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NUMERICAL ANALYSIS OF CHROMATOGRAPHIC BAND DEVELOPMENT OF ONE-COMPONENT SYSTEMS

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SUMMARY

The chromatographic diffusion coefficient of a species, the distribution coefficient of the species between the mobile and stationary phases, the initial band width and the eluent flow-rate affect the shape of the chromatogram in chromatographic band development. A numerical analysis of the fundamental diffusion equation applicable to any kind of chromatography was performed assuming that the diffusion coefficients of the species in the mobile and stationary phases are constant and the distribution coefficient is a function only of the species concentration. Some of the calculated results were compared with experimental ones. Although the discussion is limited to one-component systems, the calculations give basic knowledge for the evaluation of results in practical chromatography.

INTRODUCTION

In a previous paper[1] we demonstrated that the fundamental diffusion equation

$$\frac{\partial c_i\,(x,t)}{\partial t} = \frac{\partial\,[D_i\,(x,t)]}{\partial x}\cdot\frac{\partial\,[c_i\,(x,t)]}{\partial x} - \frac{\partial\,[v_i\,(x,t)\;c_i\,(x,t)]}{\partial x} \qquad (1)$$

is applicable to any kind of chromatography, where $c_i\,(x,t)$ is the concentration of species i at x (distance from the original point) and t (time), $D_i\,(x,t)$ the chromatographic diffusion coefficient of species i at x and t and $v_i\,(x,t)$ the velocity of species i at x and t. This equation is accurate, but is difficult to solve mathematically. The mathematical difficulties are alleviated if $D_i\,(x,t)$ and $v_i\,(x,t)$ are assumed to be constant. On the basis of these assumptions, the equation was solved in order to obtain expressions for the isotopic mole fraction and concentration profiles in a two-component chromatogram under the limiting conditions associated with isotope separation systems[2–4].

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However, in the case of heterogeneous chromatography such as ion-exchange chromatography, $D_i\ (x,t)$ and $v_i\ (x,t)$ may be affected by various factors, and their constancy will rarely hold. In a heterogeneous column, $D_i\ (x,t)$ and $v_i\ (x,t)$ are expressed by[5]

$$D_i\ (x,t) \cdot \frac{\partial c_i\ (x,t)}{\partial x} = D_i^{\mathrm{m}}\ (x,t) \cdot \frac{\partial}{\partial x}\left[\frac{\alpha c_i\ (x,t)}{\alpha + d_i}\right] + D_i^{\mathrm{s}}\ (x,t) \cdot \frac{\partial}{\partial x}\left[\frac{d_i c_i\ (x,t)}{\alpha + d_i}\right] \tag{2}$$

$$v_i\ (x,t) = \alpha v_i^{\mathrm{m}}\ (x,t)/(\alpha + d_i) \tag{3}$$

where α is the void fraction in the column, superscripts m and s are for the mobile and stationary phases, respectively, and d_i is the distribution coefficient of species i between the mobile and stationary phases, which is described by eqn. 4:

$$d_i = \frac{c_i^{\mathrm{s}}\ (x,t)}{c_i^{\mathrm{m}}\ (x,t)} \cdot (1 - \alpha) \tag{4}$$

$c_i\ (x,t)$ is defined by eqn. 5:

$$c_i\ (x,t) = \alpha c_i^{\mathrm{m}}\ (x,t) + (1 - \alpha)\ c_i^{\mathrm{s}}\ (x,t) \tag{5}$$

As is obvious from eqns. 2 and 3, $D_i\ (x,t)$ and $v_i\ (x,t)$ are not essentially constant. The former has a particularly complex form. In special cases, the form of $D_i\ (x,t)$ becomes simpler. If $D_i^{\mathrm{m}}\ (x,t)$ and $D_i^{\mathrm{s}}\ (x,t)$ are constant, eqn. 2 simplifies to eqn. 6:

$$D_i\ (x,t) \cdot \frac{\partial\ [c_i\ (x,t)]}{\partial x} = \frac{\partial}{\partial x}\left[\frac{\alpha D_i^{\mathrm{m}} + d_i D_i^{\mathrm{s}}}{\alpha + d_i} \cdot c_i\ (x,t)\right] \tag{6}$$

