

Modelling of displacement chromatography using non-ideal isotherms

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ABSTRACT

The chromatographic transport problem in the displacement separation of multi-component mixtures leads to a set of coupled, non-linear partial differential equations. Neglecting axial dispersion, the set of equations can be solved using a transformation of variables (h or ω transformation) for the case that the multi-component distribution function is considered to be ideal (Langmuirean). If intermolecular interactions (non-idealities) are taken into account in the description of the multi-component distribution equilibrium, such a transformation of variables is no longer possible. The displacement separation of binary mixtures was analysed by applying shock-wave theory to the problem of non-ideal distribution isotherms. A description of the separation as a function of time and distance was obtained (development graph). Experimental results pertaining to the separation of Na–K mixtures using Li as the carrier and Rb as the displacer are presented. Quantitative agreement with predicted development graphs was obtained if non-idealities were taken into account, whereas the use of multi-component Langmuir isotherms yielded agreement with experimental results over only a limited composition range.

INTRODUCTION

The merits of the displacement mode of chromatography were already recognized by the pioneers of separation science [1,2]. The ability to concentrate sample components in the course of a separation is a particularly important asset of the technique. Owing to both theoretical and technical problems, the advantages of the displacement mode were overshadowed by the success of linear elution chromatography. It was not until the early 1980s that displacement chromatography was revived from its quiescent state, when Horváth and co-workers [3–5] demonstrated that by using modern high-performance liquid chromatographic (HPLC) equipment, the advantages of the displacement mode could be successfully exploited.

In displacement chromatography, the column is first equilibrated with an eluent weaker than any of the feed components (the carrier); the feed mixture is then introduced followed by an eluent stronger than any of the constituents of the feed (the displacer).

During the separation, the feed components compete for the sites on the stationary phase; on completion of the separation they are arranged in adjacent pure zones that travel at equal velocities (isotachic state). As the separation is based on mutual interferences among feed components, displacement chromatography is a non-linear technique. This causes the proper selection of the operating parameters required for attaining the isotachic state (*e.g.*, flow-rate, column length, temperature, concentration and nature of carrier and displacer) to be a complex problem.

A large number of different approaches have been proposed to model non-linear separations. Depending on their specific area of interest, different workers have proposed different solutions to the two major problems in non-linear separations: (1) how to incorporate the effect of finite rates (axial dispersion) and (2) how to model the multi-component distribution between stationary and mobile phase.

Early interest in non-linear chromatography de-

rived from regenerative operations in fixed beds. Here, mainly the first problem is tackled. Thomas [6] introduced a lumped rate constant to account for slow kinetics. An important extension to the original Thomas approach allowing for other rate-controlling steps (*e.g.*, intra- and extra-particle diffusion) was published by Hiester and Vermeulen [7]. Also, workers studying overloaded elution chromatography used mass-balance equations containing dispersion terms to predict elution profiles. Haarhof and Van de Linde [8] treated non-linearity as a perturbation to the linear solution. Guiochon and co-workers [9,10] used the numerical error introduced by their finite difference scheme to estimate axial dispersion. An exact solution has been derived for a single component following Langmuir-type kinetics, assuming that axial diffusion can be neglected [11]. Owing to the mathematical complexity, the above methods are in many instances limited to a single solute. Thus, multi-component effects, important for practical cases, are not treated by these methods. An interesting exception is the work of Phillips *et al.* [12]. Here, the displacement separation of multi-component mixtures was calculated using a model that incorporates finite mass transfer rates as well as axial diffusion. A numerical technique was employed to approximate the resulting system of coupled non-linear differential equations.

Alternatively, one can assume the column efficiency to be infinite. Hence, equilibrium is assumed and all axial dispersion is neglected. This approximation is generally called ideal chromatography. Although not infinite, the efficiency of present-day HPLC columns is high enough to allow a good comparison between predicted and experimental results [13,14]. Analytical solutions to the multi-component ideal case were obtained by Helfferich and Klein [15] and Rhee and co-workers [16,17] using a very elegant transformation of variables: h -[15] or ω -transformation [16]. Golshan-Shirazi and Guiochon [18] presented a solution to the separation of binary mixtures in the overloaded elution mode using shock theory.

The use of the ideal chromatography assumption greatly facilitates the study of non-linear multi-component problems. It is sufficiently accurate to concentrate on the second major problem: how to model the multi-component distribution between mobile and stationary phases. In the literature, the

multi-component Langmuir isotherm is used almost exclusively to describe this distribution. The great preference for this particular isotherm can be easily traced to its simple functional form (constant separation factors) and to the fact that solutions for non-linear separations of N -component mixtures can be obtained in the Langmuir case by the h - or ω -transformation. If separation factors are a function of composition, this is in general not possible. The physical basis for the use of the Langmuir isotherm, however, is weak. The different saturation coverages used for different components have been shown to be inconsistent with basic thermodynamics [19] and the assumed ideality (neglect of interparticle interactions) deserves further investigation. In a number of instances, discrepancies between experimental and predicted results in the modelling of non-linear separations have been attributed to the shortcomings of the Langmuir equation [13,20].

The aim of this work was to compare two models that describe the distribution equilibrium between stationary and mobile phases: the multi-component Langmuir isotherm on the one hand and a multi-component isotherm that accounts for two-body interactions in the stationary phase on the other. As we have recently shown, an isotherm that accounts for two-body interactions in the stationary phase can be derived from first principles for systems that belong to the same compensation class [21–23], a compensation class being defined as a group of similar compounds characterized by a common compensation temperature ($T_c = \Delta H/\Delta S$, where the enthalpy and entropy changes refer to a phase equilibrium). The non-linear system we consider is the displacement separation of binary mixtures. The modelling consists of solving the hyperbolic system of conservation laws of the ideal chromatographic approximation using shock theory. The solutions are presented in the form of development graphs, *i.e.*, plots of time *vs.* distance showing the history of the separation.

More specifically, the system we use to compare the different multi-component isotherms is the displacement separation of K–Na mixtures on an ion-exchange column, using Li as the carrier and Rb as the displacer. We shall show that by using a multi-component isotherm that incorporates non-idealities, a good prediction of the displacement separation is obtained for all compositions of the

K-Na feed. The use of ideal (Langmuir) isotherms in the modelling is shown to yield an adequate description of the separation over only a limited range of composition of the binary feed.

