back to Moses, or at least to Aristotle (*1*). Harm and Rumpler prepared the first synthetic industrial ion exchanger in 1903 (*2*). The development of high-capacity organic ion-exchange resins was ushered in by Adams and Holmes's discovery in 1935 that crushed phonograph records can act as ion exchangers (*3*). From that time until the present the field of ion exchange has been active and rapidly growing. Dilts's book provides a very informative introduction to the subject (*4*); we list for reference only a few of the very large number of books on the subject (*5–9*). Helfferich's

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book (*1*), although dated, provides very clear, detailed discussions of most aspects of the theory, and very extensive bibliographies.

We shall be concerned here with the problem of modeling the behavior of ion-exchange columns. Some years ago Helfferich noted the formidable nature of the problem, commenting that it seemed a general theory of column operation was hardly feasible (*10*). Improvements in the speed and memory size of computers since that time make possible the use of mathematical methods not then practical, but the problem remains a very difficult one and we here explore only a few of its facets. Our method of attack is based on that of Glueckauf (*11–13*). This uses the concept of theoretical plates, taken from the theory of distillation and used first in chromatography by Martin and Synge (*14*). Glueckauf calculates his plate heights from fundamental parameters, however, while the size of the compartments we shall partition the column into has, by the nature of the algorithms we use to represent advection, no simple interpretation. This approach, as will be seen subsequently, allows us to use fewer compartments than are required by the theoretical plate model, which very markedly decreases computer time requirements. A quite detailed discussion of Glueckauf's model is given by Helfferich (*10*); another lucid discussion of the application of theoretical plate approach is given by Samuelson (*15*).

We shall address two aspects of the problem of ion-exchange column operation. These are: 1) solving the equilibrium problem arising when one has univalent and divalent ions exchanging, which leads to a cubic equation; and 2) reducing the amount of time required to integrate the differential equations by using a modified algorithm to model advection.

ANALYSIS

In the following sections we first compare the exact and the numerical results for the advection of a solute through a column in the absence of ion exchange. We then work out the equations for the operation of an ion-exchange column in which a univalent ion is being exchanged with another univalent ion. This is followed by the analysis of a column in which a univalent ion and a divalent ion are undergoing exchange. We then turn to the problem of reducing the quite excessive numerical dispersion which results from the usual theoretical plate analysis to obtain the advection term. This leads us to the examination of a number of so-called asymmetrical upwind algorithms recommended by Leonard (*16, 17*) for representing the advective terms in our equations. These algorithms have been shown to provide major reductions in numerical dispersion without loss of mathematical stability in the modeling of the movement of non-ionic solutes in groundwater (*18–20*) and in the modeling of column separations involving non-ionic solutes (*21, 22*). They turn out to be somewhat more touchy with regard to mathematical stability when used on the coupled pair of sets of differential equations needed to model ion-exchange column operation.

Numerical comparisons are made between the various algorithms for representing advection, and a modification to improve stability is proposed and tested. Numerical results on the distributions of Na^+ and Ca^{2+} are obtained and presented graphically.

Numerical computations were all done on a Zenith 150 personal computer; programs were written in GW BASIC and compiled with the IBM compiler. A typical run with a column partitioned into 20 compartments required 31 min of computer time.

Numerical Dispersion in the Theoretical Plate Model. Representation of Advection

In this section we examine and solve exactly the theoretical plate model for the displacement of a solute from a column without ion exchange. These results are compared with the exact solution of the problem.

Let us consider the displacement of solute from the column shown in Fig. 1. We let v be the volumetric flow rate of liquid through the column, and V_w be the volume of one of the compartments into which the column is partitioned. We assume no dispersion aside from that associated with the assumption that each compartment is well-mixed. We assume that the solute is initially present at a concentration c_0 throughout the column, and that its concentration in the displacing liquid is c_∞. Then the equations governing the concentrations in the various compartments are

$$\frac{dc_n}{dt} = \frac{v}{V_w}(c_{n-1} - c_n), \qquad n \neq 1 \tag{1}$$

$$\frac{dc_1}{dt} = \frac{v}{V_w}(c_\infty - c_1) \tag{2}$$

By induction it is easy to show that these equations have the solutions

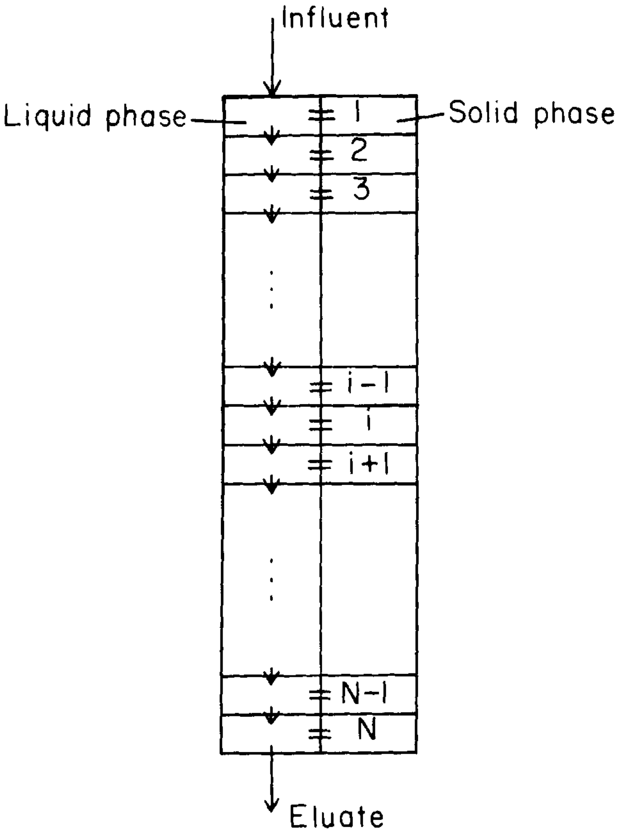

FIG. 1. The model and notation.