If d_i is also assumed to be a function of $c_i\ (x,t)$ alone, eqn. 2 reduces to eqn. 7:

$$D_i\ (x,t) = \frac{\alpha D_i^{\mathrm{m}} + d_i D_i^{\mathrm{s}}}{\alpha + d_i} - \frac{\alpha\ (D_i^{\mathrm{m}} - D_i^{\mathrm{s}})\ c_i\ (x,t)}{(\alpha + d_i)^2} \cdot \frac{dd_i}{dc_i} \tag{7}$$

As the simplest case, if d_i, D_i^{m} and D_i^{s} are constant, $D_i\ (x,t)$ has the form:

$$D_i = \frac{\alpha D_i^{\mathrm{m}} + d_i D_i^{\mathrm{s}}}{\alpha + d_i} \tag{8}$$

This is the only case where $D_i\ (x,t)$ is constant. In eqns. 6 and 7 where $D_i\ (x,t)$ and $v_i\ (x,t)$ are not constant, the mathematical solution of eqn. 1 to derive the expression for the concentration profile of species i in a chromatogram is difficult. In these cases, numerical analysis may be employed.

In the present investigation, numerical calculations based on the assumptions made in derivation of eqn. 7 were performed to show how the shape of the concentration profile of species i with reference to chromatographic band development is influenced by the chromatographic diffusion coefficient of species i, the distribution coefficient of species i between the mobile and stationary phase, the initial band width and the flow-rate of the eluent. It was assumed that species i at a constant concentration c_i^0 exists initially only in the limited range of, say, $0 < x < X_0$ and it is moved by the action of an external force without further input of species i.

ANALYSIS AND RESULTS

The calculations were carried out on the basis of finite difference equations. The derivatives in eqn. 1 are approximated by eqns. 9–11

$$\frac{\partial [c_i(x,t)]}{\partial t} \approx \frac{c_i(x,t+\Delta t) - c_i(x,t)}{\Delta t} \tag{9}$$

$$\frac{\partial [D_i(x,t)]}{\partial x} \cdot \frac{\partial [c_i(x,t)]}{\partial x} \approx \frac{1}{2(\Delta x)^2} \cdot \{[D_i(x+\Delta x,t) + D_i(x,t)] \cdot [c_i(x+\Delta x,t) - c_i(x,t) - D_i(x,t) + D_i(x-\Delta x,t)] \cdot [c_i(x,t) - c_i(x-\Delta x,t)]\} \tag{10}$$

$$\frac{\partial [v_i(x,t)\, c_i(x,t)]}{\partial x} \approx \frac{v_i(x+\Delta x,t)\, c_i(x+\Delta x,t) - v_i(x-\Delta x,t)\, c_i(x-\Delta x,t)}{2\Delta x} \tag{11}$$

with Δx and Δt, which are small elements of x and t, respectively. Substitution of the above three equations into eqn. 1 leads to eqn. 12:

$$c_i(x,t+\Delta t) = c_i(x,t) + \frac{\Delta t}{2(\Delta x)^2} \cdot \{[D_i(x+\Delta x,t) + D_i(x,t)] \cdot [c_i(x+\Delta x,t) - c_i(x,t)] - [D_i(x,t) + D_i(x-\Delta x,t)] \cdot [(c_i(x,t) - c_i(x-\Delta x,t)]\} - \frac{\Delta t}{2\Delta x} \cdot [v_i(x+\Delta x,t)\, c_i(x+\Delta x,t) - v_i(x-\Delta x,t)\, c_i(x-\Delta x,t)] \tag{12}$$

If $c_i(x,t)$ is known at $t = \mathrm{t}$ [as the initial condition, the value of $c_i(x, 0)$ is given], $d_i(x,t)$ can be calculated since it is assumed in the derivation of eqn. 7 that $d_i(x,t)$ is a function of $c_i(x,t)$ alone (the functional form of d_i against c_i will be presented later). $D_i(x,t)$ and $v_i(x,t)$ are then calculated from $d_i(x,t)$ according to eqns. 7 and 3, respectively. By use of $c_i(x,t)$, $D_i(x,t)$ and $v_i(x,t)$, we can obtain $c_i(x,t+\Delta t)$ at

