Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Equilibrium Principle of Displacement Chromatography

Kunihiko Takeda[a]; Hatsuki Onitsuka[a]; Heiichiro Obanawa[a]; Fumiaki Kawakami[a]; Mitsunaga Sasaki[a]
[a] URANIUM ENRICHMENT LABORATORY ASAHI CHEMICAL INDUSTRY CO., LTD., HYUGA-SHI, JAPAN

To cite this Article Takeda, Kunihiko , Onitsuka, Hatsuki , Obanawa, Heiichiro , Kawakami, Fumiaki and Sasaki, Mitsunaga(1988) 'The Equilibrium Principle of Displacement Chromatography', Separation Science and Technology, 23: 14, 2329 — 2347

To link to this Article: DOI: 10.1080/01496398808058457

URL: http://dx.doi.org/10.1080/01496398808058457

SEPARATION SCIENCE AND TECHNOLOGY, 23(14 & 15), pp. 2329-2347, 1988

The Equilibrium Principle of Displacement Chromatography

KUNIHIKO TAKEDA, HATSUKI ONITSUKA,
HEIICHIRO OBANAWA, FUMIAKI KAWAKAMI, and
MITSUNAGA SASAKI

URANIUM ENRICHMENT LABORATORY
ASAHI CHEMICAL INDUSTRY CO., LTD.
1-1 TAKESHIMA, HYUGA-SHI 883, JAPAN

Abstract

Displacement chromatography, an alternate method to elution chromatography in terms of operation, is described. The principle of displacement is conveniently explained using the concept of an "addend" which is regarded as a species essential to any equilibrium reaction consisting of association of two species and its reverse reaction. Microscopic equilibria in a chromatographic column can be characterized by use of reduction potential strengths ($\Delta\mu^\circ$ and $\Delta\mu$) and its derived quantities, S and L potentials that we introduced for expression of equilibria. The method for evaluating the separation factor of displacement chromatography is also described. Further, a profile of simulated separation produced by iterative applications of the distribution function to the multistage equilibrium in the column is presented.

INTRODUCTION

The kinetic principles and theory of chromatography have been fully studied and developed by Giddings (*1*) and other workers and successfully applied to a number of experiments. More specific discussions have been directed to some fields of chromatography, such as ion exchange (*2*) and isotope separation (*3*).

For the equilibrium principles and the theory of chromatography, a simple case of linear distribution was described by Rieman and Walton (*4*). Helfferich and Klein (*5*), using separation factors, made a full theoretical analysis of nonlinear chromatography involving multiple components which interfere with their mutual sorption, referring to various assumable cases of displacement as well as elution. At nearly the same time, a more mathematical analysis of similar nonlinear systems was made using Langmuir isotherm parameters by Amundson et al. (*6*). However, chromatographic systems dealt with by these references are restricted to those involving only sorption/desorption equilibria of relevant species with no other type of equilibrium. As far as displacement chromatography is concerned, they do not refer to a means to predict how displacement can be established for separation of a given sample mixture. Furthermore, since those treatments use equilibrium constants, the order of simultaneous equations is identical to the number of sorption/desorption equilibria involved, making it rather hard to attain a single, true answer for multicomponent systems.

This study considers, in terms of thermodynamics, whether or not systems involving concurrence of various reactions, such as complexation, redox, and so forth, in addition to sorption/desorption, may undergo displacement operation. Some examples of displacement are presented together with a novel theoretical approach which may simplify equilibrium calculations.

THE ADVANTAGES OF DISPLACEMENT CHROMATOGRAPHY

As a separation method, elution chromatography is more common than displacement chromatography. This is because the former can achieve a higher degree of separation and is easier to operate due to a higher degree of freedom. In displacement chromatography, the entire adsorption band of sample components to be separated has to be kept constant in length during migration through the bed, while in elution chromatography the individual adsorption bands are allowed to broaden during migration. It follows that the concentrations of components should be much higher in displacement development. The calculated results of the degree of separation and concentration of a component are exemplified for the two operating methods in Figs. 1a and 1b, respectively. Here, the chromatographic column was supposed to be subdivided into many stages horizontally for stepwise calculations, and each stage was supposed to consist of the stationary and mobile phases occupying 25 and 75% by volume, respectively, based on the total volume of the stage. In the displacement, the selectivity constants of two components to be separated based on the front circulating agent were set at 10.0 and 10.1

while their corresponding constants based on the rear circulator were equally set at 55.0. Under these conditions, the degree of separation and concentrations were calculated as the number of stages passed by the rear circulator was varied. In the elution, the selectivity constants of two components to be separated based on the developing agent were set at 10.0 and 10.1. As is well known, a single developer is used in elution while two different developers are used as front and rear circulators in displacement, as described above.

Figures 1a and 1b reveal that displacement gives rise to a lower degree of separation but a much higher concentration of a recovered component. For example, if it is intended to obtain the target component at a separation degree of 5.0, development by 20,000 steps may be necessary for displacement, compared with 7000 steps for elution. This means that displacement may require approximately threefold the time of separation. On the other hand, the concentration ratio of the eluate to the feed for displacement is 1.0, much higher than that for elution which is about 0.015 on the average.

Avoidance of high dilution (approximately sixty-sevenfold dilution) of the feed to the effluent volume may well be considered to be more than compensation for the threefold time of separation. In short, elution is more suitable for analytical separations where emphasis is placed on degree of separation rather than concentration, while displacement is more advantageous for industrial separations which require production-scale fractionations.

