Multicomponent Equilibrium Theory for Ion-Exchange Columns Involving Reactions

The multicomponent equilibrium theory for ion-exchange columns (chromatography) has been extended to systems accompanied by reactions in either or both phases. Based on the concept of coherence of concentration waves in the original theory, the proposed approach includes a systematic way to determine the thermodynamic variance and a general mathematical formulation to construct the composition path grid by means of numerical techniques. With proper adjustments, this approach can be applied as well to adsorption columns involving reactions. As a practical example, a comparison of predicted and observed effluent histories for an anion-exchange system with dissociation-association reactions is shown.

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Introduction

Most practical ion-exchange operations for separation of ionic components are carried out in columns (fixed beds). Theories for predicting column performance of ion exchange (as well as adsorption), which is essentially a kind of chromatography, have been developed for four decades. The early theories (Wicke, 1939; Wilson, 1940; DeVault, 1943; Weiss, 1943; Glückauf, 1946) were based on the premise of local equilibrium between the mobile and stationary phases. Later, refinements have fallen into two categories. One of these emphasizes the column dynamics associated with kinetic and dispersive effects for single-solute adsorption or binary ion exchange. The other, in contrast, focuses on the chromatographic patterns pertinent to interaction among species under the condition of local equilibrium in multicomponent systems. The latter, known as "multicomponent equilibrium theory," has attracted much practical interest since many applications involve multicomponent systems.

The multicomponent equilibrium theory was developed around 1970 based on the concept of propagation of concentration "waves" (variations) in fixed beds. Klein, Tondeur, and Vermeulen (Klein et al., 1967; Tondeur and Klein, 1967; Tondeur, 1970) established certain design procedures for ion-exchange columns. Helfferich (1967, 1968) generalized the theory by introducing the concept of "coherence" of concentration waves for general sorption processes as well as a mathematical tool, the "h-transform," for ion exchange with constant separation factors. With emphasis on ion exchange but including adsorption, this theory was summarized in a comprehensive monograph by Helfferich and Klein (1970). Independently, Rhee et al. (1970) dealt with Langmuir-type adsorption using an equivalent approach with discussion mainly of mathematics. Recently, the theory has been experimentally tested by Clifford and Weber (1978, 1982) for anion exchange and by Wang and Huang (1983) for cation exchange. They confirmed the theoretical predictions of the chromatographic patterns, except for systems accompanied by reactions.

Fixed-bed sorption processes involving reactions in the bulk phases have been studied for 20 years (Magee, 1963; Kočiřík, 1967; Collins and Deans, 1968; Deans et al., 1970; Bunge and Radke, 1975; Schweich et al., 1978, 1980). However, discussions of multicomponent systems are still quite limited. For ion exchange, a few recent investigations discovered certain interesting phenomena. Golden and coworkers (1974) studied ternary cation exchange accompanied by complex formation in the solution phase and found that selectivity reversals may be enhanced by such reactions. Klein (1981) dealt with systems with other types of reactions and presented certain important concepts for their modeling. Helfferich and Bennett (1984a, b) predicted theoretically and confirmed experimentally pH excursions occurring in anion-exchange columns with buffers undergoing dissociation-association reactions. These studies established a conceptual basis for incorporation of reactions into multicomponent equilibrium theory. However, the approaches were restricted to simple systems and the mathematical formulations were in case-by-case forms. Recently, Bryant and coworkers (1986) developed a numerical simulation of an aque-

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ous solution flowing through a porous mineral medium. Although they focused on precipitation-dissolution reactions which differ in nature from common ionic reactions within one phase, their mathematical formulation includes ion exchange with reactions in the mobile phase. They did not consider any reaction in the stationary phase since they recognized ion exchange as chemisorption in which ions are bonded to the solid surface, rather than free to diffuse and react with one another as in the "pores" of common ion exchangers.

This paper proposes a systematic approach which leads to a general, in contrast to case-by-case, mathematical formulation for multicomponent ion exchange accompanied by reactions in either or both phases. In this approach, numerical techniques are used to handle the nonlinearity essentially stemming from reaction equilibria. With appropriate adjustments, this approach is also applicable to adsorption columns involving reactions (in addition to chemisorption). Application of this expanded theory to anion exchange accompanied by dissociation-association reactions is in progress. For illustration, the Appendix presents an example comparing predicted and observed effluent histories for a chloride/carbonate buffer system on a strong-base resin Amberlite IRA-400.

Theoretical Basis

The multicomponent equilibrium theory (Helfferich and Klein, 1970) analyzes the development and propagation of concentration waves in a column with two basic concepts: wave velocity and coherence, both derived from conservation of materials. These concepts, together with the equilibrium properties of a particular system, lead to a grid of "composition paths," which are operation-independent and serve as a powerful tool for predicting column performance. The theory will be briefly reviewed here to introduce the basic concepts and notation.

Premises

The primary assumption of the equilibrium theory is, as its name indicates, that local equilibrium between the mobile and stationary phases is maintained at all times at an isothermal condition throughout the column. In addition, axial dispersion resulting from both molecular diffusion and hydrodynamic mixing is disregarded. For further simplification, a uniformly packed column and a constant bulk-flow rate are assumed here; these, however, can be relaxed without much difficulty.

Basic equations

Consider an n-component column and denote the concentrations of species i in the mobile and stationary phases as c_i and $\bar{c}_i$, respectively. Selecting appropriate reference concentrations c and $\bar{c}$ or the two phases, respectively, one can define normalized concentrations x_i and y_i as well as a parameter γ as follows:

$$x_i \equiv c_i/c \quad y_i \equiv \bar{c}_i/\bar{c} \quad \gamma \equiv (1-\epsilon)\bar{c}/(\epsilon c) \tag{1}$$

where ϵ is the fractional void volume of the column. For ion exchange, c may be chosen as the total concentration (normality) of the solution; $\bar{c}$, as the capacity (in terms of normality) of the exchanger. Although normality is a more convenient unit of c_i and $\bar{c}_i$ for ion exchange without reactions, molarity is a better choice for systems with reactions, and thus will be used hereafter.