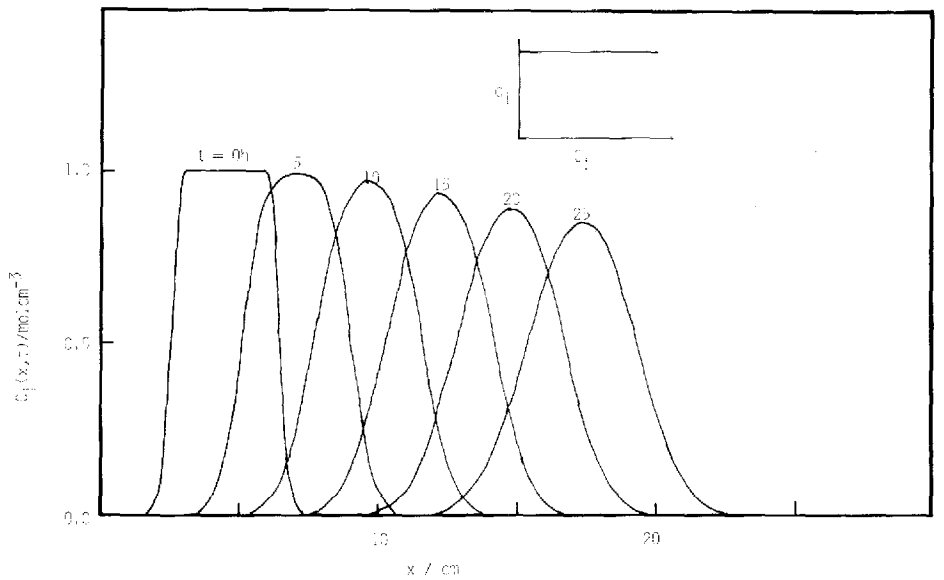

Fig. 1. Influence of d_i *vs.* c_i function on the shape of the concentration profile: plot of $c_i\,(x,t)$ against x where $d_i = 6.675$; $D_i^m = 1.027 \cdot 10^{-4}$ cm²/sec; $D_i^s = 5.137 \cdot 10^{-6}$ cm²/sec; $\alpha = 0.35$; $v' = 3.6$ ml/cm² · h.

$t + \Delta t$. Repetition of the above treatment yields the change in the shape of the concentration profile of species i with time. In the numerical calculations the initial band chromatogram was modelled as illustrated in Fig. 1 (see the band at $t = 0$); *i.e.*, both sides of the chromatogram were approximated by Gaussian functions. The Δx and Δt values used in the calculations were approximately 0.02 cm and 0.003 h, respectively.

Influence of the relationship between $d_i\,(x,t)$ and $c_i\,(x,t)$ on the shape of the concentration profile

The distribution coefficient $d_i\,(x,t)$ of species i between the mobile and stationary phases may be altered by change of $c_i\,(x,t)$, because the activity coefficient of species i is expected to vary in both phases with change of $c_i(x,t)$. Therefore, the change in the shape of the concentration profile of species i with t was traced for several different functional relationships between $d_i\,(x,t)$ and $c_i\,(x,t)$. $d_i\,(x,t)$ was approximated by a second-order function of $c_i\,(x,t)$. The values of D_i^m and D_i^s were chosen in such a way that $D_i^m/D_i^s = 50$ and $D_i = 1.0 \cdot 10^{-5}$ cm²/sec at $c_i = 0.0$. The values were estimated from eqn. 8. In Fig. 1, the change in shape of the concentration profile is plotted against t, *i.e.*, x, for the special case where $d_i\,(x,t)$ is a constant independent of $c_i\,(x,t)$. It is seen that the concentration profiles are gaussian in shape, and become broader with increasing t. In Fig. 2, the change in concentration profile with increasing t is shown for two cases where $d_i\,(x,t)$ increases monotonously with $c_i\,(x,t)$. It is obvious that in both cases the concentration profile shows a sharp boundary at the rear and changes gently at the front. Comparison of the concentration profiles for the two different types of d_i *vs.* c_i functions indicates that the shape of the concentration profile as well as the migration velocity of the band differ for