$$c_n(t) = (c_0 - c_\infty) \exp\left(\frac{-v}{V_w} t\right) \cdot \sum_{m=0}^{n-1} \left(\frac{vt}{V_w}\right)^m \frac{1}{m!} + c_\infty \tag{3}$$

and that $c_n(t)$ has a point of inflection when

$$t = (n - 1)V_w/v \tag{4}$$

This we use to denote the time at which the middle of the front marking the boundary between the original solution and the displacing solution moves through the nth compartment. We obtain a measure of the thickness of the front by determining the times at which d^2c_n/dt^2 goes through an extremum. The time interval during which the front is passing through the nth compartment, as measured by this procedure, is given by

$$\Delta t_n = \sqrt{n-1}\, V_w/v \tag{5}$$

This result, an ever-increasing thickness of the front as it moves down the column, is in contradiction to the result one obtains by integrating the partial differential equation which corresponds to Eq. (1),

$$\frac{\partial c}{\partial t}(x,t) = -\frac{v}{A}\frac{\partial c}{\partial x} \tag{6}$$

where A = cross-sectional area of column. The general solution to this equation is

$$c(x,t) = f\left(x - \frac{v}{A}t\right) \tag{7}$$

and for our system we have

$$c(x,t) = c_0, \qquad x \geqslant vt/A \tag{8}$$

$$= c_\infty, \qquad x \geqslant vt/A \tag{9}$$

Since we have not included any dispersive term in Eq. (6), the front remains infinitely sharp indefinitely as it moves down the column. The broadening of the front which we find in the model described by Eqs. (1) and (2) is intrinsic in the nature of this mathematical representation and constitutes numerical dispersion.

For a column partitioned into N compartments we have

$$V_w = LA/N \tag{10}$$

where L = column length
A = column cross section

This gives a front width of

$$\Delta t = \frac{\sqrt{N-1}}{N}\,\frac{LA}{v} \tag{11}$$

As has long been known, decreasing the front width by a factor of $1/a$ requires increasing N by a factor of a^2. Therefore, if we wish to model columns yielding narrow fronts, we must use very large values of N. These, in turn, require very small values of Δt if one is numerically integrating the differential equations modeling the column. Computer costs become excessive for these systems, and algorithms which reduce the numerical dispersion resulting from the theoretical plate model would be highly desirable.

We shall therefore explore three somewhat more elaborate formulas for representing advection; these are

$$-\mathrm{v}\frac{\partial c}{\partial t} \approx \frac{\mathrm{v}}{\Delta x}\left(-\frac{1}{2}c_{n-2} + 2c_{n-1} - \frac{3}{2}c_n\right) \tag{12}$$

$$\approx \frac{\mathrm{v}}{\Delta x}\left(-\frac{1}{8}c_{n-2} + \frac{7}{8}c_{n-1} - \frac{3}{8}c_n - \frac{3}{8}c_{n+1}\right) \tag{13}$$

$$\cong \frac{\mathrm{v}}{\Delta x}\left(-\frac{1}{6}c_{n-2} + c_{n-1} - \frac{1}{2}c_n - \frac{1}{3}c_{n+1}\right) \tag{14}$$

where v = linear velocity of liquid. The first of these representations is Leonard's QUICK algorithm (*16*); the other two are discussed in an earlier paper of ours (*19*). All three of these were found to reduce numerical dispersion quite markedly below that resulting from use of the simple algorithm

$$-\mathrm{v}\frac{\partial c}{\partial t} \cong \frac{\mathrm{v}}{\Delta x}(c_{n-1} - c_n) \tag{15}$$

on which the theoretical plate model is based. These were being used for the modeling of the movement of a single, nonionic solute, however, so it is not immediately evident that they will prove satisfactory in dealing with the more complex coupled systems of equations resulting from the modeling of ion exchange. In the next sections we develop the equations governing equilibrium, electrical neutrality, and mass balance; then we use these with the above algorithms for modeling advection to model the operation of an ion-exchange column.

Univalent-Univalent Ion Exchange

Our ion exchange process is taken as

$$\mathrm{Na}S + \mathrm{Li}^+(\mathrm{aq}) \rightleftharpoons \mathrm{Li}S + \mathrm{Na}^+(\mathrm{aq}) \tag{16}$$

where S^- represents an anionic binding site in the ion exchanger, and NaS and LiS represent univalent cations bound at these sites. The equilibrium relationship for Eq. (16) we take as

$$K = \frac{c_{\mathrm{Li}}[\mathrm{Na}^+]}{c_{\mathrm{Na}}[\mathrm{Li}^+]} \tag{17}$$

where c_{Li} = moles of bound Li^+ per liter of exchanger
c_{Na} = moles of bound Na^+ per liter of exchanger
$[\mathrm{Na}^+]$ = molar concentration of Na^+ in the liquid phase
$[\mathrm{Li}^+]$ = molar concentration of Li^+ in the liquid phase

Note that K is not the thermodynamic equilibrium constant; it includes activity coefficients and can be expected to vary with varying concentrations as illustrated, for example, in Dilts's book (*4*). This, incidentally, presents no problem in the following analyses; one simply uses a concentration-dependent K.