THE CONCEPT OF AN "ADDEND"

In order to explain the principles of displacement chromatography, the new concept of an "addend" is used (*7*, *8*), as discussed in the next paragraph. Suppose that various reactions, such as acid-base, redox, and complex formation, occur simultaneously in the liquid phase in a chromatographic column. These reactions as well as ion exchange and other adsorptions can be expressed in a similar additive form as follows:

1. Redox reaction:

$$M^{m+} + \nu \cdot e^{-} \rightleftharpoons \mathrm{M}^{(m-\nu)+} \qquad (1)$$

2. Complex-formation reaction:

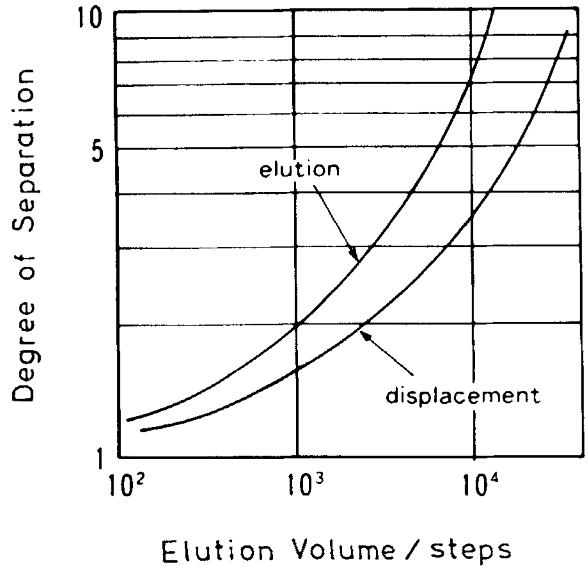

FIG. 1a. Comparison between elution and displacement, indicated by dependence of the degree of separation on elution volume in the case of the separation factor ε = 0.01.

$$(\mathrm{M}\cdot\mathrm{L}_n)^{\nu-} + \mathrm{L}^{l-} \rightleftharpoons (\mathrm{M}\cdot\mathrm{L}_{n+1})^{(\nu+l)-} \tag{2}$$

3. Acid-base reaction:

$$\text{Base} + \mathrm{H}^+ \rightleftharpoons \text{acid} \tag{3}$$

4. Ion-exchange reaction:

$$(\mathrm{M}\cdot\mathrm{L}_n)^{\nu-} + \nu\cdot\mathrm{R}^+ \rightleftharpoons (\mathrm{M}\cdot\mathrm{L}_n)\cdot\mathrm{R}\nu \tag{4}$$

5. Chelating-resin reaction:

$$\mathrm{M}^{m+} + \mathrm{R}_\mathrm{L}^{l-} \rightleftharpoons \mathrm{M}\cdot\mathrm{R}_\mathrm{L}^{(l-m)-} \tag{5}$$

6. Physical adsorption:

$$\mathrm{M} + \nu\cdot\mathrm{As} \rightleftharpoons \mathrm{M}\cdot(\mathrm{As})\nu \tag{6}$$

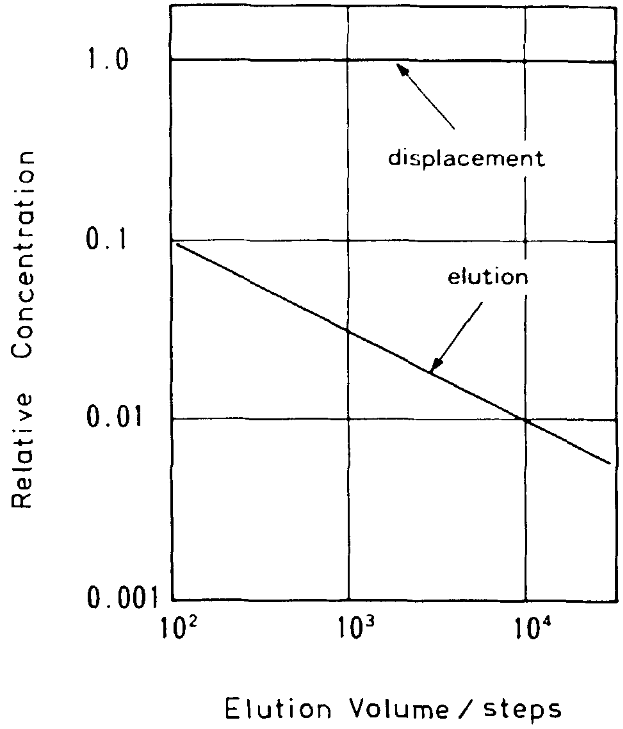

FIG. 1b. Comparison between elution and displacement, indicated by dependence of the concentration of a component to be separated on elution volume.

where M^{m+}, M, L^{l-}, R^+, R_L^{l-}, and As represent a metal ion, a molecule, a ligand, a fixed ionic group, a fixed chelating group, and an adsorption site, respectively, and ν is commonly used to denote both the stoichiometric coefficient of a reaction and the charge number of a metal-complex ion.