The governing equations consist of material balances and equilibrium relations:

Material balances

$$(\partial x_i/\partial t)_z + \gamma(\partial y_i/\partial t)_z + v^\circ(\partial x_i/\partial z)_t = 0 \quad i = 1,2,\ldots,n \tag{2}$$

Equilibria

$$y_i = f_i(x_1, x_2, \ldots, x_n) \quad i = 1,2,\ldots,n \tag{3}$$

For ion exchange, the thermodynamic "variance" (Klein, 1981), namely, the number of independent concentration variables at equilibrium, is $n-1$ instead of n since the n species are subject to an electroneutrality constraint in each phase.

Wave velocity

The travel of a concentration wave can be observed by tracing a constant concentration value within it. By this way, the "wave velocity" of a specified concentration within a "diffuse wave" (gradual variation) can be derived from the material balance (Eq. 2) as:

$$v_{xi} \equiv (\partial z/\partial t)_{xi} = v^\circ/[1 + \gamma(\partial y_i/\partial x_i)_z] \tag{4}$$

If the wave is a discontinuous "shock wave" (abrupt variation), its velocity should be derived from an integral material balance. The result is:

$$v_{\Delta xi} \equiv (\partial z/\partial t)_{\Delta xi} = v^\circ/[1 + \gamma(\Delta y_i/\Delta x_i)] \tag{5}$$

where Δ indicates the difference between the two sides of the discontinuity.

Coherence

A wave in a multicomponent system can be viewed as a superposition of single-component waves, one for each component. "Coherence" (Helfferich, 1967, 1968; Helfferich and Klein, 1970) is an asymptotically stable state at which all single-component waves travel jointly. Accordingly, in a coherent wave, all existing components have the same wave velocity:

$$v_{xi} = v_{yi} = v \quad \text{or} \quad v_{\Delta xi} = v_{\Delta yi} = v_\Delta \quad \text{for all } i \tag{6}$$

Substitution of Eqs. 4 and 5 in Eqs. 6 results in the following differential and integral coherence conditions, respectively:

$$(\partial y_i/\partial x_i)_z = (\partial y_i/\partial x_i)_t = \lambda \quad \text{for all } i \tag{7}$$

$$\Delta y_i/\Delta x_i = \Lambda \quad \text{for all } i \tag{8}$$

Composition paths

Combination of the differential coherence condition (Eq. 7) and a differential expression derived from the equilibrium relations (Eq. 3) leads to an eigenvalue problem as follows:

$$\text{det.}\,(F - \lambda I) = 0 \quad F \equiv \{\partial y_i/\partial x_j\} \tag{9}$$

where F is the Jacobian matrix associated with the equilibrium relations (Eq. 3).

For a physically-plausible ion-exchange system of n counterions subject to an electroneutrality constraint, Eq. 9 normally results in $n - 1$ distinct real positive eigenvalues along with $n - 1$ eigenvectors. Each eigenvalue λ indicates the retardation of ion exchange in a coherent wave. The set of eigenvectors define $n - 1$ directions at each particular point in the $(n - 1)$-dimensional composition space, say, expressed by the mobile-phase concentrations $\{x_i\}$. Consequently, the eigenvectors of all points in the composition space establish $n - 1$ families of composition paths, along which a gradual variation is a coherent wave. The grid of composition paths, dependent only on the equilibrium properties, serve as a powerful tool for predicting column behavior. In addition, the integral coherence condition (Eq. 8) provides a complementary formula for shock waves.

Composition route

Since a wave is a variation of composition, it can be mapped onto the composition space. With reference to the direction of wave propagation, the resulting "composition route" starts with the upstream composition, traces the composition variation within the wave, and ends with the downstream composition. However, a special case arises for a shock wave, of which the mapping results in only two points representing the upstream and downstream compositions, respectively. For better visualization, a fictitious straight route between the two composition points may be employed. The composition route of a coherent wave with gradual variation lies on a composition path. Thus, the composition profile or history of such a wave can be easily established if the grid of composition paths along with the associated eigenvalues is available. For a coherent shock wave, however, the end points of its route in general lie on the same path only if the latter is a straight line; otherwise, the former must be predicted separately using the integral coherence condition.

Expansion of Theory

Approach

There are two primary tasks in the extension of multicomponent equilibrium theory to systems with reactions. One is to determine the variance of the system; the other, to deal with the reaction terms in the material balances. For the variance, Klein (1981) and Helfferich and Bennett (1984a, b) used an intuitive knowledge of the independent equilibrium relations. This knowledge, however, itself may be the real problem for a complicated system. This paper proposes a systematic approach by which one can determine the variance prior to listing all independent equilibrium relations. For the reaction terms, Golden et al. (1974) and Klein (1981) handled this problem by writing the material balances with respect to certain conserved entities, whose concentrations are linear combinations of those of actual species. This study generalizes such an approach by identifying the conserved entities as certain fundamental segments, called "moieties," of species in the system. In addition, a "reaction matrix" devised previously (Hwang and Helfferich, 1987) is used as a compact mathematical expression of the reactions in each phase. An example in the Appendix illustrates this approach.