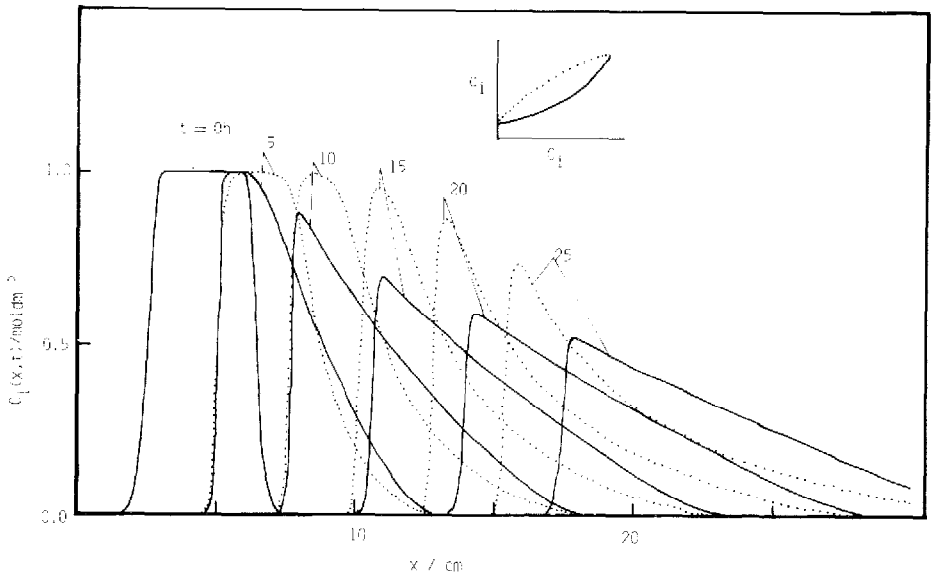

Fig. 2. Influence of d_i *vs.* c_i function on the shape of the concentration profile: plots of $c_i\,(x,t)$ against x. ———, $d_i = 1.716c_i^2 + 1.709c_i + 3.250$; -------, $d_i = -1.716c_i^2 + 5.141c_i + 3.250$; $D_i^m = 7.024 \cdot 10^{-5}$ cm²/sec; $D_i^s = 3.512 \cdot 10^{-6}$ cm²/sec; $\alpha = 0.35$; $v^{ll} = 3.6$ ml/cm² · h.

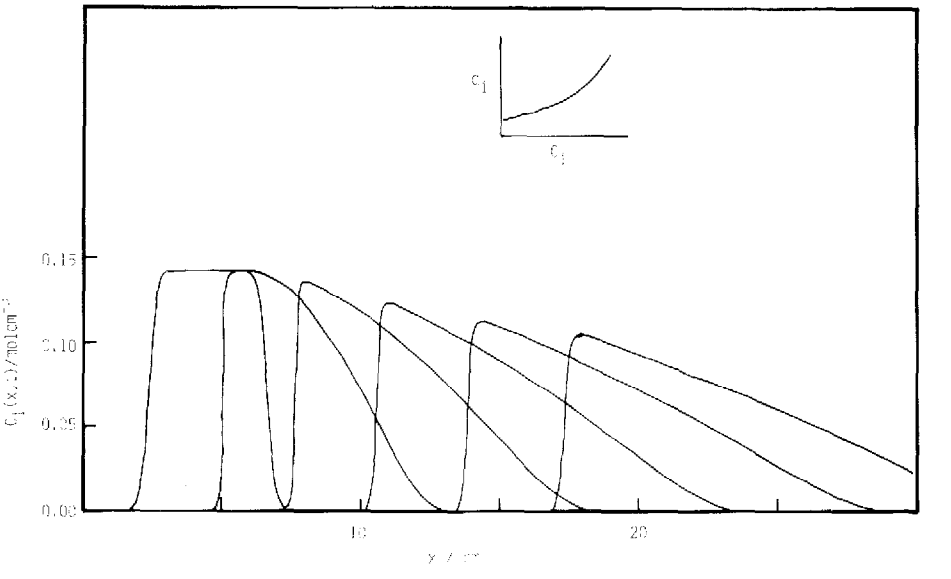

Fig. 3. Influence of d_i *vs.* c_i function on the shape of the concentration profile in the mobile phase: plo of $c_i^m\,(x,t)$ against x. Symbols and parameter values as in Fig. 2 (——).