The electrical neutrality requirement gives us

$$c_{\mathrm{Na}} + c_{\mathrm{Li}} = S_0 \tag{18}$$

where S_0 = moles of univalent anionic sites per liter of exchanger.

The mass balance relationships can be written as

$$m_{\mathrm{Na}} = V_w[\mathrm{Na}^+] + V_s c_{\mathrm{Na}} \tag{19}$$

and

$$m_{\mathrm{Li}} = V_w[\mathrm{Li}^+] + V_s c_{\mathrm{Li}} \tag{20}$$

where M_{Na} = moles of Na^+ in the compartment of the column being considered
m_{Li} = moles of Li^+ in the compartment
V_w = volume of aqueous phase in the compartment
V_s = volume of ion exchanger in the compartment

We then use Eqs. (18)–(20) to eliminate $[\mathrm{Li}^+]$, $[\mathrm{Na}^+]$, and c_{Na} from Eq. (17). Rearranging the resulting equation then yields a quadratic equation for c_{Li},

$$V_s(K-1)c_{\mathrm{Li}}^2+[(1-K)V_sS_0-m_{\mathrm{Na}}-m_{\mathrm{Li}}K]c_{\mathrm{Li}}+Km_{\mathrm{Li}}S_0=0 \tag{21}$$

or

$$Ac_{\mathrm{Li}}^2+Bc_{\mathrm{Li}}+C=0$$

Solution of this then gives

$$c_{\mathrm{Li}}=(-B-\sqrt{B^2-4AC})/2A \tag{22}$$

(It turns out that one must use the minus sign to avoid negative concentrations.)

From this, given the mole numbers of Na^+ and Li^+ in the compartment, we can calculate all the concentrations in the aqueous and solid phases when these have equilibrated. The aqueous concentrations are then involved in advection as the ions move down the column.

If the column is initially allowed to come to equilibrium with a large excess of solution having molar concentrations $[\mathrm{Na}^+]_0$ and $[\mathrm{Li}^+]_0$, then the initial values of the concentrations in the ion exchanger are given by

$$c_{\mathrm{Li}}^0=\frac{K[\mathrm{Li}^+]_0S_0}{[\mathrm{Na}^+]_0+K[\mathrm{Li}^+]_0} \tag{23}$$

$$c_{\mathrm{Na}}^0=\frac{[\mathrm{Na}^+]S_0}{[\mathrm{Na}^+]+K[\mathrm{Li}^+]} \tag{24}$$

Univalent-Divalent Ion Exchange

We take as our ion-exchange process

$$2\mathrm{Na}S+\mathrm{Ca}^{2+}(\mathrm{aq})\rightleftharpoons \mathrm{Ca}S_2+2\mathrm{Na}^+(\mathrm{aq}) \tag{25}$$

The equilibrium expression is then

$$K=\frac{[\mathrm{Na}^+]^2c_{\mathrm{Ca}}}{[\mathrm{Ca}^{2+}]c_{\mathrm{Na}}^2} \tag{26}$$

where the notation is similar to that used in the previous section.

The electrical neutrality requirement for solid phase yields

$$2c_{\mathrm{Ca}} + c_{\mathrm{Na}} = S_0 \tag{27}$$

The mass balance relationships are

$$m_{\mathrm{Na}} = V_w[\mathrm{Na}^+] + V_s c_{\mathrm{Na}} \tag{28}$$

and

$$m_{\mathrm{Ca}} = V_w[\mathrm{Ca}^{2+}] + V_s c_{\mathrm{Ca}} \tag{29}$$

Use of Eqs. (27)–(29) to eliminate all the variables from Eq. (25) except c_{Ca} and rearranging then yields a cubic equation,

$$a_3 c_{\mathrm{Ca}}^3 + a_2 c_{\mathrm{Ca}}^2 + a_1 c_{\mathrm{Ca}} + a_0 = 0 \tag{30}$$

where

$$a_3 = -4(V_w K + V_s)V_s \tag{31}$$

$$a_2 = 4[V_w K(m_{\mathrm{Ca}} + V_s S_0) - V_s(m_{\mathrm{Na}} - V_s S_0)] \tag{32}$$

$$a_1 = -V_w K S_0(4m_{\mathrm{Ca}} + V_s S_0) - (m_{\mathrm{Na}} - V_s S_0)^2 \tag{33}$$

$$a_0 = V_w K m_{\mathrm{Ca}} S_0^2 \tag{34}$$

We originally hoped that this equation could be solved by a suitably chosen simple numerical method—Newton's method or a modification thereof, or various other iterative methods. This turned out not to be the case; the methods we tested worked over portions of the ranges of parameters of interest, but over other portions either failed to converge or converged too slowly to be of use. It was therefore necessary to solve the cubic by the exact method developed independently by S. del Ferro and by N. Tartaglia in the 16th century and first published by Cardano (*23*); a more accessible reference is Uspensky (*24*).

Tartaglia's method turned out to be quite tractable. Although it requires the use of complex arithmetic (including square and cube roots of complex numbers), subroutines for this are readily programmed. We found this approach to be fast and accurate over almost the entire range of parameters tested. It was necessary to test all three roots for suitability; if there is a pair which are complex conjugates, one uses the single real root. If all roots are real, one takes the one which makes all concentrations positive.