THEORY

General description of the problem for non-ideal isotherms

Let us consider a system consisting of m components. The molar concentrations of the i th component in the mobile and stationary phase are denoted by c_i and n_i , respectively. Let z be the distance along the column measured from the inlet and let t denote time with $t = 0$ corresponding to the entry of the sample into the column. The variables z and t are made dimensionless by the length L of the column and by L/U , where U is the constant interstitial velocity of the eluent. Neglecting axial dispersion, the conservation law for the i th component is

$$\frac{\partial c_i}{\partial z} + \frac{\partial c_i}{\partial t} + v \cdot \frac{\partial n_i}{\partial t} = 0 \quad (1)$$

where

$$v = (1 - \varepsilon)/\varepsilon \quad (2)$$

ε being the void fraction. To relate stationary phase concentrations to mobile phase concentrations, we introduce the separation factors α_{ij} . To allow for intermolecular interactions in the stationary phase, these separation factors are no longer considered to be constants (the usual assumption), but are a function of all the stationary phase concentrations n_1, n_2, \dots, n_m . It is, of course, here that non-ideality enters into the problem. The separation factors are thus defined by

$$\frac{n_i}{c_i} = \alpha_{ij}(n_1, \dots, n_m) \frac{n_j}{c_j} \quad i, j = 1, \dots, m \quad (3)$$

Consistency demands that

$$\alpha_{ij} = 1/\alpha_{ji} \quad \text{for all } i, j \quad (4)$$

and

$$\alpha_{ij}\alpha_{jl} = \alpha_{il} \quad \text{for all } i, j, l \quad (5)$$

We have a total of m conservation laws (1) relating the $2m$ concentrations in the stationary and mobile

phases: c_i and n_i . One would like to eliminate m of the unknowns by using eqns. 3, 4 and 5, and in view of the general dependence of α_{ij} on the n_j , it is natural to try to express the c_i in terms of the n_j . However, as we choose to describe the distribution equilibrium using the separation factors that are ratios, there are not enough independent eqns. 3, 4 and 5 to do so. This implies that the set of eqns. 1–5 by itself is not sufficient to determine the development of a separation from its initial conditions. Additional knowledge of the distribution equilibrium needs to be specified for a deterministic description.

To clarify this point, let $C(z, t) \equiv \sum_{i=1}^m c_i(z, t)$ and $N(z, t) \equiv \sum_{i=1}^m n_i(z, t)$ be the total concentrations in the mobile and stationary phases, respectively. From eqn. 3, one obtains

$$C = \sum_{j=1}^m c_j = \sum_{j=1}^m \alpha_{ij}(n_1, \dots, n_m) \frac{n_j}{n_i} \cdot c_i \quad (6)$$

and hence

$$c_i = C \cdot \frac{n_i}{\sum_{j=1}^m \alpha_{ij}(n_1, \dots, n_m) n_j} \quad i = 1, \dots, m \quad (7)$$

Thus, a knowledge of the total mobile phase concentration is required in order to express the c_i in the n_j . By adding eqns. 1, it follows that C satisfies

$$\left(\frac{\partial}{\partial z} + \frac{\partial}{\partial t} \right) C + v \cdot \frac{\partial N}{\partial t} = 0 \quad (8)$$

By substituting eqn. 7 in eqn. 1, we obtain

$$\left(\frac{\partial}{\partial z} + \frac{\partial}{\partial t} \right) \left\{ C \cdot \frac{n_i}{\sum_{j=1}^m \alpha_{ij}(n_1, \dots, n_m) n_j} \right\} + v \cdot \frac{\partial n_i}{\partial t} = 0 \quad i = 1, \dots, m \quad (9)$$

Thus, the system of eqns. 8 and 9 can be solved if the total concentration in the stationary phase N is known as a function of (z, t) or, more generally, if N is given in terms of all the stationary phase concentrations $N(n_1, \dots, n_m)$, because the system of equations then consists of $m + 1$ equations for the $m + 1$ unknowns: n_1, \dots, n_m and C .

Non-ideal distribution isotherms with constant total stationary phase concentrations

In this section we derive a specialized form of eqn. 8 for the case that $\mathbf{N}(z, t)$ is constant. This situation applies to our experimental system: the ion-exchange separation of homovalent ions. Here, electroneutrality requires that the exchanger is always occupied by the same number of ions. Substituting $\mathbf{N}(z, t) \equiv \mathbf{N}$ constant into eqn. 8 shows that \mathbf{C} is constant along curves: $t - z = \text{constant}$. Hence:

$$\mathbf{C}(t, z) = \tilde{\mathbf{C}}(\tau), \quad \tau = t - z \quad (10)$$

for some function $\tilde{\mathbf{C}}$. Since the linear velocity is unity with respect to the frame (z, t) , eqn. 10 implies that a sudden change in the total mobile phase concentration moves with the linear velocity of the eluent. Hence, the total mobile-phase concentration can be determined from the conditions at the inlet $z = 0$. By substitution of this function in eqn. 9, a coupled non-linear system of m equations for the m stationary phase concentrations n_i results.

It will be advantageous to use dimensionless concentrations x_i, y_i defined by

$$x_i \equiv c_i/\mathbf{C}, \quad y_i \equiv n_i/\mathbf{N} \quad (11)$$

Further, it will be helpful to use the independent variables (τ, ζ) that are related to (t, z) by

$$\tau = t - z \quad (12)$$

$$\zeta = z$$

Then, for fixed ζ , $\partial/\partial\tau = \partial/\partial t$ and for fixed τ , $\partial/\partial\zeta = \partial/\partial t + \partial/\partial z$. Hence, we obtain from eqn. 9

$$\frac{\partial}{\partial\tau} \cdot y_i + \frac{\tilde{\mathbf{C}}(\tau)}{v\mathbf{N}} \cdot \frac{\partial}{\partial\zeta} \left\{ \frac{y_i}{\sum_{j=1}^m \alpha_{ij}(y_1, \dots, y_m)y_j} \right\} = 0 \quad i = 1, \dots, m \quad (13)$$

where we used the identity

$$\frac{\partial}{\partial\zeta} \tilde{\mathbf{C}}(\tau) = \left(\frac{\partial}{\partial t} + \frac{\partial}{\partial z} \right) \tilde{\mathbf{C}} = 0$$

which follows from eqn. 8 if \mathbf{N} is constant. Also, the separation factors are now considered as functions of the dimensionless stationary phase concentrations y_i . By the definition of the y_i , we have

$$\sum_{i=1}^m y_i = 1 \quad (14)$$

and hence one of the y_i can be eliminated immediately. We shall eliminate y_m . Using eqns. 4 and 5, we find for every $i = 1, \dots, m-1$

$$\frac{y_i}{\sum_{j=1}^m \alpha_{ij}y_j} = \frac{y_i}{\alpha_{im} + \sum_{j=1}^{m-1} (\alpha_{ij} - \alpha_{im})y_j} = \frac{\alpha_{mi}y_i}{1 + \sum_{j=1}^{m-1} (\alpha_{mj} - 1)y_j} \quad (15)$$