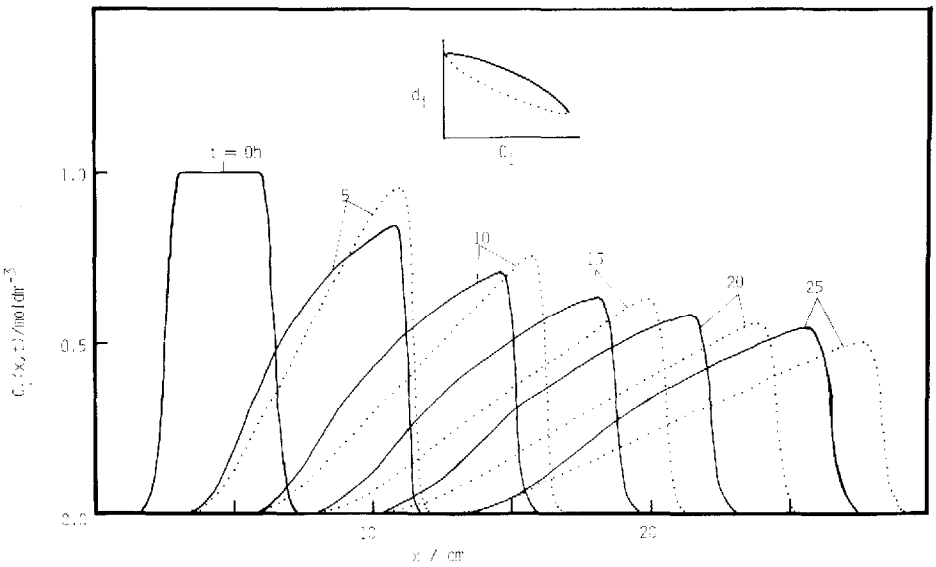

Fig. 4. Influence of d_i *vs.* c_i function on the shape of the concentration profile: plots of c_i (x,t) against x. ———, $d_i = -1.716c_i^2$ $1.709c_i + 6.675$; -------, $d_i = 1.716c_i^2 - 5.141c_i + 6.675$; $D_i^m = 1.027 \cdot 10^{-4}$ cm²/sec; $D_i^s = 5.137 \cdot 10^{-6}$ cm²/sec; $\alpha = 0.35$; $v^{l'} = 3.6$ ml/cm² · h.

the differing types of functions. Fig. 3 shows the change in the concentration profile in the mobile phase with t for the case of the d_i *vs.* c_i function drawn as solid lines in Fig. 2. These profiles correspond to elution of chromatographic bands, *i.e.*, they have a broad boundary at the frontal part and a sharp one at the rear. In Fig. 4, the change in the concentration profile is illustrated for two cases where d_i (x,t) decreases monotonously with increasing c_i (x,t). In contrast to Fig. 2, the concentration profile has a sharp boundary at the frontal part and broadens at the rear.

Influence of D_i (x,t) on the shape of the concentration profile

The calculations were carried out for three cases where $D_i = 1 \cdot 10^{-5}$, $5 \cdot 10^{-6}$ and $1 \cdot 10^{-6}$ cm²/sec at $c_i = 0.0$. For each D_i the values of D_i^m and D_i^s were estimated from eqn. 8. The ratio of D_i^m/D_i^s was kept constant at 20. In Fig. 5 are shown the concentration profiles 20 h after the start. As expected, the larger is the value of D_i, the broader is the profile.

Influence of initial band width on the shape of the concentration profile

The change in the concentration profile with time was calculated for different initial band widths. Fig. 6a shows the results for the case were d_i is an increasing function of c_i, and Fig. 6b for the case where d_i is a decreasing function of c_i. It is apparent that the larger is the initial band width the steeper is the sharp edge of the profile. The slowly changing rear boundary has the same form at the lower concentration level despite the different band width.