Not only these six reactions but other ones occurring in solution can be expressed uniformly as

$$A + \nu X \rightleftharpoons D \tag{7}$$

where A and D denote an acceptor and an adduct, respectively, and X is termed an "addend," which represents an electron, a ligand, a proton, a fixed ionic group, a fixed chelating group, or an adsorption site, depending on the type of reaction involved. Equation (7) implies that the equilibrium state of each reaction can be expressed as

$$\Delta\mu_X = \Delta\mu^\circ_{X,A/D} + \frac{RT}{\nu}\ln(a_A/a_D) \tag{8}$$

where

$$\Delta\mu_X \equiv \mu^\circ_X - \mu_X \tag{9}$$

and

$$\Delta\mu^\circ_{X,A/D} \equiv \mu^\circ_X + \frac{1}{\nu}(\mu^\circ_A - \mu^\circ_D) \tag{10}$$

and where μ°_X, μ°_A, and μ°_D are the standard chemical potentials of X, A, and D. $\Delta\mu_X$ and $\Delta\mu^\circ_{X,A/D}$ are termed here the reduction potential strengths at any given state and at the standard state. (The subscripts of these symbols will be omitted hereafter unless necessary.) Table 1 lists $\Delta\mu$ and $\Delta\mu^\circ$ for various reactions represented by activities and various kinds of equilibrium constant including redox potential, acidity constant, and stability constant (*9*).

It is quite common that redox reactions and complexation are directly expressed in an additive form like Eq. (7). But it may seem strange to express ion exchange in this manner since it is generally represented by the form $A + \nu X = D + C$. Obviously a fixed ionic group of ion-exchange resin is accompanied by the equivalent charge of counterions, which has traditionally required ion exchange to take the above form

TABLE 1

Expressions of $\Delta\mu$ and $\Delta\mu^\circ$ in Terms of Conventional Physicochemical Constants and Quantities[a]

Type of reaction	Addend	$\Delta\mu$	$\Delta\mu^\circ$
Redox	Electron	FE	FE°
Acid/base	Proton	$fRT \cdot \mathrm{pH}$	$-f(RT/\nu)\mathrm{p}K_a$
Complexation	Ligand	$fRT \cdot \mathrm{pL}$	$-f(RT/\nu)\mathrm{p}K_L$
Anion exchange	Resin-fixed anion	$-RT\ln a_R$	$(RT/\nu_R)\ln K$
Cation exchange	Resin-fixed cation	$-RT\ln a_R$	$(RT/\nu_R)\ln K$
Chelation	Resin-fixed chelating group	$-RT\ln a_R$	$(RT/\nu_R)\ln K$
Precipitation	Counterion	$-RT\ln a$	$-f(RTn/m)\mathrm{p}K_{SP}$
Biphasic liquid equilibrium	Solvent	$-RT\ln a$	$(RT/\nu)\ln K$

[a] $f = 2.303$.

where a fixed ionic group or groups are always associated with a counterion. But, as is well known, Nernst teaches us to express a redox reaction in the additive form Ox + ne^- $\rightleftharpoons$ Red, regardless of the fact that no electron exists in solution by itself and that another pair of redox species must be involved in the system. And an intensive quantity, redox potential, derived from the above additive form, is conveniently used to characterize the thermodynamic property of any redox system concisely. In this analogy it is not irrational for ion exchange to be regarded as the combination of two concurrent reactions which are no more divisible and exemplified by $A_1^- + R^+ \rightleftharpoons A_1 \cdot R$ and $A_2^- + R^+ \rightleftharpoons A_2 \cdot R$, A_1^- and A_2^- being different exchangeable anion species. Therefore, if a reference exchangeable ion like Cl^- is supposed, ion exchange of a complex ion generally expressed as

$$(M \cdot L_n)^{\nu-} + \nu R^+Cl^- \rightleftharpoons (M \cdot L_n)R\nu + \nu Cl^- \tag{11}$$

can be simply written as Eq. (4).

In a multi-equilibrium system where a number of liquid-phase and liquid/solid biphasic reactions occur simultaneously with a number of chemical species present, the distribution of each species, acting as the adduct in Eq. (7), can be calculated by multiple use of Eq. (8). That is, the distribution function of any one species of interest is written as

$$T_{i,n_j} = \exp\left((S_P - L_P)/RT\right) \tag{12}$$

where

$$S_P \equiv \sum_j \sum_{n_j} (\nu_{i,n_j} \Delta\mu^\circ_{i,n_j}) \tag{13}$$

and

$$L_P \equiv \sum_j \sum_{n_j} (\nu_{i,n_j} \Delta\mu_j) \tag{14}$$

and where i and j denote a given "bare" species acting as the initial acceptor and an arbitrary addend, respectively, and n_j denotes the order of stepwise association of the jth addend with the species i. The symbols ν_{i,n_j} and $\Delta\mu^\circ_{i,n_j}$ are the abbreviations of $\nu_{i,(n_1,n_2,\ldots,n_j,\ldots,n_J)}$ and $\Delta\mu^\circ_{i,(n_1,n_2,\ldots,n_j,\ldots,n_J)}$ which have the respective orders of stepwise association, n_1, $n_2, \ldots,$ $n_j, \ldots,$ and n_J, for all the addend species, 1, 2, ..., j, ..., and J, and indicate the stoichiometric coefficient and standard reduction potential strength, respectively, for the association reaction,

$$A_{i,n_j-1} + \nu_{i,n_j} \cdot j \rightleftharpoons A_{i,n_j} \tag{15}$$

where $n_j = 1, 2, \ldots, N_j$, with N_j being the maximum association number of addend j to the species i, and A_{i,n_j-1} and A_{i,n_j} denote the acceptor and the adduct, and their subscripts have the same meaning as in ν_{i,n_j} or $\Delta\mu^{\circ}_{i,n_j}$.