Advection and Ion Exchange

Here we combine the effects of the advective motion of the aqueous phase through the ion-exchange column with the effects of ion exchange, assumed to be at local equilibrium. (That is, the solid and aqueous phases in any given compartment are taken as being at equilibrium with respect to ion transport between them.) We examined in detail the theoretical plate model, then grafted on our other algorithms for representing advection. Physical dispersion is left out of our analysis, since we wish to study numerical dispersion and reduce it to the lowest feasible level. It should be noted in passing that Koussis has suggested the use of linear combinations of advection algorithms having greater or lesser numerical dispersion as a means of representing physical dispersion (*25*). Our model is diagrammed in Fig. 1.

Let $m_{\mathrm{Na},i}$ = moles of sodium in the ith compartment
$m_{\mathrm{Ca},i}$ = moles of calcium in the ith compartment
$[\mathrm{Na}^+]_i$ = concentration of sodium ion in the aqueous phase of the ith compartment, mol/L
$[\mathrm{Ca}^{2+}]_i$ = concentration of calcium ion in the aqueous phase of the ith compartment, mol/L
$c_{\mathrm{Na},i}$ = concentration of bound sodium in the solid phase of the ith compartment, mol/L
$c_{\mathrm{Ca},i}$ = concentration of bound calcium in the solid phase of the ith compartment, mol/L
V_w = volume of aqueous phase in one compartment, L
V_s = volume of ion exchanger in one compartment, L
v = volumetric flow rate, L/unit time
N = number of compartments into which the column is partitioned

Then the theoretical plate model gives

$$\frac{dm_{\mathrm{Na},i}}{dt} = v([\mathrm{Na}^+]_{i-1} - [\mathrm{Na}^+]_i) \tag{35}$$

$$\frac{dm_{\mathrm{Ca},i}}{dt} = v([\mathrm{Ca}^{2+}]_{i-1} - [\mathrm{Ca}^{2+}]_i), \qquad i = 1, 2, \ldots, N \tag{36}$$

We assume here that $[\mathrm{Na}^+]_0$ and $[\mathrm{Ca}^{2+}]_0$ are the influent concentrations of these ions.

The requirement that the solid phase be electrically neutral gives

$$c_{\mathrm{Na},i} + 2c_{\mathrm{Ca},i} = S_0 \tag{37}$$

where, as before, S_0 is the concentration of anionic sites (assumed singly charged) in the ion exchanger, in mol/L. The mass balance equations now take the form

$$m_{\mathrm{Na},i} = V_w[\mathrm{Na}^+]_i + V_s c_{\mathrm{Na},i} \tag{38}$$

$$m_{\mathrm{Ca},i} = V_w[\mathrm{Ca}^{2+}]_i + V_s c_{\mathrm{Ca},i} \tag{39}$$

The requirement of local equilibrium gives an equation essentially identical to Eq. (26),

$$K_i = \frac{[\mathrm{Na}^+]_i^2 c_{\mathrm{Ca},i}}{[\mathrm{Ca}^{2+}]_i c_{\mathrm{Na},i}^2} \tag{40}$$

K_i is subscripted since it varies with the sodium and calcium ion concentrations through their effects on activity coefficients. We shall neglect this in the following, but it could fairly readily be included.

The same procedure used to derive Eq. (30) above is then used to obtain a cubic equation in $c_{\mathrm{Ca},i}$,

$$a_3 c_{\mathrm{Ca},i}^3 + a_2 c_{\mathrm{Ca},i}^2 + a_1 c_{\mathrm{Ca},i} + a_0 = 0, \qquad i = 1, 2, \ldots, N \tag{41}$$

where

$$a_3 = -4(V_w K_i + V_s)V_s \tag{42}$$

$$a_2 = 4[V_w K_i(m_{\mathrm{Ca},i} + V_s S_0) - V_s(m_{\mathrm{Na},i} - V_s S_0)] \tag{43}$$

$$a_1 = -V_w K_i S_0(4m_{\mathrm{Ca},i} + V_s S_0) - (m_{\mathrm{Na},i} - V_s S_0)^2 \tag{44}$$

$$a_0 = V_w K_i m_{\mathrm{Ca},i} S_0^2 \tag{45}$$

An ion-exchange run on the column is then modeled as follows. The initial state of the column is assumed given (concentrations of both ions in the liquid and solid phases of all compartments), as is the composition of the solution being used to elute the column. Equations (35) and (36) are then integrated forward one increment in time, Δt. The new values of the $m_{\mathrm{Na},i}$ and $m_{\mathrm{Ca},i}$ are substituted into Eqs. (42)–(45), and the new values of the $c_{\mathrm{Ca},i}$ are calculated by solving the cubics, Eq. (41). Equations (37)–(39) are solved for the other concentrations; these are given by

$$c_{\mathrm{Na},i} = S_0 - 2c_{\mathrm{Ca},i} \tag{46}$$

$$[\mathrm{Ca}^{2+}]_i = (m_{\mathrm{Ca},i} - V_s c_{\mathrm{Ca},i})/V_w \tag{47}$$

$$[\mathrm{Na}^+]_i = (m_{\mathrm{Na},i} - V_s S_0 + 2V_s c_{\mathrm{Ca},i})/V_w \tag{48}$$

If one is using a concentration-dependent equilibrium constant in Eq. (40), one would next calculate a corrected value of K_i and repeat the process of determining the concentrations, iterating as necessary to obtain convergence. (We did not do this.) One is then ready to integrate Eqs. (35) and (36) one more step Δt forward in time and repeat the calculation of the concentrations. And so on, until the run is complete.