Classification of species

For ion exchange accompanied by reactions, the coupling relationship among species can be divided according to their importance to column performance into three classes: sorption (ion exchange of counterions as well as sorption of coions and neutral molecules), reactions, and electric coupling. Thus, the species can be conveniently classified into three groups:

- *Sorbable species* include all counterions as well as those coions or neutral molecules which are significantly sorbed by the exchanger. This is the primary group with respect to the chromatographic phenomenon and is the only one whose members are common to both phases.
- *Reactive species* include nonsorbable and fixed species which are involved in reactions with sorbable species so that their concentrations may vary during the sorption process. Species which are involved in both sorption and reactions are counted in the first group rather than this one.
- *Inactive species* are ionic species which are neither sorbable nor reactive, but coupled with the other species by the electroneutrality requirement. This group includes nonreactive coions which are essentially excluded from the exchanger and nonreactive fixed ionic groups. These species are chromatographically indistinguishable. Thus, all such coions will be treated as a lumped species with its concentration measured in terms of normality; so will all such fixed groups.

The concentration of the inactive fixed group is a constant during a column operation; that of the inactive coion may vary only if the total concentration of the solution is changed at the column entrance. Accordingly, the concentrations of the inactive species are parameters rather than variables with respect to the sorption-reaction process. As a matter of fact, a system with reactions may contain no inactive species if all coions are either sorbable or reactive and all fixed ionic groups are involved in reactions. For convenience, sorbable species together with reactive ones will hereafter be referred to as "active species."

Systems

Consider an ion-exchange system containing n and $\bar{n}$ active species in the solution and the exchanger, respectively. Among these species, there are $\tilde{n}$ sorbable species, $n - \tilde{n}$ reactive ones in the solution, and $\bar{n} - \tilde{n}$ reactive ones in the exchanger. Also, there are certain reactions whose number must be less than that of the species and will be denoted by $n - m$ for the solution phase and $\bar{n} - \bar{m}$ for the exchanger phase.

Moieties

For the solution phase, the n species can be viewed as consisting of m conserved "moieties" which remain intact in the $n - m$ reactions (Hwang and Helfferich, 1987). For example, species $CO_3^=$, HCO_3^-, H_2CO_3, and H^+ can be considered as consisting of moieties CO_3 and H in different proportions. For the exchanger phase, similarly, there are $\bar{m}$ moieties. Suppose $\tilde{m}$ of these moieties constitute the $\tilde{n}$ sorbable species and are common to both phases; such moieties will hereafter be referred to as "sorbable moieties." Accordingly, there are $m - \tilde{m}$ nonsorbable moieties in the solution and $\bar{m} - \tilde{m}$ fixed ones in the exchanger. Sorbable moieties are conserved in the entire system but not conserved within each phase, whereas nonsorbable and fixed moieties are conserved within each respective phase.

Equilibria

For a system with reactions, the following two types of equilibria must be taken into account:

- Reaction equilibria within each phase: one for each reaction. Obviously, there are $n - m$ such equilibrium relations for the solution phase and $\bar{n} - \bar{m}$ relations for the exchanger phase.
- Sorption equilibria between the two phases: ion-exchange equilibria for counterions, and possibly, other sorption equilibria for coions and neutral molecules.

For a simple system, one may be able to write all independent sorption equilibria by intuition (Golden et al., 1974; Klein, 1981; Helfferich and Bennett, 1984a, b). For a complicated system, however, it will be of great help if the number of independent relations can be determined prior to listing those relations.

Variance

For the system of concern, the total number of concentration variables of active species in both phases is $n + \bar{n}$. At equilibrium, the reaction equilibria give $n - m$ and $\bar{n} - \bar{m}$ constraints for the solution and the exchanger phases, respectively. Also, conservation of the nonsorbable and fixed moieties in each respective phase provides $m - \tilde{m}$ and $\bar{m} - \tilde{m}$ reaction-coupling constraints in the two phases, respectively. In addition, there is an electroneutrality constraint for each phase. As a result, the number of independent concentration variables in each phase is $\tilde{m} - 1$, the same for both phases. This implies that, even though one may be able to formally write as many as $\tilde{n}$ sorption equilibrium relations, only $\tilde{m} - 1$ of them are independent. Thus, the variance of the system is $\tilde{m} - 1$, and the column behavior should be mathematically described by $\tilde{m} - 1$ sorption equilibrium relations and $\tilde{m} - 1$ material balance equations.

The variance obtained above is based on the active species, and thereby, corresponds to the composition variations resulting intrinsically from the sorption-reaction process. For clarity, this value will be referred to as "sorption variance" when necessary. For a system with an inactive coion (lumped), however, the concentration of this coion may change if the total concentration of the solution is changed at the column entrance. Such a change will lead to a composition variation in which the concentrations of the active species may also vary owing to the coupling by the electroneutrality condition. Such a composition variation, not counted in the sorption variance, corresponds to a zero eigenvalue λ defined by Eq. 7. This wave travels at the bulk-flow velocity without any retardation. Consequently, the "total variance" of such a system is $\tilde{m}$.

Mathematical formulation

For the ion-exchange system under consideration, the following notation of indices will be employed: $i = 1, 2, \ldots, \tilde{n}$ for sorbable species, $i = \tilde{n} + 1, \ldots, n$ for nonsorbable reactive species, $i = \tilde{n} + 1, \ldots, \bar{n}$ for fixed reactive species, and $i = 0$ for the lumped inactive species if it exists, in each phase; also, $k = 1, 2, \ldots, \tilde{m}$ for sorbable moieties, $k = \tilde{m} + 1, \ldots, m$ for nonsorbable moieties, and $k = \tilde{m} + 1, \ldots, \bar{m}$ for fixed moieties; moreover, $\ell = m + 1, \ldots, n$ for reactions in the solution and $\ell = \bar{m} + 1, \ldots, \bar{n}$ for those in the exchanger.