Equation (12) is very comprehensive because the species of interest hold a plural number of addends of any kind j. The L_P, termed L-potential, is given by the sum of the individual potential strengths $\Delta\mu_j$ for this multi-equilibrium system, while the S_P, termed S-potential, is that of the individual standard potential strengths $\Delta\mu^{\circ}_{i,n_j}$ of the equilibrium reactions involved. Two important features of Eq. (12) are summarized in the following statements. One is that the sum total of standard reduction potential strengths $\Delta\mu^{\circ}_{i,n_j}$, which refer to such various types of equilibrium as acid-base, redox, complex formation, and ion exchange, can govern the distribution of any adduct species regardless of their normally different, physicochemical treatments. Another is that $\Delta\mu_j$ or, more commonly, the activities of addends are the only factor that can be varied to adjust the distribution of the species because $\Delta\mu^{\circ}_{i,n_j}$ is predetermined for each equilibrium reaction.

The procedure for determining the concentration of an individual adduct species, C_{i,n_j}, is described as follows for a multi-equilibrium system where a plural number of different metal ions as acceptor are present together with a plural number of addend species. Here, activity is supposed to be equal to the concentration for simplicity. C_{i,n_j} is given by the relation

$$C_{i,n_j} = \frac{C_{i,T} T_{i,n_j}}{\sum_{j=1}^{J} \sum_{n_j=0}^{N_j} T_{i,n_j}} \tag{16}$$

where $C_{i,T}$ is the total concentration of the ith metal species. Since the values of $C_{i,T}$, J, and N_j are all given, C_{i,n_j} is determined by the distribution function T_{i,n_j}. And T_{i,n_j} is a function of $\Delta\mu_j$ or concentrations of relevant free addends, $C_{j,0}$. After all, C_{i,n_j} is a function of $C_{j,0}$. So, the next thing to be done is to indicate how $C_{j,0}$ is determined.

In order to consider the material balance of a given addend species j, a function indicating it is formulated as

$$f_j = \sum_{i=1}^{I} \sum_{n_j=1}^{N_j} \nu_{i,n_j} C_{i,n_j} + C_{j,0} - C_{j,T} \tag{17}$$

where $C_{j,T}$ is the total concentration of addend j and is predetermined. Because C_{i,n_j}, given by Eq. (16), is a function of $C_{j,0}$, and because v_{i,n_j} is predetermined, f_j is also a function of $C_{j,0}$. Since f_j should be zero, convergence calculations of f_j to zero should yield the true root of $C_{j,0}$. The calculations should be executed in parallel with those with respect to all other addend species because their free concentrations affect the results of calculation with respect to the individual addend j. This procedure is suitable for iterative calculations for hundreds of equilibrium stages which may amount to more than ten thousand times, because the function T_{i,n_j} increases smoothly, making it easy to attain the answer. At any rate, the paired expression of ion exchange as well as other reactions involved makes multi-equilibrium systems much more wieldy in combination with the additivity of $\Delta\mu^\circ$ and $\Delta\mu$.

THE EQUILIBRIUM PRINCIPLE OF DISPLACEMENT CHROMATOGRAPHY

(1) Formation of Boundaries and an Adsorption Band

In displacement chromatography, the adsorption band of a substance to be separated must be confined between the front and rear boundaries. A schematic diagram of the mechanism of displacement is illustrated in Fig. 2. Formation of boundaries before and behind the adsorption band to inhibit the substance from diffusing out of it is the prerequisite for displacement. In Fig. 2, species F and B are used for forming the adsorption band of species M to be separated, and species X is an addend in this chromatographic system. Now it is supposed that species M represents collectively all the sample components to be separated. The sorbable species M is desorbed at the moment it accepts X, while it is adsorbed on releasing X. The addend donor B, which has a lower affinity for X than for M, is supplied above the band in the form of BX. At the rear boundary, B gives X to the adsorbed M, resulting in its desorption. The formed species MX is carried down by the solution, going through the band. In front of the band is placed previously the addend acceptor F, which has a higher affinity for X than for M. At the front boundary, F strips MX of X, allowing the freed M to be adsorbed.

It should be noted that species B, M, and F in Fig. 2 all correspond to the acceptor A used in Eq. (7), while BX, MX, and FX all belong to the adduct D used in the same equation. Although B, M, and F are each the acceptor of each association reaction, in their mutual relation B must be