The numerical integration was done by means of a standard predictor-corrector method (*26*); this operates as follows.
Starter formula:

$$y(t_1) = y(t_0) + \frac{dy}{dt}[y(t_0),t_0]\Delta t \tag{49}$$

Predictor:

$$y^*(t_{n+1}) = y(t_{n-1}) + \frac{dy}{dt}[y(t_n),t_n]2\Delta t \tag{50}$$

Corrector:

$$y(t_{n+1}) = y(t_n) + \left\{\frac{dy}{dt}(t_n) + \frac{dy}{dt}[y^*(t_{n+1}),t_{n+1}]\right\}\frac{\Delta t}{2} \tag{51}$$

Here

$$t_n = n\Delta t \quad \text{and} \quad \frac{dy}{dt}(t_n) = \frac{dy}{dt}[y(t_n),t_n]$$

As will be seen in the section on results, use of Eqs. (35) and (36) to describe advection leads to a good deal of spreading of the elution front from numerical dispersion. In the numerical integration scheme we therefore replaced Eqs. (35) and (36) with one of the following three pairs of equations obtained from Eqs. (12)–(14).

$$\frac{dm_{\mathrm{Na},i}}{dt} = v\left(-\frac{1}{2}[\mathrm{Na}^+]_{i-2} + 2[\mathrm{Na}^+]_{i-1} - \frac{3}{2}[\mathrm{Na}^+]_i\right) \tag{52}$$

$$\frac{dm_{\mathrm{Ca},i}}{dt} = v\left(-\frac{1}{2}[\mathrm{Ca}^{2+}]_{i-2} + 2[\mathrm{Ca}^{2+}]_{i-1} - \frac{3}{2}[\mathrm{Ca}^{2+}]_i\right) \tag{53}$$

or

$$\frac{dm_{\mathrm{Na},i}}{dt} = v\left(-\frac{1}{8}[\mathrm{Na}^+]_{i-2} + \frac{7}{8}[\mathrm{Na}^+]_{i-1} - \frac{3}{8}[\mathrm{Na}^+]_i - \frac{3}{8}[\mathrm{Na}^+]_{i+1}\right) \quad (54)$$

$$\frac{dm_{\mathrm{Ca},i}}{dt} = v\left(-\frac{1}{8}[\mathrm{Ca}^{2+}]_{i-2} + \frac{7}{8}[\mathrm{Ca}^{2+}]_{i-1} - \frac{3}{8}[\mathrm{Ca}^{2+}]_i - \frac{3}{8}[\mathrm{Ca}^{2+}]_{i+1}\right) \quad (55)$$

or

$$\frac{dm_{\mathrm{Na},i}}{dt} = v\left(-\frac{1}{6}[\mathrm{Na}^+]_{i-2} + [\mathrm{Na}^+]_{i-1} - \frac{1}{2}[\mathrm{Na}^+]_i - \frac{1}{3}[\mathrm{Na}^+]_{i+1}\right) \quad (56)$$

$$\frac{dm_{\mathrm{Ca},i}}{dt} = v\left(-\frac{1}{6}[\mathrm{Ca}^{2+}]_{i-2} + [\mathrm{Ca}^{2+}]_{i-1} - \frac{1}{2}[\mathrm{Ca}^{2+}]_i - \frac{1}{3}[\mathrm{Ca}^{2+}]_{i+1}\right) \quad (57)$$

These advection algorithms resulted in quite marked decreases in numerical dispersion, as will be seen in the next section. It was found, however, that in the context of the ion-exchange problem they exhibit instabilities for some values of the system parameters; these show up as oscillations in the concentration profiles in the column and "wiggles" in the concentrations in the elution front as it comes off the column. Examples of this behavior will be shown in the next section. In a few of the runs the instabilities were sufficiently severe to result in program crashes—error conditions caused by negative or complex concentrations. Some way of increasing the mathematical stability of the algorithm used to model advection was obviously needed.

In another connection Koussis had suggested to us the use of linear combinations of advection algorithms of greater and lesser numerical dispersivity as a cheap and effective way to model physical dispersion (*25*). This led us to try linear combinations of the simple, extremely stable, very dispersive theoretical plate algorithm (Eq. 1) with one of the less dispersive but also less stable algorithms (Eq. 12, 13, or 14). We therefore tested two types of combined algorithms,

$$-v\frac{\partial c}{\partial x} \approx a \cdot [1] + (1 - a) \cdot [13] \quad (58)$$

and

$$-v\frac{\partial c}{\partial x} \approx a \cdot [1] + (1 - a) \cdot [14] \qquad (59)$$

where $0 < a < 1$. Relatively small components of the theoretical plate algorithm (Eq. 1) were found to eliminate the instability problems, and yielded elution fronts which were substantially narrower than those resulting from the use of the theoretical plate algorithm alone.

COMPUTATIONS AND RESULTS

A program to carry out the numerical work was written in GW BASIC, the equivalent of BASICA, and run on a Zenith 150 microcomputer. A run in which the column was represented by 20 compartments and in which two column volumes of eluting liquid were passed into the column required about 3 h of computer time when the program was run in interpreted GW BASIC. These long running times for the program encouraged us to acquire a BASICA compiler; this reduced the amount of computer time for a run like that described above to about 30 min.

We next examined some representative results. We considered the elution of an ion-exchange column nearly saturated with Ca^{2+} by elution with relatively concentrated NaCl solutions. It was assumed in all cases that the volume of the column was 20 L; 10 L of which was solid ion exchanger and 10 L of which was mobile aqueous phase. The ion-exchange resin was assumed to contain 3.0 mol/L of univalent anionic sites. The column was assumed to be brought to equilibrium initially with a very large volume of solution having $[Ca^{2+}] = 0.20\ M$, $[Na^+] = 0.05\ M$, and $[Cl^-] = 0.45\ M$. The other parameters in the model are indicated in the figure legends.