Reaction matrices

Consider the solution phase and denote species i and moiety k as A_i and S_k, respectively. The species and the reactions can be expressed by linear combinations as follows:

$$A_i = \sum_{k=1}^{m} (\mu_{ki} S_k) \quad i = 1, 2, \ldots, n \tag{10}$$

$$\sum_{i=1}^{n} (\nu_{\ell i} A_i) = 0 \quad \ell = m + 1, m + 2, \ldots, n \tag{11}$$

where the $\{\mu_{ki}\}$ are "reaction-coupling factors" and the $\{\nu_{\ell i}\}$ are stoichiometric coefficients. In many studies of chemical reactions (e.g., Aris, 1965), species (compounds) are regarded as composed of elements and are expressed by a set of equations similar to Eqs. 10 with each coefficient representing the number of atoms of an element in a species. However, such a coefficient matrix usually has a rank smaller than the total number of elements since some elements are coupled (e.g., C and O in a carbonate system). This means there are some redundant equations, which can be eliminated by an algebraic manipulation. In terms of moieties, Eqs. 10 are equivalent to the result of such a manipulation, and the matrix $\{\mu_{ki}\}$ has a rank m, equal to the total number of moieties. Note that a μ_{ki} may become a negative integer for compensation in some cases (see the example in the Appendix). Combination of the two integer matrices $\{\mu_{ki}\}$ and $\{\nu_{\ell i}\}$ yields an n-by-n "reaction matrix" (Hwang and Helfferich, 1987) which gives a compact representation of the reactions in the solution. Similarly, the reactions in the exchanger can be expressed by an $\bar{n}$-by-$\bar{n}$ reaction matrix composed of two integer matrices $\{\bar{\mu}_{ki}\}$ and $\{\bar{\nu}_{\ell i}\}$.

Equations in terms of species

The basic equations of the equilibrium theory are material balances and equilibrium relations. For ion exchange with reactions, the former consists of differential material balances with reaction terms and reaction couplings derived from conservation of the moieties; the latter, of sorption equilibria (for counterions, and possibly, coions and neutral molecules), reaction equilibria, and electroneutrality constraints. These equations are:

Differential material balances:

Sorbable species

$$(\partial x_i/\partial t) + \gamma(\partial y_i/\partial t) + v^\circ(\partial x_i/\partial z) = R_i + \gamma \bar{R}_i \qquad i = 1, 2, \ldots, \tilde{n} \tag{12}$$

Nonsorbable reactive

$$(\partial x_i/\partial t) + v^\circ(\partial x_i/\partial z) = R_i \qquad i = \tilde{n} + 1, \ldots, n \tag{13}$$

Fixed reactive

$$(\partial y_i/\partial t) = \bar{R}_i \qquad i = \tilde{n} + 1, \ldots, \bar{n} \tag{14}$$

Reaction couplings:

Solution

$$\sum_{i=1}^{n} \mu_{ki} R_i = 0 \qquad k = 1, 2, \ldots, m \tag{15}$$

Exchanger

$$\sum_{i=1}^{\bar{n}} \bar{\mu}_{ki} \bar{R}_i = 0 \qquad k = 1, 2, \ldots, \bar{m} \tag{16}$$

Sorption equilibria:

$$g_j(\{y_i\}) = f_j(\{x_i\}) \quad j = 1, 2, \ldots, \tilde{n} \tag{17}$$

Reaction equilibria:

$$\text{Solution} \quad \prod_{i=1}^{n} x_i^{\nu_{\ell i}} = K_\ell \quad \ell = m + 1, \ldots, n \tag{18}$$

$$\text{Exchanger} \quad \prod_{i=1}^{\bar{n}} y_i^{\bar{\nu}_{\ell i}} = \bar{K}_\ell \quad \ell = \bar{m} + 1, \ldots, \bar{n} \tag{19}$$

Electroneutrality constraints:

$$\text{Solution} \quad \sum_{i=1}^{n} z_i x_i + \omega x_0 = 0 \tag{20}$$

$$\text{Exchanger} \quad \sum_{i=1}^{\bar{n}} \bar{z}_i y_i + \omega y_0 = 0 \tag{21}$$

In the above equations, R_i and $\bar{R}_i$ are normalized reaction terms (by c and $\bar{c}$, respectively); K_ℓ and $\bar{K}_\ell$ are normalized reaction equilibrium constants in terms of normalized concentrations; z_i and $\bar{z}_i$ are valences of species; ω is the charge sign (+1 or −1) of coions and fixed ionic groups. The sorption equilibria (Eq. 17) are written in a form more general and more convenient for ion exchange than Eqs. 3. The parameters x_0 and y_0 take a zero value if there is no inactive species in the corresponding phase.

The proposed approach is to rewrite the equations in terms of the sorbable moieties, and thereby eliminate the reaction terms since moieties are conserved with respect to the reactions. Because moiety concentrations are indirectly subject to the electroneutrality, only $\tilde{m} - 1$ of the $\tilde{m}$ sorbable moieties are independent. In accordance with the variance, these $\tilde{m} - 1$ independent concentration variables will be chosen to write $\tilde{m} - 1$ differential material balances and $\tilde{m} - 1$ sorption equilibria.