The α_{mj} are now considered as a function of \vec{y} , where \vec{y} is the column vector of all independent stationary phase concentrations in the system. Substituting eqn. 15 into eqn. 13, we finally obtain the following coupled system of $m-1$ non-linear partial differential equations for the $m-1$ unknowns y_1, \dots, y_{m-1}

$$\frac{\partial}{\partial\tau} \cdot y_i + \frac{\tilde{\mathbf{C}}(\tau)}{v\mathbf{N}} \cdot \frac{\partial}{\partial\zeta} \left\{ \frac{\alpha_{mi}(\vec{y})y_i}{1 + \sum_{j=1}^{m-1} [\alpha_{mj}(\vec{y}) - 1]y_j} \right\} = 0 \quad i = 1, \dots, m-1 \quad (16)$$

The concentrations at the inlet of the column $\zeta = 0$ are known at every time t . Hence

$$\vec{y}(\tau, \zeta = 0) \quad (17)$$

is given.

Some remarks seem appropriate. First, one can, in principle, derive a system of coupled non-linear partial differential equations which is completely analogous to eqn. 16, but which instead of y_i and α_{ij} involves x_i and α_{ij} . However, if the separation factors are not constants, they will in general be specified as functions of the stationary-phase concentrations y_i , rather than in terms of the mobile phase concentrations x_i . Therefore, the system of eqns. 16 for y_i and α_{ij} is in general more useful than the analogous system for x_i and α_{ij} . In the case of Langmuir isotherms, the separation factors are constants and both systems are equally useful, although most workers use the system involving the mobile phase concentrations.

Second, we note that if $\tilde{\mathbf{C}}(\tau)$ is constant, *i.e.*, if the total mobile phase concentration at the inlet is constant, the system has the form

$$\frac{\partial y_i}{\partial\tau} + \frac{\partial}{\partial\zeta} F_i(\vec{y}) = 0 \quad i = 1, \dots, m-1 \quad (18)$$

where the F_i are given by

$$F_i(\vec{y}) = \frac{\tilde{C}}{\nu N} \frac{\alpha_{mi}(\vec{y})y_i}{1 + \sum_{j=1}^{m-1} [\alpha_{mj}(\vec{y}) - 1]y_j} \quad (19)$$

Eqn. 18 is called a hyperbolic system if the $(m-1) \times (m-1)$ matrix $\mathbf{A}(\vec{y}) = (\mathbf{A}_{ij}(\vec{y}))$ given by $\mathbf{A}_{ij}(\vec{y}) = \partial F_i / \partial y_j(\vec{y})$, has $m-1$ real eigenvalues $\lambda_1(\vec{y}), \dots, \lambda_{m-1}(\vec{y})$ for every state \vec{y} . Whether eqn. 18 actually is a hyperbolic system depends on the separation factors $\alpha_{ij}(\vec{y})$, but in the case of constant separation factors (Langmuir) and for the non-ideal distribution isotherm studied in this paper, this is generally so. If the total mobile phase concentration at the inlet is a function of time, the functions F_i depend explicitly on τ through the factor $\mathbf{C}(\tau)$. Then, the system of eqns. 18 is not hyperbolic. In the experiments considered in this paper the total concentration $\mathbf{C}(\tau)$ is, although not constant, piecewise constant, and the theory of hyperbolic systems can still be used.

Solution method for binary mixtures

We consider a binary mixture of K and Na with Li as the carrier and Rb as the displacer. The total stationary phase concentration is constant and the number of components is $m = 4$. The numbering of the components will be in sequence of decreasing affinity for the stationary phase. Thus, y_1, y_2, y_3, y_4 correspond to Rb, K, Na and Li, respectively. The numbering convention implies that

$$\alpha_{ij} < 1 \text{ for } i > j \quad (20)$$

We consider the conservation laws 13 for two different isotherms, namely the ideal Langmuir isotherms for which the α_{ij} are independent of the concentrations and the non-ideal isotherms derived in refs. 21–23 that depend on all y_i according to

$$\alpha_{ij}(y_1, y_2, y_3, y_4) = \exp \left[\frac{-(1-T/T_c)}{RT} \sum_{k=1}^4 (f_{ik} - f_{jk})y_k \right] \quad (21)$$

In eqn. 21, T is the absolute temperature and R is the gas constant. T_c is the so-called compensation temperature of the class of compounds under consideration and the f_{ij} are dimensionless parameters describing the two-body interaction between com-

ponents i and j in the stationary phase. It is important to note that the f_{ij} are structural parameters and do not depend on the composition of the mixture or on the temperature. This is in contrast to the Langmuir case, where it is assumed that multi-component isotherms can be constructed using data obtained from measurements of single-component isotherms; an assumption that has been shown to be untenable [19,24]. It is shown in the cited references that the above distribution isotherm resembles the Fowler–Guggenheim approach [25] to multi-component adsorption, except that in our case the interaction energies are temperature dependent.

For $t < 0$ the column contains only the carrier ($y_4 = 1$). Then, for $0 < t < t_e$, the mixture enters the column and for $t > t_e$ there is only the displacer ($y_1 = 1$). Hence, we have the following boundary condition at the inlet, $x = \zeta = 0$, for the state vector $\vec{y} = (y_1, y_2, y_3, y_4)^T$:

$$\begin{aligned} \vec{y}(\tau, 0) &= (0, 0, 0, 1)^T \equiv \vec{y}^I \text{ (initial state)} \\ \vec{y}(\tau, 0) &= (0, y_2^F, y_3^F, 0)^T \equiv \vec{y}^F \text{ (feed state)} \\ \vec{y}(\tau, 0) &= (1, 0, 0, 0)^T \equiv \vec{y}^E \text{ (end state)} \end{aligned} \quad (22)$$

where the superscript T (transpose) is used to indicate that column vectors are implied.

Let the total mobile phase concentration corresponding to the initial, feed and end state be given by $\mathbf{C}^I, \mathbf{C}^F$ and \mathbf{C}^E , respectively. It follows from eqn. 10 that there are three regions in the (z, t) plane in which the total mobile-phase concentration is equal to one of these values (see Fig. 1):

$$\begin{aligned} \mathbf{C}(t, z) &= \mathbf{C}^I \text{ for } t < z \\ \mathbf{C}(t, z) &= \mathbf{C}^F \text{ for } z < t < z + t_e \\ \mathbf{C}(t, z) &= \mathbf{C}^E \text{ for } t > z + t_e \end{aligned} \quad (23)$$

The conservation laws 13 thus differ in these three regions of the (z, t) plane. We note that although the governing eqn. 13 has τ as an independent variable, we shall use time t in the final results and in the plot by using the transformation of eqn. 12.