Influence of eluent flow-rate, $v^{l'}$, on the shape of the concentration profile

The effect of the eluent flow-rate on the concentration profile was examined

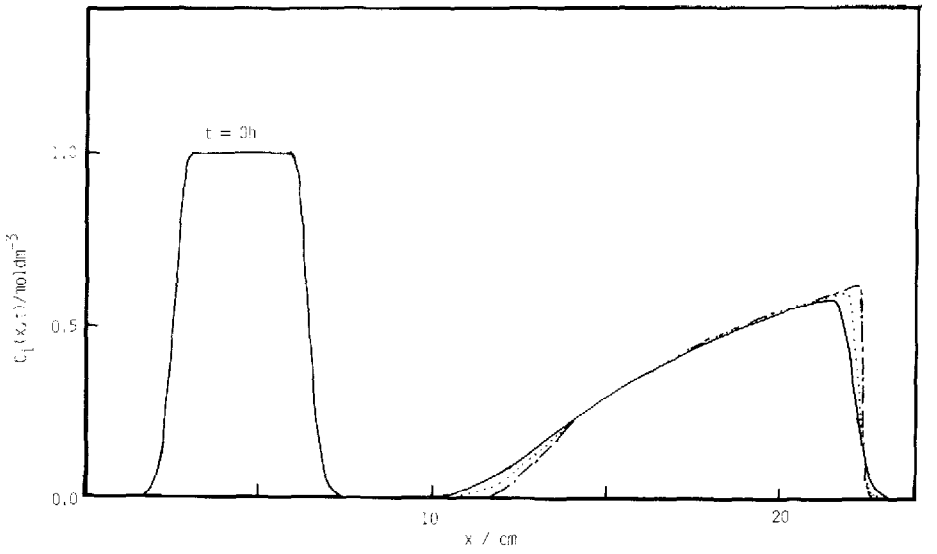

Fig. 5. Influence of D_i on the shape of the concentration profile 20 h from the start: plots of $c_i(x,t)$ against x. ———, $D_i = 1 \cdot 10^{-5}$ cm²/sec at $c_i = 0$; -------, $D_i = 5 \cdot 10^{-6}$ cm²/sec at $c_i = 0$; —·—·—, $D_i = 1 \cdot 10^{-6}$ cm²/sec at $c_i = 0$; $d_i = -1.716c_i^2 - 1.709c_i + 6.675$; $\alpha = 0.35$; $v^{1'} = 3.6$ ml/cm² · h.