Equations in terms of sorbable moieties

Let s_k and q_k denote the normalized concentrations (by c and $\bar{c}$, respectively) of the sorbable moiety k in the solution and the exchanger, respectively. These concentrations can be related to the species concentrations as follows:

$$s_k = \sum_{i=1}^{n} \mu_{ki} x_i \quad q_k = \sum_{i=1}^{\bar{n}} \bar{\mu}_{ki} y_i \quad k = 1, 2, \ldots, \tilde{m} \tag{22}$$

Choosing $\tilde{m} - 1$ independent sorbable moieties with indices $k = 1, 2, \ldots, \tilde{m} - 1$, multiplying each species material balance in Eqs. 12, 13, and 14 by μ_{ki} or $\bar{\mu}_{ki}$, then summing over all species for each phase, one eliminates the reaction terms and obtains the following equations:

$$(\partial s_k/\partial t) + \gamma(\partial q_k/\partial t) + v^\circ(\partial s_k/\partial z) = 0$$
$$k = 1, 2, \ldots, \tilde{m} - 1 \tag{23}$$

The species concentrations $\{x_i\}$ and $\{y_i\}$ can be in principle expressed in terms of the sets of independent sorbable-moiety concentrations $\{s_k\}$ and $\{q_k\}$, respectively. Thus, one can rewrite the sorption equilibria (Eq. 17) as follows:

$$g_h[y_1(\{q_k\}), y_2(\{q_k\}), \ldots, y_{\tilde{n}}(\{q_k\})]$$
$$= f_h[x_1(\{s_k\}), x_2(\{s_k\}), \ldots, x_n(\{s_k\})]$$
$$h = 1, 2, \ldots, \tilde{m} - 1 \tag{24}$$

Wave velocity

Except for different concentration variables, Eq. 23 is formally identical to Eq. 2 and, in a more general form, Eq. 24 is equivalent to Eq. 3. Consequently, an expression of wave velocity formally identical to Eq. 4 can be derived from Eqs. 23 and 24:

$$v_{sk} \equiv (\partial z/\partial t)_{sk} = v^\circ/[1 + \gamma(\partial q_k/\partial s_k)_z] \tag{25}$$

This expression means that one observes the concentration waves by tracing the sorbable moieties instead of the species. Similarly, if the wave is a shock wave, its velocity can be related to moiety concentrations as follows:

$$v_{\Delta sk} \equiv (\partial z/\partial t)_{\Delta sk} = v^\circ/[1 + \gamma(\Delta q_k/\Delta s_k)] \tag{26}$$

In practice, it is usually easier to measure the moiety concentrations (e.g., total CO_3 in a system with $CO_3^=$, HCO_3^-, and H_2CO_3) since they are not coupled by reactions.

Coherence

In terms of the concentration waves of the sorbable moieties, the coherence criterion says that, in a coherent wave, all individual waves of the sorbable-moiety concentrations travel jointly. This statement leads to the following differential and integral coherence conditions, respectively:

$$(\partial q_k/\partial s_k)_z = (\partial q_k/\partial s_k)_t = \lambda \quad \text{for all } k = 1, 2, \ldots, \tilde{m} \tag{27}$$

$$\Delta q_k/\Delta s_k = \Lambda \quad \text{for all } k = 1, 2, \ldots, \tilde{m} \tag{28}$$

The differential condition (Eq. 27) provides the basis for constructing the composition path grid as will be described in the following paragraphs. With the same calculation for the conversion between species and moiety concentrations, the integral condition (Eq. 28) supplies a complementary tool to predict the behavior of coherent shock waves, which are in general not guided by the composition paths.

Eigenvalue problem at coherence

The differential coherence condition (Eq. 27) together with the sorption equilibria (Eq. 24) results in an eigenvalue problem as follows:

$$\det. (G - \lambda I) = 0 \quad G \equiv \{\partial q_h/\partial s_k\} \tag{29}$$

where G is the Jacobian matrix of order $\tilde{m} - 1$ by $\tilde{m} - 1$ associated with the sorption equilibria (Eq. 24).

Referring to the composition space expressed by the solution-phase concentrations $\{s_k\}$, the following procedures are proposed to obtain the eigenvalues and the eigenvectors for a particular composition point:

1. Select a physically accessible point $\{s_k\}$ in the composition space—to be discussed later.

2. Convert $\{s_k\}$ ($\tilde{m} - 1$ elements) to $\{x_i\}$ (n elements).
3. Select $\tilde{m} - 1$ independent sorption equilibrium relations among $\tilde{n}$ possible ones of Eqs. 17 and rearrange the indices to constitute Eqs. 24.
4. Calculate $\tilde{m} - 1$ elements of $\{y_i\}$ ($\bar{n}$ elements) from the sorption equilibria.
5. Calculate the other elements of $\{y_i\}$ and then convert $\{y_i\}$ to $\{q_k\}$ ($\tilde{m} - 1$ elements).
6. Establish the Jacobian matrix G in the eigenvalue problem (Eq. 29) from $\{s_k\}$ and $\{q_k\}$ obtained above.
7. Solve the eigenvalue problem, possibly using an available package of computer programs.

Convenient formulas for use in the various steps are discussed later.

Physically accessible composition region

In terms of $\{s_k\}$, the physically accessible region in the ($\tilde{m} - 1$)-dimensional composition space is bounded by $\tilde{m}$ hypersurfaces (of $\tilde{m} - 2$ dimensions) specified by the equations $s_k = 0$ with $k = 1, 2, \ldots, \tilde{m}$. Since $s_{\tilde{m}}$ is not selected as a concentration coordinate, the equation $s_{\tilde{m}} = 0$ is an implicit one. Unfortunately, an explicit form of this equation in terms of the concentration coordinates $\{s_k\}$ with $k = 1, 2, \ldots, \tilde{m} - 1$ is in general unavailable. Thus, after prescribing a point $\{s_k\}$ (certainly, nonnegative in all $\tilde{m} - 1$ elements), one has to check the following criterion of physical accessibility: the corresponding $\{x_i\}$ (see next paragraph) must be nonnegative in all n elements and lead to a nonnegative $s_{\tilde{m}}$, calculated using the first one of Eqs. 22. A physically accessible $\{s_k\}$ should lead to a physically accessible $\{q_k\}$ provided that all sorption equilibrium relations are physically plausible.