It is physically obvious, and it can also be verified explicitly, that concentration velocities are smaller than the linear velocity of the eluent, which is equal to 1 with respect to the dimensionless z and t that we use. Hence, below the line $t = z$ only the carrier is present.

The boundary condition 22 consists of three

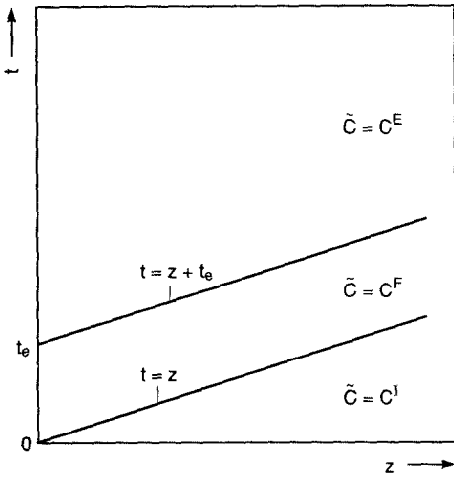


Fig. 1. Schematic diagram of the solution of eqn. 8 in the (t, z) plane showing zones of different total concentration.

constant states separated by discontinuities at $t = 0$ and $t = t_e$. A system of conservation laws with as boundary (or initial) condition two constant states separated by a discontinuity is known as a Riemann problem. Hence, for not too large values of z , the solution of our problem can be obtained by separately solving two Riemann problems corresponding to the aforementioned discontinuities. For larger values of z the solutions of the two Riemann problems will, of course, interact.

Let us first consider the Riemann problem corresponding to the discontinuity at $t = 0$ (it might be helpful to refer to Fig. 2 at this point). Since for $t < z$ the state is known to consist of pure Li, only the region $z < t < z + t_e$ is of interest. Hence, we take $\mathbf{C} = \mathbf{C}^F$ in eqn. 13. The displacer obviously plays no role in the distribution process at $\tau = 0$, so that we may put $y_1 \equiv 0$ eqn. 13. Further, using eqn. 14, one of the remaining components, for which we choose y_4 , can be eliminated. Using eqn. 16, the following set of two conservation laws, involving only y_2 and y_3 , remains:

$$\frac{\partial y_i}{\partial \tau} + \frac{\partial}{\partial \zeta} F_i(\vec{y}) = 0 \quad i = 2, 3 \quad (24)$$

where $\vec{y} = (y_2, y_3)^T$ and

$$F_i(\vec{y}) = \frac{C^F}{vN} \cdot \frac{\alpha_{4i}(\vec{y})y_i}{1 + [\alpha_{42}(\vec{y}) - 1]y_2 + [\alpha_{43}(\vec{y}) - 1]y_3} \quad i = 2, 3 \quad (25)$$

From the general mathematical theory of hyperbolic systems [26–28], it is known that the solution of a Riemann problem for a system of two components consists of three constant states, \vec{y}^v , $v = 1, 2, 3$, with \vec{y}^1 the left, \vec{y}^2 the intermediate and \vec{y}^3 the right state, separated by two shocks and/or simple waves. For the Riemann problem at $\tau = 0$, we have $\vec{y}^1 = (y_2^F, y_3^F)$. Simple waves are continuous transitions which depend on (τ, ζ) only through the ratio τ/ζ . It turns out that for both the ideal Langmuir isotherm and the non-ideal isotherm, all transitions between constant states are shocks. If $s^1 < s^2$ denote the shock speeds, then mass conservation leads to the following jump relationships across the shocks:

$$s^v(y_i^v - y_i^{v+1}) = F_i(\vec{y}^v) - F_i(\vec{y}^{v+1}) \quad i = 2, 3 \quad (26)$$

These are four equations for the four unknowns s^1 , s^2 , y_2^2 and y_3^2 . Numbers in superscripts are again used to indicate states. Thus, s^1 refers to the shock between left and intermediate states, y_3^2 is the stationary phase concentration of the third component in the intermediate state, etc. For $v = 2$, we add eqns. 26 for $i = 2, 3$. After substitution of eqn. 25 and of $\vec{y}^3 = (0, 0)$ and by using $y_2^F + y_3^F = 1$, one deduces that

$$s^2 = C^F/vN \quad (27)$$

This value of the speed of the fastest shock is thus independent of the isotherm used. By substituting eqn. 27 into eqn. 26, s^1 and y_2^2, y_3^2 can be calculated. As can be expected, the intermediate state always consists of pure Na, so that $\vec{y}^2 = (0, 1)$. The speed s^1 depends on the functional dependence of the α_{ij} on the concentrations \vec{y} and hence is different for different isotherms.

Fig. 2 shows a schematic development graph in the (z, t) plane. The shocks $t = z$ and $t = z + t_e$ between regions of different total mobile phase concentration move at the velocity of the mobile phase ($= 1$ in our coordinates) and are seen to overtake the shocks with speed s^1 [at point $Q = (z_Q, t_Q)$] and with speed s^2 [at point $R = (z_R, t_R)$]. As a result, the shock speeds change suddenly to values \tilde{s}^1 and \tilde{s}^2 which follow from the jump relations 26, but now with C^F replaced by C^E . In particular the fastest shock now has speed

$$\tilde{s}^2 = C^E/vN \quad (28)$$

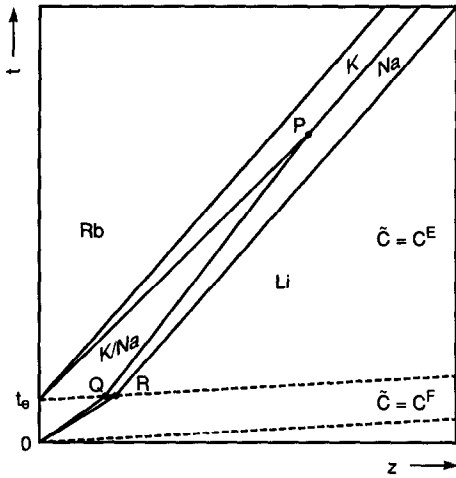


Fig. 2. Development graph of the ion-exchange separation of a binary mixture showing the three characteristic points P, Q and R.