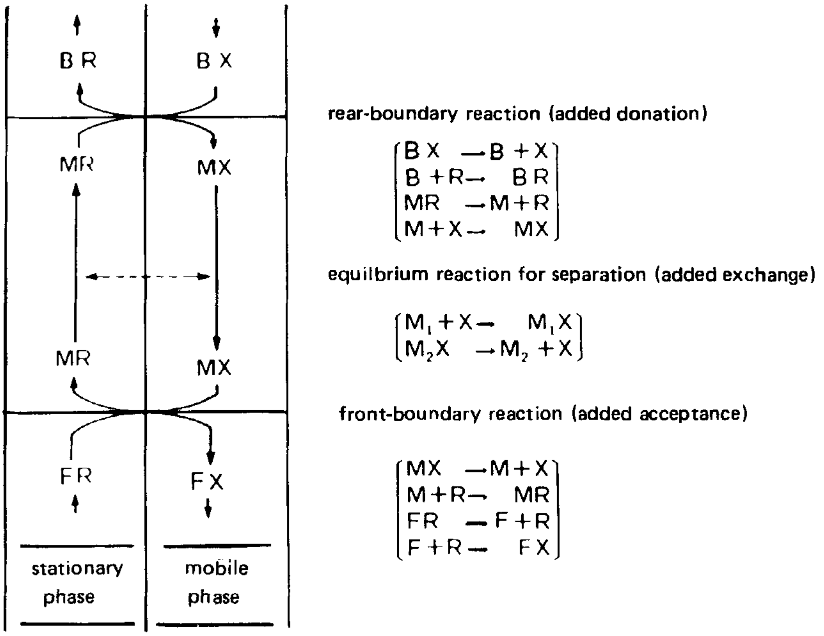

FIG. 2. Mechanism of displacement and reactions in the three regions of an adsorption band. M and M_i (i = 1, 2) denote any component and an individual component to be separated, and X, B, and F denote an addend, an addend donor, and an addend acceptor.

X-donating against M while F must be X-accepting against M. This donation/acceptance capability is determined by a difference in $\Delta\mu^{\circ}_{\mathrm{X,A/D}}$ (see Eq. 10) between the addend acceptors (B and M, or M and F). Generally speaking, if the different in $\Delta\mu^{\circ}$, denoted simply by $\Delta(\Delta\mu^{\circ})$, is not less than 2 kJ/mol, then a boundary is formed sharply enough to operate displacement.

In the upper right of Fig. 2, reactions of individual species at the rear boundary are shown, and in the lower right those at the front boundary. In the middle right it is shown that in the adsorption band, exchange of X or its competitive acceptance occurs between different species (denoted by M_1 and M_2) representing individual components to be separated.

Examples of displacement and elution are represented in Table 2 by sets of an addend, a donor, and an acceptor involved. In elution the addend donor for components to be separated is identical to the addend acceptor. This necessitates the value of $\Delta(\Delta\mu^{\circ})$ for either boundary to be

TABLE 2

Three Fundamental Species in Some Specific Cases of Displacement Chromatography

Components to be separated	Main sorbable species	Addend[a]	Donor	Acceptor	Mode of chromatography
Metal complex ions	$MCl_n^{-(n-m)}$	R^{+} [b]	Cl^-	Cl^-	Elution
Rare earth elements	R_E^{3+}	$R(COO^-)_n$ [c]	NH_4^+	Cu^{2+}	Displacement
Carbon isotopes	HCO_3^-	H^+	Cl^-	OH^-	Displacement
Uranium isotopes	$UO_2(VI)Cl_n^{-(n-2)}$	e^-	TiO^{2+}	Fe^{3+}	Displacement

[a] The discriminative addend.

[b] A fixed ionic group.

[c] A dissociated aminopolycarboxylic acid.

smaller than 2 kJ/mol, resulting in its broadening. The situation is opposite in displacement where both boundaries are formed very sharply. In a chromatographic system of rare earth ions using NH_4^+ (as B) and Cu^{2+} (as F), and in that of carbon isotopes using Cl^- (as B) and OH^- (as F), respectively, displacement can be established. Another example of displacement shown in Table 2 is a redox chromatography system for separation of uranium isotopes (*10*). In this case an electron, a TiO^{2+} ion, and a Fe^{3+} ion are used as the addend, species B and F, respectively. However, a TiO^{2+} ion is supplied in the form of BX, or the associated species of TiO^{2+} plus e^-, which is nothing but Ti^{3+}, because a free electron is very transitory.

L- and S-potentials (see Eqs. 12 to 14) can be used to foresee more quantitatively if two boundaries and an adsorption band are formed in a specified chromatographic system. Calculations of multistage equilibria are again based on the distribution function. It is supposed that a large number of stages are formed by horizontal subdivision of the column and that an individual equilibrium is set up on each stage (*11*). Equilibrium calculations are executed for every stage from the first one to the last, which constitutes one-step calculations, and then shifts to the next step. This stepwise shift corresponds to a chromatographic operation termed "development." That is, completion of the one-step calculations is followed by an imaginary descent of the solution by the height of a stage. This means that the portion of the solution on the lowest stage is pushed out of the column. This effluent corresponds to a portion of effluent observed in actual operation. At the same time, the liquid-phase volume of the first stage, which is now vacant, is supposed to be refilled with the feed developer solution. The equilibrium calculations are then repeated for all stages as the second step. Such iteration of equilibration-and-shift cycles simulates the actual chromatographic operation.

Figure 3 shows L-potentials of imaginary fractions eluted stepwise (*12*). Here, a carbon-isotope separation system is exemplified in order to predict distribution of the carbonic species involved. L_P was determined by computer-aided simulating calculations for each step of imaginary development. In the notation $L_P(m,n)$ and $S_P(m,n)$ $(0 \leqslant m, n \leqslant 2)$, the first number in parentheses refers to the association number of OH^- to aqueous carbon dioxide H_2CO_3 and the second one to that of fixed-ionic groups RN^+. Thus, $L_P(1,0)$ refers to L_P of a bicarbonate ion since H_2CO_3 plus OH^- is euqal to $H_3CO_4^-$ or HCO_3^- plus H_2O. In a similar manner it can be understood that $L_P(2,0)$, $L_P(1,1)$, and $L_P(2,2)$ indicate CO_3^{2-}, $RN^+ \cdot HCO_3^-$, and $(RN^+)_2 \cdot CO_3^{2-}$, respectively. It should also be noted that the potential difference, $S_P - L_P$, of a given adduct indicates how stable it is.