Conversion between species and moiety concentrations

The equations relating species and moiety concentrations in each phase consist of the reaction couplings (conservation of moieties), the reaction equilibria, and the electroneutrality constraint. Since the normalized concentrations of both nonsorbable and fixed moieties are parameters rather than variables, symbols different from those for sorbable moieties will be employed: $\{r_k\}$ and $\{\bar{r}_k\}$ for the nonsorbable and the fixed moieties, respectively. These concentrations can be related to the species concentrations in the same way as Eqs. 22 except for k greater than $\tilde{m}$.

For the solution phase, the n elements of $\{x_i\}$ can be obtained by solving the following n simultaneous equations, provided that the $\tilde{m} - 1$ elements of $\{s_k\}$ are given:

$$i = 1, 2, \ldots, n \begin{cases} \sum_i (\mu_{ki} x_i) = s_k & k = 1, 2, \ldots, \tilde{m} - 1 \\ \sum_i (-\omega z_i x_i) = x_0 & (\tilde{m}\text{th eq.}) \\ \sum_i (\mu_{ki} x_i) = r_k & k = \tilde{m} + 1, \ldots, m \\ \prod_i^P (x_i^{\nu_{\ell i}}) - K_\ell \prod_i^R (x_i^{-\nu_{\ell i}}) = 0 & \ell = m + 1, \ldots, n \end{cases} \tag{30}$$

In the above equations, the electroneutrality condition (Eq. 20) has been rearranged so that the coefficients $-\omega z_i$ of counterions (main species) take positive values. The reaction equilibrium expression (Eq. 18) has also been rearranged to avoid zero values (for vanishing species) occurring in the denominator. In the rearranged form, the superscript P indicates the multiplication over all products, with positive $\nu_{\ell i}$; the superscript R, over all reactants, with negative $\nu_{\ell i}$.

For the exchanger phase, the $\tilde{m} - 1$ independent sorption equilibria result in $\tilde{m} - 1$ elements of $\{y_i\}$ while leaving the other $\bar{n} - \tilde{m} + 1$ elements unknown. These unknowns can be obtained by solving the last three ($\bar{n} - \tilde{m} + 1$ equations) of the following set similar to Eqs. 30:

$$i = 1, 2, \ldots, \bar{n} \begin{cases} \sum_i (\bar{\mu}_{ki} y_i) = q_k & k = 1, 2, \ldots, \tilde{m} - 1 \\ \sum_i (-\omega \bar{z}_i y_i) = y_0 & (\tilde{m}\text{th eq.}) \\ \sum_i (\bar{\mu}_{ki} y_i) = \bar{r}_k & k = \tilde{m} + 1, \ldots, \bar{m} \\ \prod_i^P (y_i^{\bar{\nu}_{\ell i}}) - \bar{K}_\ell \prod_i^R (y_i^{-\bar{\nu}_{\ell i}}) = 0 & \ell = \bar{m} + 1, \ldots, \bar{n} \end{cases} \tag{31}$$

Then, the $\tilde{m} - 1$ elements of $\{q_k\}$ can be calculated using the first one ($\tilde{m} - 1$ equations) of the above equation set.

Jacobian matrix of sorption equilibria

The Jacobian matrix G, defined in Eq. 29 and associated with the sorption equilibria (Eq. 24), can be established by solving the following matrix equation:

$$EG = D \tag{32}$$

where

$$\begin{aligned} D &\equiv \{\partial f_h/\partial s_k\}_{(\tilde{m}-1)\times(\tilde{m}-1)} \\ &= \{\partial f_h/\partial x_i\}_{(\tilde{m}-1)\times n}\{\partial x_i/\partial s_k\}_{n\times(\tilde{m}-1)} \\ E &\equiv \{\partial g_h/\partial q_k\}_{(\tilde{m}-1)\times(\tilde{m}-1)} \\ &= \{\partial g_h/\partial y_i\}_{(\tilde{m}-1)\times \bar{n}}\{\partial y_i/\partial q_k\}_{\bar{n}\times(\tilde{m}-1)} \end{aligned} \tag{33}$$

The partial derivatives $\{\partial f_h/\partial x_i\}$ and $\{\partial g_h/\partial y_i\}$ can be evaluated by direct differentiation of the respective function in the sorption equilibrium relations (Eq. 24). The derivatives $\{\partial x_i/\partial s_k\}$ can be obtained by solving the following equations, which are derived by differentiating Eqs. 30:

$$\begin{cases} \sum_i [\mu_{hi}(\partial x_i/\partial s_k)] = \delta_{hk} & h = 1, 2, \ldots, \tilde{m} - 1 \\ \sum_i [-\omega z_i(\partial x_i/\partial s_k)] = 0 & (\tilde{m}\text{th eq.}) \\ \sum_i [\mu_{hi}(\partial x_i/\partial s_k)] = 0 & h = \tilde{m} + 1, \ldots, m \\ \sum_i^P \left\{\nu_{\ell i} x_i^{\nu_{\ell i}-1}\left[\prod_{j\neq i}^P (x_j^{\nu_{\ell j}})\right](\partial x_i/\partial s_k)\right\} & \\ \quad + \sum_i^R \left\{K_\ell \nu_{\ell i} x_i^{-\nu_{\ell i}-1}\left[\prod_{j\neq i}^R (x_j^{-\nu_{\ell j}})\right](\partial x_i/\partial s_k)\right\} = 0 & \ell = m + 1, \ldots, n \end{cases} \tag{34}$$

where δ_{hk} is the Kronecker delta which takes the value 1 if $h = k$ and the value 0 otherwise. The above equations are linear with respect to $\{\partial x_i/\partial s_k\}$, which therefore can be evaluated easily once the values of $\{x_i\}$ have been obtained from Eqs. 30. By a similar way, the derivatives $\{\partial y_i/\partial q_k\}$ can be calculated.