Next consider the Riemann problem at $\tau = t_e$. There, Li is absent so that $y_4 \equiv 0$. By eliminating y_3 using $y_3 = 1 - y_1 - y_2$, one obtains a coupled system of two conservation laws involving only y_1 and y_2 . Again, it can be shown that only shocks occur at the transitions between the constant states \vec{y}^v , $v = 1, 2, 3$. One now has $\vec{y}^1 = (1, 0)^T$ and $\vec{y}^3 = (0, y_2^2)^T$ while the intermediate state \vec{y}^2 and the shock speeds s^1 and s^2 follow from the jump equations

$$s^v(\vec{y}^v - \vec{y}^{v+1}) = F_i(\vec{y}^v) - F_i(\vec{y}^{v+1}) \quad (29)$$

$$i = 1, 2, \quad v = 1, 2$$

with

$$F_i(\vec{y}) = \frac{C^E}{vN} \cdot \frac{\alpha_{3i}(\vec{y})y_i}{1 + [\alpha_{31}(\vec{y}) - 1]y_1 + [\alpha_{32}(\vec{y}) - 1]y_2} \quad (30)$$

$$i = 1, 2$$

In particular, if $y_1^2 + y_2^2 = 1$, then eqn. 29 with $v = 1$ implies that

$$s^1 = C^E/vN \quad (31)$$

If $y_1^2 + y_2^2 < 1$, then by choosing $v = 1$ and adding over $i = 1, 2$ the same result is obtained. Further, it is easy to verify that the intermediate state always consists of pure K so that $\vec{y}^2 = (0, 1)$. Contrary to s^1 , the speed s^2 of the fastest shock depends on the isotherm used.

As can be seen from Fig. 2, the fastest shock corresponding to the Riemann problem at $\tau = t_e$ moves faster than the slowest shock emanating from $\tau = 0$. Hence, the latter is overtaken by the former. At the point of intersection [point P = (z_p, t_p) in Fig. 2], we have yet another Riemann problem. In this problem the left state consists of pure K, whereas the right state consists of pure Na. Hence, only y_2 and y_3 are relevant. After eliminating y_3 using $y_2 + y_3 = 1$, we obtain a single conservation law involving only y_2 . Hence, there is only one shock emanating from point P, separating the pure K and Na states. The shock speed, s^1 , follows from

$$s^1(y_2^1 - y_2^2) = F_2(\vec{y}^1) - F_2(\vec{y}^2) \quad (32)$$

where

$$F_2(\vec{y}) = \frac{C^E}{vN} \cdot \frac{\alpha_{32}(\vec{y})y_2}{1 + [\alpha_{32}(\vec{y}) - 1]y_2} \quad (33)$$

By substituting $y_2^1 = 1$, $y_2^2 = 0$, one finds that

$$s^1 = C^E/vN \quad (34)$$

Hence, we conclude (*cf.*, Fig. 2) that for $z > z_p$ four pure states are found that are separated by shocks with equal speeds given by eqn. 34 and independent of the isotherms. Point P is thus the point of complete separation and for $z > z_p$ the isotachic state is attained. Although the isotachic state and the speeds of the shocks separating the pure states for $z > z_p$ are independent of the isotherm used, the position of point P does depend on the isotherms since P is the intersection of the fastest shock emanating from $\tau = t_e$ and the slowest shock emanating from $\tau = 0$. These shocks have speeds that do depend on the isotherm.

Some remarks concerning the computation method outlined above seem appropriate. In general, one does not know beforehand whether a transition between two constant states is a shock or a simple wave. Physically, that is determined by the different magnitudes of the stationary phase concentrations as fixed by the multi-component isotherm. Mathematically, the relative magnitudes of the eigenvalues of the Jacobian matrices $A(\vec{y}^v)$ and $A(\vec{y}^{v+1})$ determine whether a given transition is a shock or a simple wave. As remarked above, all transitions for both the ideal and the non-ideal isotherms were found to be shocks.

It is well known that in the Langmuir case, *i.e.*, the case that separation factors are constant, computations are facilitated by using the so-called h - or ω -transformation [15, 16]. The new dependent variables, ω_i , have the useful property that for a given Riemann problem involving an arbitrary number of components each of them changes across only one of the shocks or simple waves. Dependent variables with this property always exist for a Riemann problem involving only two dependent variables, and therefore we could have made use of them. However, for such small systems the jump relations 26 are just as simple. But for Riemann problems involving more than two dependent variables, the existence of the ω_i s is very special and in fact one can show that for the non-ideal isotherms given by eqn. 21 they do not exist [29].

EXPERIMENTAL

Materials

All alkali metal salts used were nitrates of Suprapur or comparable quality (Merck, Darmstadt, Germany). The salts were dried overnight at 80°C and cooled to ambient temperature in a desiccator before weighing. High-purity deionized water (> 18 M Ω) was used to make up the solutions. Quartz glassware was used throughout.

All experiments were performed using a polystyrene-divinylbenzene-based strong cation exchanger (IC PAK C, Millipore-Waters, Milford, MA, USA), which was purchased prepacked in a 50 mm \times 4.6 mm I.D. column. The total ion-exchange capacity of the column and the column void fraction were determined to be 7.22 μ equiv. and 0.42, respectively, using techniques described previously [22].

Apparatus

A modified PU4100 liquid chromatograph (Philips Analytical Chromatography, Cambridge, UK) was used for separations by displacement chromatography. A schematic diagram of the displacement system is shown in Fig. 3. The valves indicated represent a Model 5011P solvent selection switch (A), two Model 7030 three-port valves (B and C) and a Model 7125 six-port injection valve (D), all obtained from Rheodyne (Cotati, CA, USA). A needle valve (E) from Scientific Systems (State

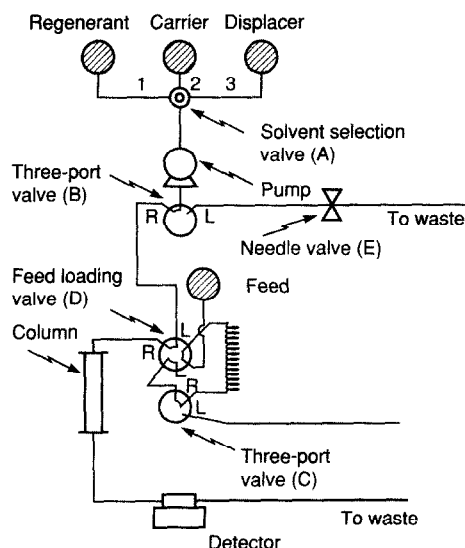


Fig. 3. Diagram of the experimental set-up used for displacement separations. Operational procedures are described in the text.