In Figs. 2, 3, and 4 are shown eluate concentrations of Cl^-, Na^+, and Ca^{2+} as functions of time elapsed since the initiation of elution. In these runs the advection term is represented by 0.3 × Eq. (1) + 0.7 × Eq. (13) which, as we shall see shortly, very markedly reduces numerical dispersion but still avoids instability. Note that in these three figures the abscissa has its origin at 5 min. We find that the widths of the Cl^- and Na^+ fronts are narrowed as *N*, the number of compartments into which the column is partitioned, increases from 10 to 40, the width of the peak in the Ca^{2+} concentration decreases, and its height increases. Intuitively, this is what one would expect, and it is in qualitative agreement with Tamamushi's findings (*22*) for gas chromatography columns. The width of the Cl^- front gives a measure of the extent of the numerical dispersion. In the absence of numerical dispersion, the Cl^- curves would show an

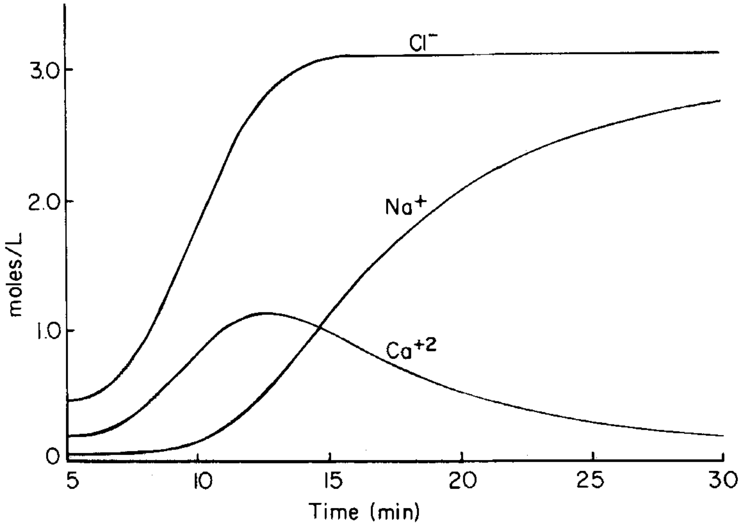

FIG. 2. Plots of effluent [Ca^{2+}], [Na^{+}], and [Cl^{-}] versus time. V_w = 1.0 L, V_s = 1.0 L, S_0 = 3.0 *M*, $K_{Ca/Na}$ = 4.0, N = 10, v = 1.0 L/min, initial [Na^{+}] = 0.05 *M*, initial [Ca^{2+}] = 0.20 *M*, influent [Na^{+}] = 3.0 *M*, influent [Ca^{2+}] = 0.05 *M*, Δt = 0.025 min, a = 0.3 in Eq. (58).

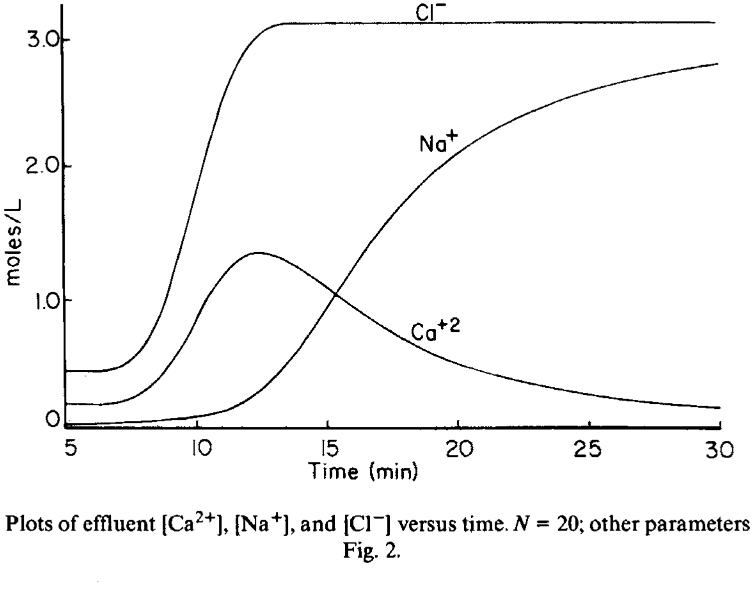

FIG. 3. Plots of effluent [Ca^{2+}], [Na^{+}], and [Cl^{-}] versus time. N = 20; other parameters as in Fig. 2.

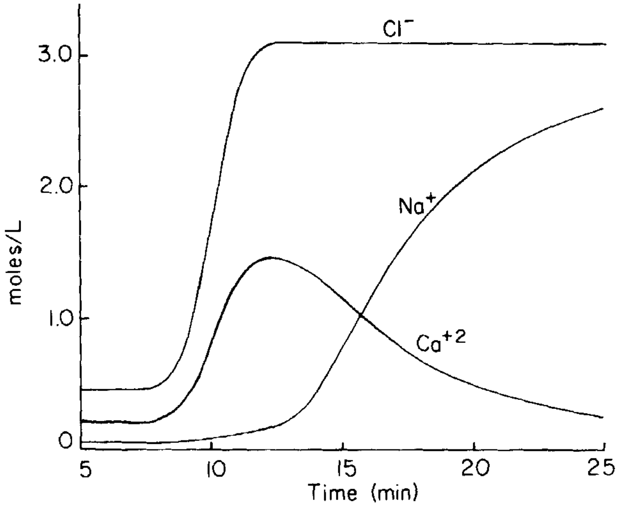

FIG. 4. Plots of effluent $[Ca^{2+}]$, $[Na^+]$, and $[Cl^-]$ versus time. $N = 40$; other parameters as in Fig. 2.

infinitely sharp step in concentration, since no physical dispersion is included in our model. The much greater width of the Na^+ front is a measure of the "chemical dispersion" of the system; we shall be concerned with this later.