Composition paths

As in the multicomponent equilibrium theory for systems without reactions, one can construct a composition path grid by selecting some composition points and linking the resulting eigenvectors of the same families. Owing to the nonlinearity of the reaction equilibria, this construction in general calls for numerical techniques even for systems with the simplest sorption equilibria such as ion-exchange equilibria with constant separation factors. For instance, numerical approximation techniques were employed in previous studies for bivariant systems (Golden et al., 1974; Helfferich and Bennett, 1984b). Such approximations are essentially numerical integration methods, similar to those for solving ordinary differential equations. These techniques can in principle be extended to systems with higher variances, but computation procedures may become too complicated to be of practical interest. Moreover, even if a nonlinear grid in more than two dimensions can be constructed, using it to predict column performance may be difficult if an appropriate orthogonalization of the grid is unavailable. For systems with reactions, unfortunately, one can hardly anticipate an orthogonalization as simple as the h-transformation (Helfferich, 1967, 1968; Helfferich and Klein, 1970) used for systems without reactions. Practical techniques to overcome this problem are still under development. Fortunately, some practically important applications, such as "frontal analysis," for a high-variant system can be handled with a sequence of bivariant subsystems (Helfferich and Klein, 1970), whose composition path grids can be constructed by the proposed approach. This is because, for such a situation, only a bivariant subsystem consisting of part of the species is involved in each coherent wave.

Numerical techniques

To construct the composition paths for a system with reactions, one in general needs numerical techniques for both solving the eigenvalue problem at each selected composition point and establishing the path grid from the resulting eigenvectors.

For obtaining the eigenvalues and eigenvectors, numerical methods are called for to solve the nonlinear equation sets (Eqs. 30 and 31), the linear equation sets (Eqs. 34 and 32), and the eigenvalue problem (Eq. 29). All of these computation tasks can be carried out by conventional methods (e.g., Carnahan et al., 1969). More conveniently, an available package of computer programs, such as the IMSL package (IMSL Inc., 1980), can be used.

For constructing the path grid, a numerical integration technique is needed. For example, a point-by-point approximation was used previously (Helfferich and Bennett, 1984b) for a bivariant system. In this method, a starting point is chosen on an edge of the physically accessible composition region and the eigenvalues and eigenvectors at this point are calculated. Then, a second point is located by advancing a small distance along one of the eigenvectors. Following one family of the eigenvectors at a time, one can establish an approximated composition path at a time by repeating the above two steps until reaching another edge. Thus, with several starting points, one can construct a composition path grid by repeating these procedures. Some systems, however, may call for special manipulation as will be discussed later.

For demonstration, a grid of composition paths calculated with these numerical techniques is presented in the Appendix for a bivariant system of anion exchange accompanied by dissociation-association reactions in both solution and exchanger phases. Such a composition path grid along with the integral coherence condition (Eq. 28) gave a satisfactory prediction of the column performance in a column experiment.

Discussion

The proposed approach is formulated in a general aspect. Specific applications of this general formulation are beyond the scope of this paper. However, certain facets of the applications in general are to be discussed here.

Data required

The data required for constructing a grid of composition paths are:

- Reference concentrations for both phases (c and $\bar{c}$).
- Number of species in solution (n), that in exchanger ($\bar{n}$), and number of sorbable species ($\tilde{n}$).
- Number of moieties in solution (m), that in exchanger ($\bar{m}$), and number of sorbable moieties ($\tilde{m}$)—these values are determined from number of reactions in each phase.
- Valences of species in both phases ($\{z_i\}$ and $\{\bar{z}_i\}$).
- Charge sign of coions and fixed ionic groups (ω) and normalized concentrations of the lumped inactive species (x_0 and y_0).
- Reaction matrices of both phases ($\{\mu_{ki}\}$, $\{\nu_{\ell i}\}$, $\{\bar{\mu}_{ki}\}$, and $\{\bar{\nu}_{\ell i}\}$).
- Normalized concentrations of nonsorbable and fixed moieties ($\{r_k\}$ and $\{\bar{r}_k\}$).
- Normalized equilibrium constants of reactions in both phases ($\{K_\ell\}$ and $\{\bar{K}_\ell\}$).
- Functional forms of sorption equilibrium relations ($\{f_k\}$ and $\{g_k\}$) in terms of normalized concentrations along with associated parameters.

For predicting the column performance using the composition paths, additional data needed are:

- Initial composition in the column, as a function of location if not uniform.
- Feed composition at the column entrance, as a function of time if not constant.
- Fractional void volume of the column (ϵ) and bulk-flow velocity of the solution in the column (v^o).

Activity coefficients in exchanger phase

The equilibrium constants of reactions used in the mathematical formulation are based on concentrations (molarities), rather than on activities, of the species. Although these parameters are not strictly constant, assuming them as constants is usually a good approximation since the concentration ranges of many applications are quite narrow. In the exchanger phase, however, such a constant may deviate significantly from the true reaction constant based on activities (the true constants for the two phases are the same if based on the same standard states). Owing to the chemical and electric properties of the exchanger matrix as well as high concentration and ionic strength, the activity coefficients of the species in the exchanger may be far from unity, and thereby, have to be either determined experimentally or estimated theoretically. For the purpose of calculating reaction constants, however, one needs only the quotients of activity coefficients as correction factors, rather than the individual activity coefficients of all species.