College, PA, USA) was installed in the waste line. The pressure differential across the needle valve was adjusted to match the prevailing column pressure drop to allow for switching without influencing the flow-rate delivered by the pump. All tubing used was Tefzel (Omnifit, Cambridge, UK). A feed loop of 2.58 ml was installed within the thermostated compartment of the PU4100 column oven accessory. The column effluent was led to an LDC Conductometer Mark III (LDC/Milton Roy, Riviera Beach, FL, USA). The conductivity signal was differentiated with respect to time using a differentiator built in-house and fed to a Philips PU6030 data capture unit. A Philips PU6000 integration system together with a P3202 computer were used for data processing.

Optionally, fractions could be collected using a Model 201 fraction collector (Gilson, Villiers le Bel, France). Collected fractions were analysed using a PU4100 chromatograph equipped with a PU4700 autoinjector.

Procedure

The set-up described in the previous section allows a five-position cyclic operation of the displacement system. In the following, the respective positions of the valves A, B, C and D are indicated in

parentheses (refer to Fig. 3). In the load position (2, R, R, R) the carrier solution is loaded on to the column. In the flush position (3, R, L, L) the carrier is flushed from the system and replaced by the displacer up to valve C. The total concentrations of carrier, feed and displacer typically range from 0.5 to 2.5 mM. In the feed position (3, L, R, R) the feed loop is filled using a large syringe with the feed solution by flushing with at least five feed-loop volumes. It should be noted that displacer solution is led to waste via the needle valve in the feed position. The run position (3, R, R, L) refers to the actual displacement separation. Flow-rates between 0.5 and 1.5 ml/min were used. After each displacement run, the column was regenerated (1, R, R, R) by flushing with a 0.1 M LiNO₃ solution for at least 30 min. The dead volume in the tubing was determined by replacing the column with a zero-dead-volume coupling.

Numerical calculations

A computer program was written to compute development graphs. The program decides whether a boundary is diffuse or self-sharpening. If only shocks are encountered, as in this study, all boundary trajectories can be calculated from jump relationships such as eqn. 26. Development graphs are then constructed for a number of preselected concentration ratios of the binary feed. The lengths of pure and mixed zones at the column exit are produced in a dimensional format to facilitate comparison with experimental results.

The input required by the program consists of operating parameters (column void fraction, column capacity, flow-rate, feed-loop volume, total concentrations in carrier, feed and displacer) and isotherm information. The multi-component isotherm used in this paper (eqn. 21) requires the specification of structural parameters, the compensation temperature of the class and the experimental temperature. The experimental temperature was specified as appropriate. The structural parameters for the class of alkali metal ions and the pertinent compensation temperature are listed in Table I.

TABLE I

VALUES FOR THE STRUCTURAL PARAMETERS f_{ij} OF THE COMPENSATION CLASS OF THE ALKALI METAL IONS ($T_c = 480$ K)

	Rb	K	Na	Li
Rb	0.0			
K	1.18	1.70		
Na	2.75	3.49	6.33	
Li	3.36	4.91	9.95	12.11

RESULTS AND DISCUSSION

In this section we compare experimental results with those computed using the techniques outlined in the Theory section. As these techniques are general and not restricted to ideal (Langmuir) isotherms, it is our aim to examine critically predictions obtained using different descriptions of the multi-component distribution equilibrium. In the experiments we confine ourselves to the displacement separation of binary mixtures of sodium and potassium. In all experiments Li was used as the carrier and Rb as the displacer.

The results of calculations are presented in the form of development graphs (see Fig. 4), *i.e.*, plots of dimensionless time (Ut/Z) vs. dimensionless position (z/Z). All the information required to compute a chromatogram at any time or place is contained in such a graph. Different characteristic points [*e.g.*, the point of complete separation (P)] can be read directly from the graph. Compositions pertaining to different positions in the graph can be calculated from the known location of shocks and simple waves. As can be seen from Fig. 4, and already noted in the Theory section, only shocks occur in our examples. All displacer concentrations will lead to the desired result of an isotachic train, so that separation always takes place. The displacer concentration can be used as the instrument to control the concentrations at which the pure feed components are eluted. In Fig. 4a, the concentration of the displacer is lower than that of the feed, in Fig. 4b the concentration of the displacer is equal to and in Fig. 4c higher than that of the feed. According to eqn. 23, three regions of different total concentration can be

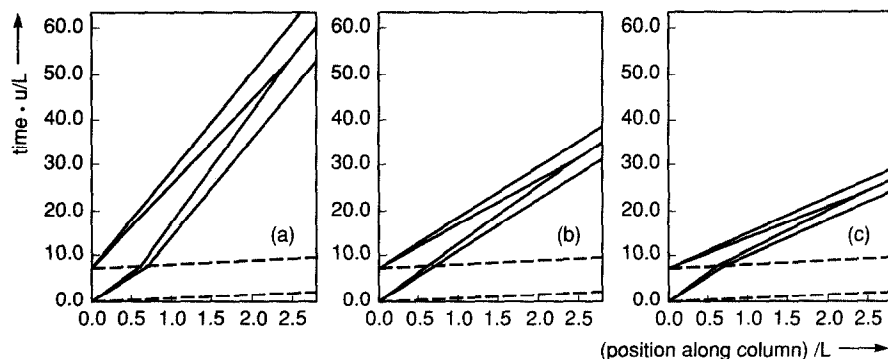


Fig. 4. Development graphs of the displacement separation of a binary mixture consisting of 1.0 mM KNO_3 and 1.0 mM NaNO_3 . The carrier is LiNO_3 (2.0 mM) and the displacer is RbNO_3 at concentrations of (a) 1.0, (b) 2.0 and (c) 3.0 mM. The column has a void volume of 0.349 ml and an ion-exchange capacity of 7.22 μequiv . The feed volume is 2.58 ml and the temperature 295 K. L is the column length and u is the linear velocity of the eluent.

distinguished. As all chromatographic velocities are smaller than U , the concentration of the displacer determines the concentrations in the separated zones. Pure zones become narrower and hence more concentrated at higher displacer concentrations, showing the capability of displacement chromatography to enrich sample components during separation.