Figures 5 and 6 plot the Cl^- effluent concentrations for models having 10, 20, and 40 compartments. In Figure 5 the theoretical plate model was used; in Fig. 6, 0.3 × Eq. (1) + 0.7 × Eq. (13). Front widths are substantially less in Fig. 6 than in Fig. 5, demonstrating the very substantial reductions in numerical dispersion which result from the use of an upwind, asymmetrical algorithm for representing advection. This makes possible very substantial savings in computer time, since the number of compartments required to obtain a given front width is reduced to about half that required by the theoretical plate model, and the size of Δt, the time increment in the numerical integration, can be doubled. The total savings in computer time required amount, therefore, to about 75%.

Figure 7 shows the dependence of the Ca^{2+} elution peak on the number of compartments, N. As N is increased, the Ca^{2+} peak becomes somewhat narrower and sharper, but chemical dispersion evidently gives it an intrinsic and rather substantial width. Kinetic effects, not included in our model, would result in still further broadening.

The effect of changing the proportions of the two advection algorithms

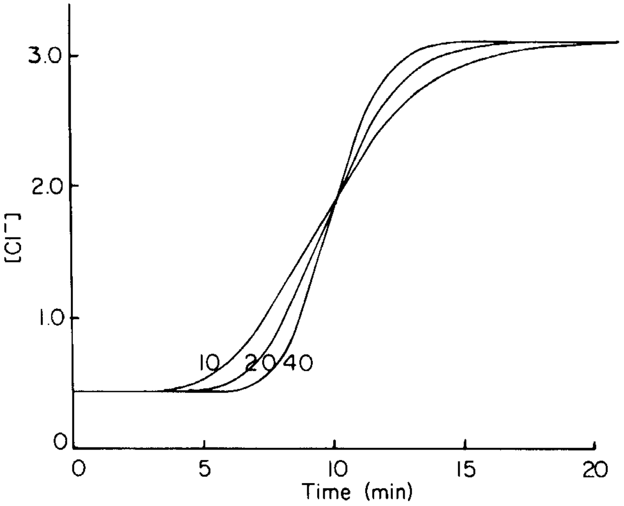

FIG. 5. Plots of effluent [Cl$^-$] versus time. Advection is represented by Eq. (1), the theoretical plate model. N = 10, 20, 40, as labeled. Other parameters as in Fig. 2.

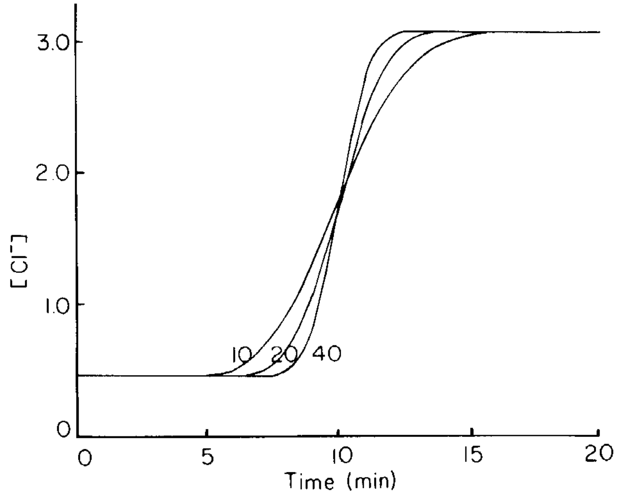

FIG. 6. Plots of effluent [Cl$^-$] versus time. Advection is represented by Eq. (58) with a = 0.3. N = 10, 20, 40, as labeled. Other parameters as in Fig. 2.

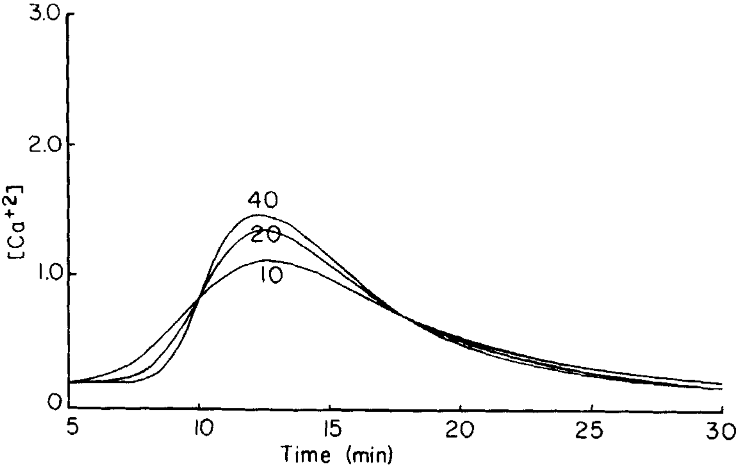

FIG. 7. Plots of effluent [Ca^{2+}] versus time. Advection is represented by Eq. (58) with $a = 0.3$. $N = 10, 20, 40$, as labeled. Other parameters as in Fig. 2.