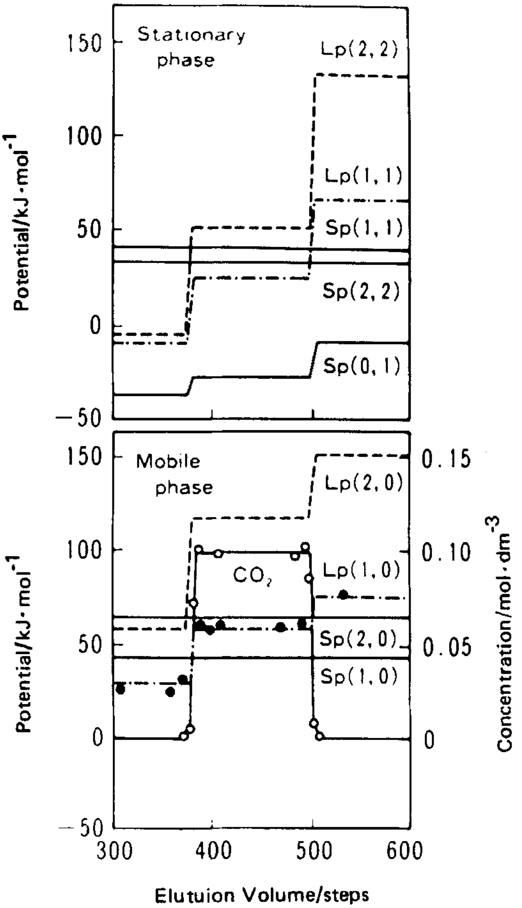

FIG. 3. Variation of L potentials with elution volume during imaginary stepwise elution.

The simulation shown in Fig. 3 started with imaginary feeding of a carbon dioxide solution to the top of a column which is packed with anion-exchange resin regenerated in advance by an alkaline solution. In the steps from the 380th to the 500th, CO_2 is considered to be the main carbonic species in the mobile phase since $S_P(1,0) < L_P(1,0)$ and $S_P(2,0) < L_P(2,0)$, while HCO_3^- is considered to be predominant in the stationary phase from the relations $S_P(1,1) > L_P(1,1)$, $S_P(2,2) < L_P(2,2)$, and most probably $S_P(0,1) \ll L_P(0,1)$. In the steps up to the 370th, HCO_3^- could be the main mobile-phase species since the $S_{SP}(1,0) \sim L_P(1,0)$ relation is reversed to $S_{SP}(1,0) > L_P(1,0)$, which means descending CO_2 may be transformed to HCO_3^-. However, most of the HCO_3^- ions in the mobile phase will not stay there but will migrate into the stationary phase from the relation $S_P(1,1) \gg L_P(1,1)$, resulting in the foramtion of the front boundary. Passing the 500th step, the stationary-phase bicarbonate ions will disappear because the potential difference $S_P(1,1) - L_P(1,1)$ turns negative. Carbon dioxide also disappears rapidly from the mobile phase. This rapid disappearance of all carbonic species ensures the formation of the rear boundary around the 500th step. After the 500th step, bicarbonate ions on the resin are desorbed, undergoing simultaneous transformation to carbon dioxide, which then flows downward.

(2) Fundamental Separation Equilibrium

It is addends that play a central role in displacement chromatography because they govern the behavior of components toward separation. They determine how both boundaries of an adsorption band are formed and how efficiently separation is attained in terms of equilibrium considerations. In this section, equilibrium reactions in solution, capable of biasing components to be separated, are described. These equilibria are fundamental in considering separation of a mixture of displacement chromatography. Therefore, they may be also termed "fundamental sepration equilibria." For example, a separation equilibrium in solution can be observed between ions of different rare earth elements (like Nd^{3+} and Pr^{3+}) through a chelating agent, which was investigated by Spedding (*13*) in their first successful chromatographic separation using a strong acid cation-exchange resin. This exchange reaction is conventionally expressed as

$$Nd^{3+} + Pr^{3+} \cdot R(COO^-)_n \rightleftharpoons Nd^{3+} \cdot R(COO^-)_n + Pr^{3+} \qquad (18)$$

where $R(COO^-)_n$ is a dissociated aminopolycarboxylic acid [as in ethylenediaminetetraacetic acid (EDTA)] acting as an addend. Equation (18) can be divided into a pair of individual reactions like Eq. (5):

$$Nd^{3+} + R(COO^-)_n \rightleftharpoons Nd^{3+} \cdot R(COO^-)_n \qquad (19)$$

$$Pr^{3+} + R(COO^-)_n \rightleftharpoons Pr^{3+} \cdot R(COO^-)_n \qquad (20)$$

Another example of separation equilibria in solution can be observed between carbon isotopes making up aqueous carbon dioxide. Since aqueous carbon dioxide is denoted by H_2CO_3, it can be represented as