In Fig. 5 the experimental results are illustrated, the first derivative of the conductivity signal being plotted against time. Compared with Fig. 4, displacement chromatograms refer to a position corresponding to the column outlet ($z = 1$). Our data correspond to the situation of incomplete separation, that is, the feed loaded is so large that the column length is insufficient for the attainment of

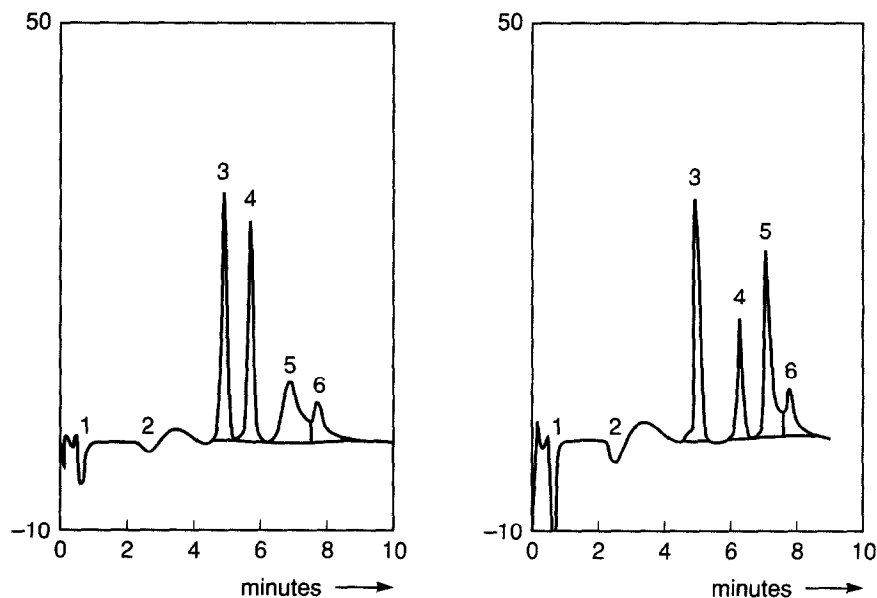


Fig. 5. Displacement chromatograms for two different K-Na mixtures on a Waters IC PAK C column (differentiated conductivity traces). The carrier was LiNO_3 (2.0 mM) and the displacer was RbNO_3 (2.0 mM). The feed was 2.58 ml of a solution containing 1.0 mM K-1.0 mM Na (right-hand side) and 0.6 mM K-1.4 mM Na (left-hand side). The flow-rate and the temperature were 1.0 ml/min and 295 K, respectively. The column had a void volume of 0.349 ml and an ion-exchange capacity of 7.22 μequiv .

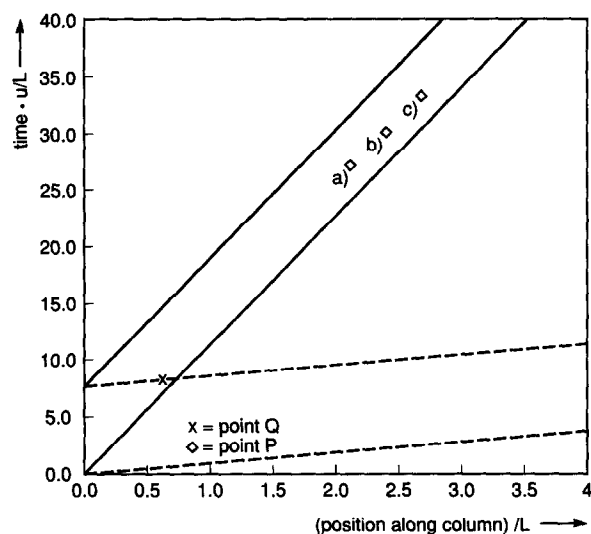


Fig. 6. Development graphs illustrating the shift of the point of complete separation with temperature [(a) 295 K; (b) 308 K; (c) 317 K] of a 1.0 mM K–1.0 mM Na mixture. The displacer is 2.0 mM RbNO₃. Other conditions as in Fig. 4.

the isotachic state. In terms of Fig. 4, the column outlet is to the left of the point of complete separation (P). On the left-hand side of Fig. 5, a displacement chromatogram of a 1.0 mM K–1.0 mM Na mixture is shown, and on the right-hand side, a chromatogram of a 0.6 mM K–1.4 mM Na mixture. The peaks numbered 3, 4 and 5 refer to the shocks from the carrier state to the pure Na state (3), the pure Na state to the mixed feed state (4) and from the mixed feed state to the pure K state. Peak 6 refers to the shock from pure K to the displacer Rb (5). Peaks 1 and 2 correspond to small changes in the total concentration that are experimentally inevitable. According to eqn. 10, they travel at the velocity of the eluent U and hence emerge at t_0 and $t_0 + t_e$. The distances between the peaks, called zone lengths and measured in millilitres of effluent, correspond to the amounts in the different states. In the following, these experimental zone lengths will be compared with predictions using different multi-component distribution functions. It should be realized that when complete separation is attained, *i.e.*, to the right of point P in Fig. 4, zone lengths are no longer a critical test of the distribution function used to model the separation.

Let us first investigate the influence of tempera-

TABLE II

COMPARISON OF CALCULATED ZONE LENGTHS (USING THE ISOTHERM OF EQN. 21 WITH EXPERIMENTALLY DETERMINED VALUES

T (K)	Na zone length (ml)	Mixed zone length (ml)	K zone length (ml)
295 (exp.)	0.64	1.25	0.65
295 (calc.)	0.64	1.30	0.64
308 (exp.)	0.60	1.40	0.57
308 (calc.)	0.57	1.44	0.57
317 (exp.)	0.56	1.46	0.54
317 (calc.)	0.53	1.52	0.53

ture. In Fig. 6, the development graphs for the separation of an Na–K mixture are given for three different temperatures. It is seen that separation becomes more difficult as temperature is increased, *i.e.*, the point of separation moves to longer column lengths. Numerical results are presented in Table II. A good comparison between the experimental results and those calculated using the multi-component isotherm of eqn. 21 is observed. The result is understandable. As the alkali metal ions belong to the same compensation class, they have, by definition, a common compensation temperature (in this case 480 K). At this temperature the stationary phase composition is equal to the mobile phase composition for all mobile phase compositions, so that all selectivity is lost. Hence, on going from low temperatures towards the compensation temperature, selectivity factors become progressively smaller, making the column length and time required for a complete separation longer.