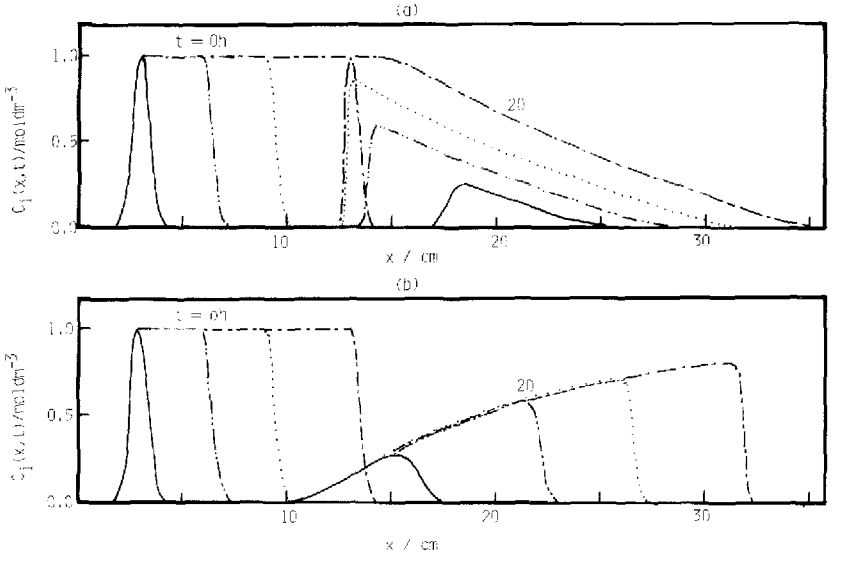

Fig. 6. Influence of initial band width on shape of concentration profile: plots of $c_i(x,t)$ against x. a, Band width: ———, 0 cm; — — —, 3 cm; -------, 6 cm; - - -, 10 cm. $d_i = 1.716c_i^2 + 1.709c_i + 3.250$; $D_i^m = 7.024 \cdot 10^{-5}$ cm²/sec; $D_i^s = 3.512 \cdot 10^{-6}$ cm²/sec; $\alpha = 0.35$; $v^{1'} = 3.6$ ml/cm² · h. b, Band widths as in a. $d_i = -1.716c_i^2 - 1.709c_i + 6.675$; $D_i^m = 1.027 \cdot 10^{-4}$ cm²/sec; $D_i^s = 5.137 \cdot 10^{-6}$ cm²/sec; $\alpha = 0.35$; $v^{1'} = 3.6$ ml/cm² · h.

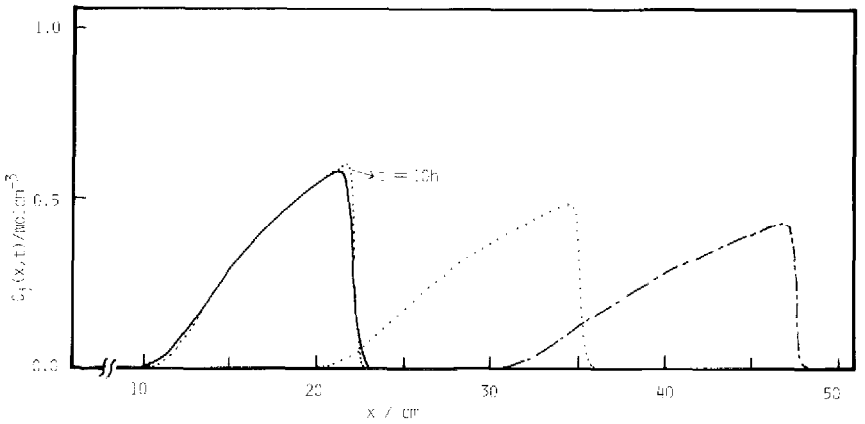

Fig. 7. Influence of $v^{1'}$ on the shape of the concentration profile: plots of $c_i(x,t)$ against x. ———, $v^{1'}$ = 3.6 ml/cm² · h; ------, $v^{1'}$ = 7.2 ml/cm² · h; — · — · —, $v^{1'}$ = 10.8 ml/cm² · h. $d_i = -1.716c_i^2 - 1.709c_i + 6.675$; $D_i^m = 1.027 \cdot 10^{-4}$ cm²/sec; $D_i^s = 5.137 \cdot 10^{-6}$ cm²/sec; $\alpha = 0.35$.

with the other parameters kept constant. The rates chosen were 3.6, 7.2 and 10.8 ml/cm² · h. The concentration profiles 20 h from the start are compared in Fig. 7. As expected, the chromatograms are shifted with the rate, but it should be noted that they are different in shape. If it is assumed, as previously[1–3], that d_i is kept constant independent of c_i, no change in shape of the concentration profile would be expected. By inspection of the concentration profiles, it is apparent that as $v^{1'}$ increases the sharp boundary becomes steeper, while the broad boundary is broadened.

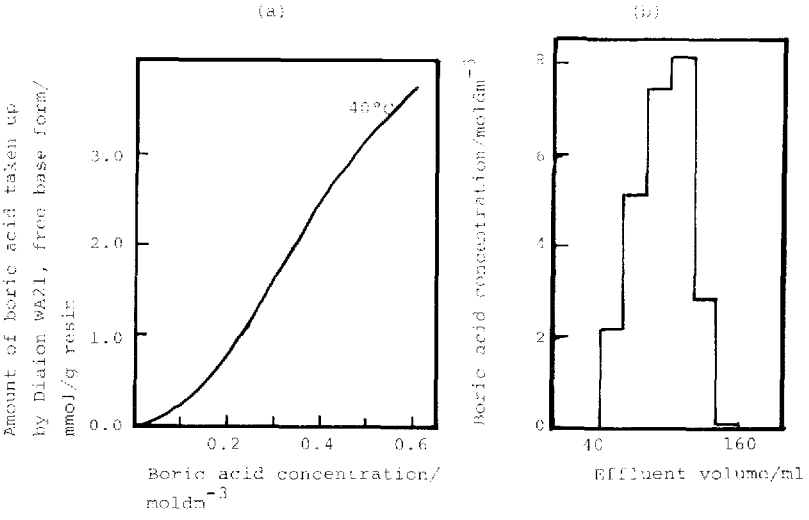

Fig. 8. Ion-exchange isotherm (a) and chromatogram (b) of boric acid. Resin: Diaison WA21, free base form. Eluent: water; flow-rate 38 ml/cm² · h. Temperature: 40°C.