$$H_2{}^{13}CO_3 + H^{12}CO_3^- \rightleftharpoons H_2{}^{12}CO_3 + H^{13}CO_3^- \qquad (21)$$

where the isotopic equilibrium constant is about 1.012. Using a proton as the addend, Eq. (21) can be divided into a pair of individual reactions like Eq. (3):

$$H^{12}CO_3^- + H^+ \rightleftharpoons H_2{}^{12}CO_3 \qquad (22)$$

$$H^{13}CO_3^- + H^+ \rightleftharpoons H_2{}^{13}CO_3 \qquad (23)$$

Equations (19), (20), (22), and (23) are all unified into the additive form Eq. (7) described above. An addend species taking a part in a separation equilibrium, like $R(COO^-)_n$ in Eqs. (19) and (20) and H^+ in Eqs. (22) and (23), can be specifically termed a "discriminative addend" since it discriminates between components to be separated, playing a critical role in separation among other addend species. When it is intended to separate different but chemically similar ions or compounds, the first thing to be done is to select a discriminative addend which has different affinities for them.

As described above in referring to Fig. 2, the ability of the acceptors B, M, and F to accept the addend X increases in the order B < M < F. This sequence can be expanded to indicate the relative accepting abilities of individual species $M_1, M_2, \ldots, M_i$, that is, $B < M_i < \ldots < M_2 < M_1 < F$ where the band of each component progresses in the increasing order of subscript numbers. The expanded sequence implies that separation of these species can be explained similarly to the boundary formation of an adsorption band as described above. However, their addend-accepting abilities are similar in magnitude, resulting in the formation of adsorption bands with some inevitable overlapping between neighboring bands.

The capability of a chromatographic system to separate components generally originates from a difference in affinity for the adsorbent. Such a difference can be directly observed in a system using a chelating resin for separating rare earth ions because fixed chelating groups themselves are the discriminative addend. The situation is not so simple in general cases because the discriminative addend is not always a fixed addend on the resin.

Consider a separation system where only two components to be separated are present together with no addend other than a discriminative addend, which may be appropriately termed an "ideal separation system." The fundamental separation equilibrium can be expressed as

$$K_0 = 1 + \varepsilon_0 = \frac{x_2/x_3}{y_2/y_3} \tag{24}$$

where ε_0 can be termed the "inherent" separation factor, and $x_2 = [M_1]$, $x_3 = [M_1X]$, $y_2 = [M_2]$, and $y_3 = [M_2X]$, all expressed in units of mole/liter. However, in actual chromatographic systems there are a number of addend species present besides the discriminative addend. For example, in the case of uranium isotope separation by redox chromatography, an electron is the discriminative addend and a fixed ionic group is among the other addends. The overall separation equilibrium attained through ion exchange can be expressed as

$$K_s = 1 + \varepsilon_s = \frac{(x_1 + x_4)/(x_2 + x_3)}{(y_1 + y_4)/(y_2 + y_3)} \tag{25}$$

where ε_s can be termed the "static" separation factor, and $x_1 = [M_1 \cdot R]$, $x_4 = [M_1X \cdot R]$, $y_1 = [M_2 \cdot R]$, and $y_4 = [M_2X \cdot R]$, all expressed again in units of mole/liter. The magnitude of ε_s, compared with that of ε_0, can be considered to indicate how efficiently the fundamental separation equilibrium is transferred to the separation equilibrium between the solid and liquid phases. At any rate, evaluation of ε_s can be made by use of Eq. (12) since it determines the distributions of all species representing either component or x_i and y_i (i = 1–4) in Eq. (25).

From Eqs. (24) and (25), ε_s is related to ε_0 by

$$\varepsilon_s = \frac{[(1 + \varepsilon_0)aX_1 + X_4](aX_2 + X_3)}{(aX_1 + X_4)[(1 + \varepsilon_0)aX_2 + X_3]}\,\varepsilon_0 \tag{26}$$

where

$$X_i = x_i + y_i \qquad (i = 1\text{–}4) \tag{27}$$

and

$$a = \frac{1 - N_0(1 + \varepsilon_0)}{1 - N_0} \tag{28}$$

and where

$$N_0 = \sum_{i=1}^{4} x_i / \sum_{i=1}^{4} X_i \tag{29}$$

In actual separations of rare earth ions or carbon isotopes, shown in Table 2, ε_s was virtually equal to ε_0 and the concentrations of species M and MX · R was observed to be negligibly low, which suggests the ideal distribution of relevant species, as illustrated in Fig. 2. However, in the case of uranium-isotope separation, ε_s was significantly lower (7) than ε_0, whose value is known to be ~0.0013. In such a chromatographic system as one for uranium-isotope separation, where $\varepsilon_0 \ll 1$ and $N_0 \ll 1$, Eq. (26) can be approximated as

$$\varepsilon_S = \zeta_l \varepsilon_0 \tag{30}$$

where

$$\zeta_l = \frac{X_1 X_3 - X_2 X_4}{(X_1 + X_4)(X_2 + X_3)} \tag{31}$$

The coefficient ζ_l can be termed the "localization coefficient." The value of ζ_l was found to range from 0.73 to 0.98 for uranium enrichment systems.

(3) Predictive Analysis of Chromatographic Separations

An example of simulated separations is illustrated in Fig. 4. This system separates rare earth ions (Pr^{3+} and N^{3+}) by using a strong acid cation-exchange resin.