We now compare the performance of the multi-component Langmuir isotherm with the isotherm of eqn. 21. Langmuir data used for the K–Na exchange were obtained by fitting frontal chromatography measurements published previously [23] to the Langmuir equation. The values used for N and α were 7.22 μmol and 0.66, respectively. In Fig. 7, the development graphs for the cases of the Langmuir isotherm and the isotherm of eqn. 21 are depicted on the left- and right-hand side, respectively. The open squares refer to the points of complete separation (P). In each plot, there are eleven such points referring to eleven equidistant K/Na ratios in the

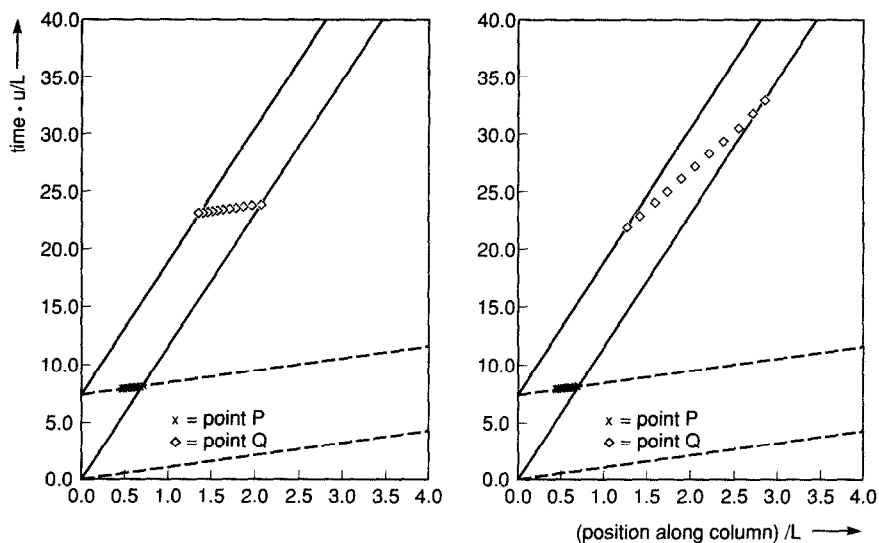


Fig. 7. Development graphs for eleven different K-Na mixtures computed using a multi-component Langmuir isotherm (left-hand side) and the isotherm of eqn. 21 (right-hand side). The points of complete separation correspond to eleven equidistant K/Na ratios in the feed ranging from 0.0 to 1.0. The total feed concentration is 2.0 mM, as is the concentration of RbNO_3 displacer. Other conditions as in Fig. 4.

feed ranging from 0.0 to 1.0. The difference between the two is apparent. In the Langmuir case, the point of complete separation is only a weak function of the feed composition, whereas a much stronger dependence on the K/Na ratio is observed for the multi-component isotherm in which interactions in the stationary phase are taken into account. Column

lengths required for complete separation *ca.* 50% higher are predicted in the latter instance for high potassium contents in the feed. In Fig. 8 the experimental results are compared with the predictions of both models. The lengths of the different zones (in millilitres) are plotted as a function of the composition of the binary feed. The left-hand side

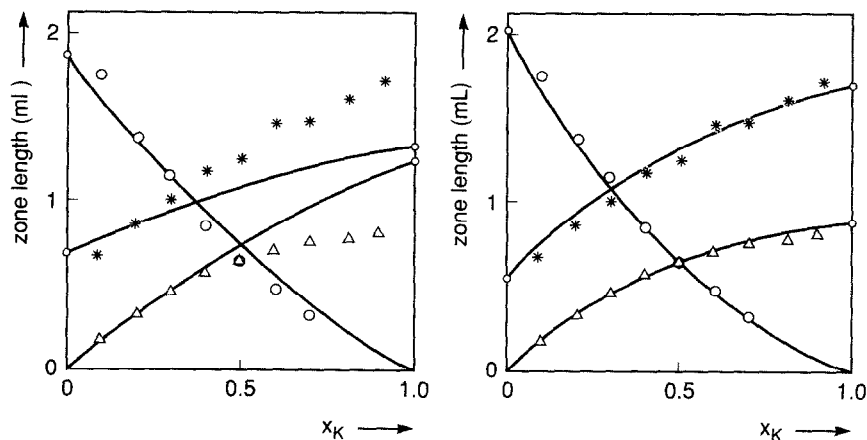


Fig. 8. Lengths of zones in the displacement separation of K-Na mixtures as a function of the potassium content of the feed. Curves in the left-hand figure are computed using a multi-component Langmuir isotherm and in the right-hand figure using the isotherm of eqn. 21. The symbols represent experimental data. Three different zone lengths can be distinguished: (\circ) the pure Na zone, ($*$) the mixed zone and (\triangle) the pure K zone. Total concentrations in carrier, feed and displacer were all 2.0 mM. Other conditions as in Fig. 5.

shows the lengths calculated using the Langmuir model, the right-hand side those calculated using the isotherm of eqn. 21. Small open circles on both the Na and K axes represent the limiting lengths of the mixed zone at very small and very high potassium contents, respectively. We feel that the results are convincing: the multi-component distribution isotherm of eqn. 21 shows good agreement with the experimental data over the complete composition range, whereas the Langmuir isotherm predicts experimental results correctly over only a limited composition range. The particular range of fit for the Langmuir isotherm strongly depends on the way Langmuir parameters are extracted from the experimental data, e.g., α -values obtained from a fit to the complete isotherm are significantly different from those derived from linear elution chromatographic data. A good prediction over the complete feed composition range is not possible, which reflects the insufficiency of the multi-component Langmuir equation to represent the competitive sorption behaviour.

From Figs. 7 and 8, it is seen that the errors made by using too simple an expression for the distribution isotherm are substantial. Research aimed at obtaining improved descriptions of competitive sorption is sparse, however [30]. As remarked in the Introduction, understanding the sorption process is the key to understanding chromatographic separations. We firmly believe that better descriptions of the distribution equilibrium, such as the isotherm of eqn. 21, are a prerequisite for the quantitative modelling of non-linear separations. Attempts to fine-tune the continuity equations by adding dispersive terms seem dubious as long as inadequate descriptions of the distribution equilibrium are used.

CONCLUSIONS

The traditional way of solving the coupled set of mass-balance equations that apply to the transport problem in displacement chromatography (*i.e.*, using the h - or ω -transformation) cannot be used if the multi-component isotherm describing the distribution between mobile and stationary phases is non-ideal.

For the separation of binary mixtures, the mass-balance equations can be solved for non-ideal isotherms using shock-wave theory, provided that

the continuity equations are recast in terms of stationary phase concentrations and that the total concentration in the stationary phase is known at every time and place.

Experimental results for the ion-exchange separation (total concentration in the stationary phase constant) of binary mixtures are only properly described across the complete composition range if non-idealities are taken into account. In extreme cases, ideal sorption behaviour predicts the column length required for complete separation to be *ca.* 50% too short.

For the quantitative modelling of displacement chromatography, multi-component distribution isotherms better than the ideal approximation are a prerequisite.

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