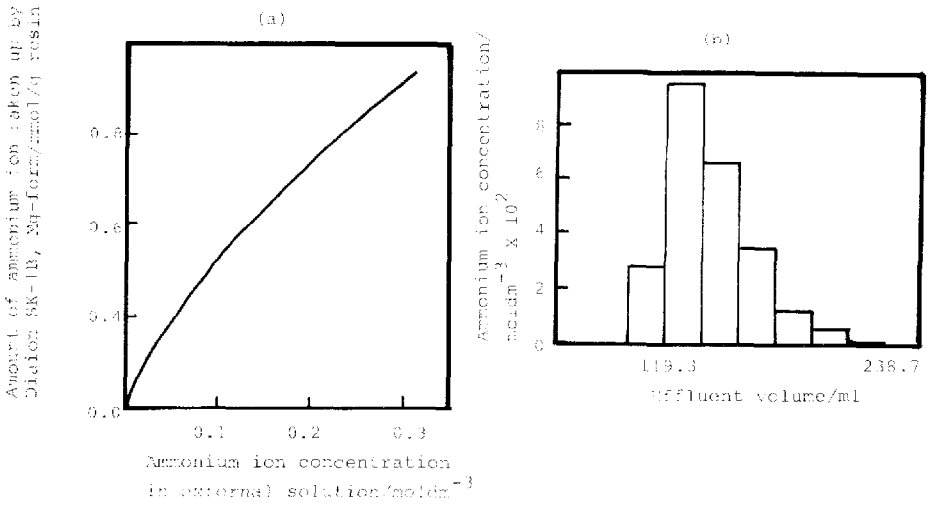

Fig. 9. Ion-exchange isotherm (a) and chromatogram (b) of ammonium ion. Resin: Diaion SK-1B, magnesium form. Eluent: water; flow-rate 38 ml/cm^2 · h. Temperature: 25°C.

DISCUSSION

It was predicted that, in the case where d_i increases with c_i, the chromatogram would show band broadening at the front and sharpening at the rear, and that the opposite behaviour would be observed in the case where d_i decreases with increasing c_i. These predictions were compared with the experimental results. In Fig. 8a and b, an observed ion-exchange isotherm of borate and its chromatogram are illustrated[6]. The adsorption isotherm obviously indicates that the d_i value should increase with increasing c_i up to 0.35 mol dm^{-3}, and then decrease. Fig. 8b was obtained for concentrations less than 0.35 mol dm^{-3}, where d_i is an increasing function of c_i. It is apparent that the frontal part is broad, while the rear is sharp. This observation is compatible with the present theoretical prediction. As another example, an observed ion-exchange isotherm of ammonium ion and its chromatogram are shown in Fig. 9a and b, respectively[7]. In this case, d_i decreases with increasing c_i over the whole concentration range. Fig. 9b shows band sharpening at the frontal part and broadening at the rear, as predicted.

Since the relationship beween d_i and c_i is obtained rather easily by a batch method, the present theoretical approaches should be useful for obtaining basic knowledge for the evaluation of results in practical chromatography. However, the present discussion was limited to a one-component chromatography, and no information was obtained about, *e.g.*, the isotopic mole fraction and concentration profiles in a two-isotope separation system. This is due to the fact that the distribution coefficient of species i, d_i, is assumed to be a function only of its concentration, c_i. In the case where the chromatographic diffusion coefficient is given by eqn. 6, which is more general than eqn. 7, it would be possible to derive information about the chromatographic behaviour in systems involving more than one species or isotopes. Numerical analyses of systems closely associated with the practical operation of two-isotope chromatography will be presented in a subsequent paper.

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