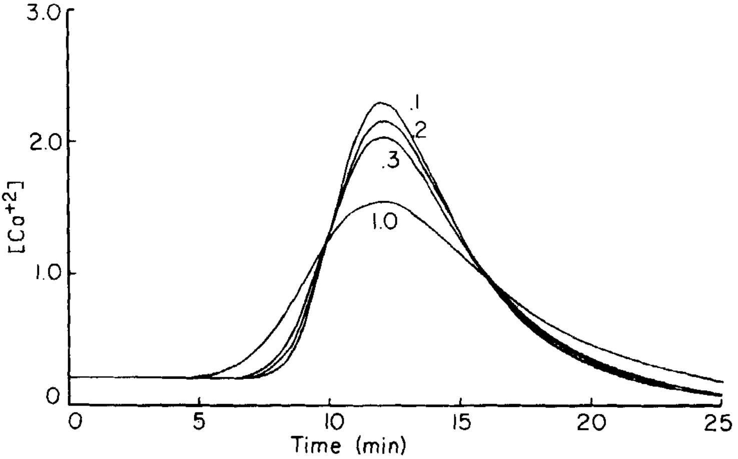

FIG. 8. Plots of effluent [Ca^{2+}] versus time. Advection is represented by Eq. (58); $a = 1, 0.3, 0.2, 0.1$ from bottom to top. Influent [Na^+] = 5.0 *M*, $N = 20$, $\Delta t = 0.05$ min; other parameters as in Fig. 2. Similar runs made with Eq. (59) representing advection are indistinguishable from these.

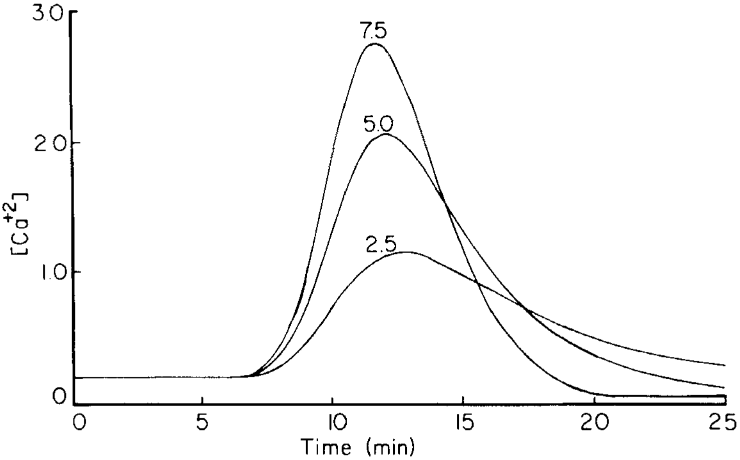

FIG. 9. Plots of effluent $[Ca^{2+}]$ versus time. Advection is represented by Eq. (58) with $a = 0.3$. $\Delta t = 0.05$ min, influent $[Na^+] = 7.5, 5.0, 2.5$ *M* (top to bottom), $N = 20$; other parameters as in Fig. 2.

used is shown in Fig. 8. The Ca^{2+} elution peak becomes progressively more narrow and tall as the proportion of the highly dispersive theoretical plate algorithm is decreased. Evidently, using such a linear combination of a dispersive and a nondispersive algorithm provides a satisfactory method for representing physical dispersion.

In Fig. 9 we see the effects of changing the NaCl concentration in the eluting solution. Increasing it results in a much narrower Ca^{2+} elution peak and in drastically reduced tailing. These results suggest that it might be advisable to hit the column initially with the highest feasible NaCl concentration, and then push this on through the column with a substantially more dilute solution; this might reduce chemicals costs and waste disposal problems.

The effects of changing the relative binding strength of Ca^{2+} relative to Na^+ are exhibited in Fig. 10. As one would expect, increasing the strength of Ca^{2+} binding broadens the elution peak and increases the extent of peak tailing.

In conclusion, we note that the use of asymmetrical upwind algorithms having low numerical dispersion can drastically reduce the amount of computation required to model ion-exchange columns having a large number of theoretical plates. Also, the solution of the cubic equation is best carried out exactly by Tartaglia's (Cardano's) method, rather than by

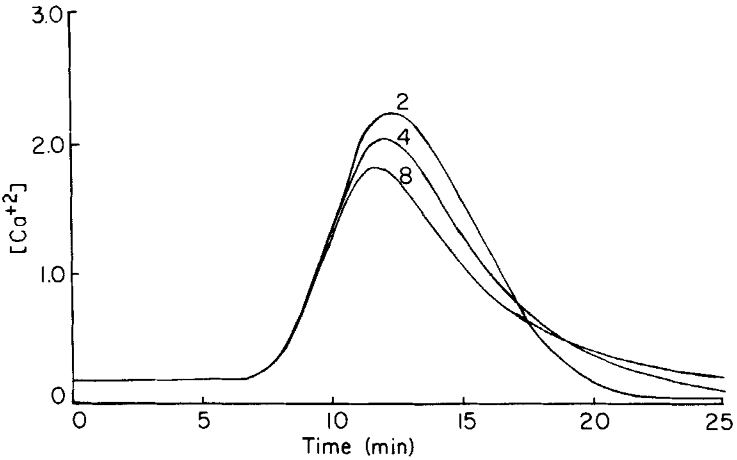

FIG. 10. Plots of effluent [Ca^{2+}] versus time. Advection is represented by Eq. (58) with $a = 3$. $\Delta t = 0.05$ min, influent [Na^+] = 5.0 *M*, $N = 20$, $K = 2$, 4, 8 from top to bottom; other parameters as in Fig. 2.

numerical approximation techniques. The resulting model can be computed in a reasonable length of time on a microcomputer 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.

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