Simulations were executed according to the following imaginary separation procedures. First, a solution of Cu^{2+} ions was supplied to a column packed with the cation-exchange resin in order to load Cu^{2+} ions on the resin. Second, a solution containing rare earth ions was supplied to the column to replace Cu^{2+} ions in the latter region of the bed. Third, an ammoniacal solution of EDTA was supplied to desorb the rare earth ions loaded on the resin. The first, second, and third procedures are called "regeneration," "adsorption," and "development," respectively. Equilibrium calculations during development were executed using an ECLIPS minicomputer, manufactured by Data General Co., with repeated applications of Eq. (12).

Although the profile shown is not novel, it is an example that the

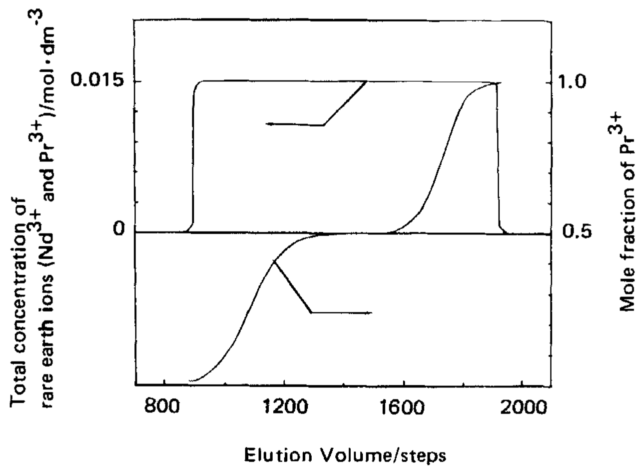

FIG. 4. Simulated profile of separation of rare earth ions by displacement using a strong acid cation-exchange resin.

present approach is effective as a tool for equilibrium calculations. Ion-exchange chromatography is traditionally considered to be based on a difference between sample components in their affinity for an ion-exchange resin. The present approach to chromatographic analysis originates in a recognition that the essence of chromatographic separations is a difference between sample components in their affinity for a particular addend. This approach seems to make a chromatographic system more wieldy, especially one involving some equilibrium reactions. In the above case, Nd^{3+} has a higher affinity for the dissociated EDTA as addend, $R(COO^-)_n$, than Pr^{3+}, so the latter is left in the backside of the adsorption band in a higher proportion than the former when it is developed by a solution containing the addend.

CONCLUSIONS

1. Displacement enables a purified component to be recovered at a concentration similar to that in a feed solution, although it needs a longer time to develop than elution. The whole evaluation of displacement, compared with elution, seems to make it more favorable for large-scale commercial separations.
2. Introduction of the "addend" concept and the potential strength

($\Delta\mu$) greatly helps in understanding how displacement can be established.

3. S- and L-potentials and the distribution function, which are derived from $\Delta\mu^\circ$ and/or $\Delta\mu$, are a powerful tool for predicting the formation of boundaries and an adsorption band, and the degree of separation for a displacement chromatography system.

4. The procedure for designing a displacement chromatography system is 1) selection of a discriminative addend which has as large a difference as possible in the affinity between the components to be separated; 2) selection of a set of an addend, an acceptor, and a donor for forming boundaries and an adsorption band; 3) examination by simulating calculations of the likelihood with which boundaries and an adsorption band could be formed; 4) estimation of the static separation factor from the inherent separation factor by use of the distribution function of Eq. (12); 5) determination of the distributions of the components on each imaginary equilibrium stage of the column in each step of simulation; and 6) drawing a separation profile by use of their distributions in the imaginary effluent of each step.

REFERENCES

1. J. C. Giddings, *Dynamics of Chromatography: Part I; Principles and Theory,* Dekker, New York, 1965.
2. F. G. Helfferich, *Ion Exchange,* McGraw-Hill, New York, 1962.
3. H. London (ed.), *Separation of Isotopes,* Newnes, London, 1961.
4. W. Rieman III and H. F. Walton, *Ion Exchange in Analytical Chemistry,* Pergamon, Oxford, 1970.
5. F. Helfferich and G. Klein, *Multicomponent Chromatography—The Theory of Interference,* Dekker, New York, 1970.
6. H. Rhee, R. Aris, and N. R. Amundson, *Philos. Trans. R. Soc., 267,* 419 (1970).
7. T. Miyake, K. Takeda, H. Onitsuka, and T. Watanabe, *Nucl. Technol., 73*(1), 116 (1986).
8. K. Takeda, M. Akiyama, F. Kawakami, and M. Sasaki, *Bull. Chem. Soc. Jpn., 59*(7), 2225 (1986).
9. L. G. Sillen and A. E. Martell, *Stability Constants of Metal-Ion Complexes* (Special Publication 17), The Chemical Society, London, 1964.
10. T. Miyake, K. Takeda, H. Onitzuka, and H. Obanawa, *Reactive Polym., 5*(1), 63 (1987).
11. A. J. P. Martin and R. L. M. Synge, *Biochem. J., 35,* 1358 (1941).
12. K. Takeda, H. Obanawa, and N. Morita, *Sep. Sci. Technol., 22*(1), 103 (1987).
13. F. H. Spedding and A. H. Deane, *The Rare Earths,* Krieger, New York, 1971, pp. 38–70.

Received by editor February 17, 1987
Revised December 22, 1987