In principle, the activity coefficients are also involved in the sorption equilibria (for ion exchange of counterions as well as sorption of coions and neutral molecules). These values must be consistent between reaction and sorption equilibria. Accordingly, sorption equilibrium relations in addition to the $\tilde{m} - 1$ independent ones, if available, may be used to determine experimentally some of the correction factors for the reaction constants. For a simple system in which each sorbable moiety is involved in only one reaction, this procedure may give all of these correction factors. In general, however, one may not be able to determine all of them because the concentrations of some species, for example, $CO_3^=$, HCO_3^-, and H_2CO_3, cannot be measured individually. Thus, one normally has to estimate some of these correction factors based on thermodynamic consideration and reasonable postulates or by best fit to the result of a column experiment.

As a first approximation, one may assume that the matrix of the exchanger has no effect on the behavior of mobile species with respect to the reaction equilibria and the effects of concentration and ionic strength in both phases are the same. With these assumptions, the reaction constant in the intraparticle "pores" of the exchanger (i.e., excluding the matrix) is identical to that in the external solution. In other words, the reaction constant based on molalities rather than molarities, that is, based on solvent content rather than bulk volume, has the same value for both phases (Helfferich and Bennett, 1984a). For this ideal situation, no activity coefficients for the exchanger phase are required for correcting the reaction constants; the only correction factor needed is the fractional pore volume or solvent content of the exchanger.

Anomalies of composition paths

For a nonreacting system with constant separation factors, the selectivity sequence of the species is fixed throughout the entire composition space (physically accessible). Also, the eigenvalues vary monotonically along each composition path and in a parallel trend along all paths of the same family. For a system with variable separation factors, Tondeur (1970) showed that the selectivity order of two species may be reversed across a certain hypersurface in the composition space. In such a situation, the eigenvalues vary monotonically along each path but in opposite trends along same-family paths on the two sides of the dividing hypersurface. In addition to such selectivity reversals, another type of anomaly may happen in systems with reactions. As Golden et al. (1974) showed in their system with complex formation in the solution phase, local extrema of an eigenvalue may occur along a composition path so that a coherent wave associated with such a path may be "composite," that is, composed of both self-sharpening and nonsharpening portions. Both anomalies, if existing, have profound consequences for column behavior and should be marked in the composition path grid.

The selectivity (or affinity) for systems with reactions are more conveniently stated with respect to moieties. Analogous to the treatments of Tondeur (1970), and Helfferich and Klein

(1970), the hypersurface across which the affinities of moieties h and k are reversed can be specified by the following equation together with the sorption equilibrium relations:

$$q_h/s_h = q_k/s_k \tag{35}$$

Such a selectivity reversal exists if the solution of these equations falls into the physically accessible region of the composition space.

For extrema of the eigenvalue along a composition path, one can mark the loci of such extrema during the point-by-point numerical computation of the path grid. Since the eigenvalue of each point is evaluated when constructing a path, variation of the eigenvalue along the path can be examined concurrently and local extrema, if any, can be identified (e.g., see Appendix). Such loci of extrema in principle form one or more hypersurfaces in the composition space.

Conclusions

A generalized approach is proposed to expand the multicomponent equilibrium theory (Helfferich and Klein, 1970) for ion-exchange columns to systems accompanied by reactions in either or both phases. Based on the concept of coherence of concentration waves in the original theory, this approach constructs the composition path grid of a system in a more general way than proposed by earlier studies (Golden et al., 1974; Klein, 1981; Helfferich and Bennett, 1984a,b), which were restricted to simple systems.

The improvement is in two facets. First, a systematic way has been formulated to determine the thermodynamic variance of a system prior to listing all independent equilibrium relations, which often cause confusion if the system is complicated. Second, a general, in contrast to case-by-case, mathematical formulation has been established to construct a composition path grid by means of numerical techniques. In this formulation, the concept of conserved moieties of species is used to eliminate the reaction terms in the material balances. Also, a reaction matrix devised previously (Hwang and Helfferich, 1987) is employed as a compact representation of the reactions in each phase. With proper adjustments, the proposed approach is also applicable to adsorption columns involving reactions in the bulk phases.

Certain limitations of this theory in its present form should be noticed. First, the numerical techniques for construction and utilization of composition path grids have so far been limited to bivariant systems (with two-dimensional grids). However, some important applications for a high-variant system can be handled with a sequence of two-dimensional grids for its bivariant subsystems, as mentioned earlier. Second, the theory calls for adjustments if a third phase such as gas or precipitate (Klein, 1986) is generated in the column. In such a situation, the wave velocity is affected by the variation of the volume fraction of the liquid and by the velocity of the third phase, which may be stagnant or move slower than the bulk liquid velocity.

Acknowledgment

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Appendix

For illustration of the proposed approach, a bivariant system of anion exchange with dissociation-association reactions is presented here as an example. This example system consists of a strong-base anion exchanger, Amberlite IRA-400, and a sodium chloride/carbonate buffer solution. For simplicity, lump dissolved CO_2 and H_2CO_3 into a single species H_2CO_3 and assume no gas bubbles in the column. Also, assume that sorption of the coions Na^+ and H^+ and of the neutral molecules H_2CO_3 is negligible compared with ion exchange of counterions. The species in this example system are listed in Table A1 with classification and indices. For both phases, the dissociation-association reactions, the moieties, and the reaction matrices defined accordingly are also listed in Table A1. Note that, even though involved in a reaction, the solvent water is not considered as a species since its concentration is essentially constant. For consistency (keeping that the sum of the numbers of moieties and of reactions equals the number of species), OH is not counted as a moiety and OH^- is assigned a negative reaction-coupling factor with respect to the moiety H since OH^- consumes, rather than yields, one H in the neutralization (reverse of the ionization of water). Similar arrangements may also be needed for other situations, for instance, systems with precipitates which are not counted as species.

Variance

Since there are three sorbable moieties ($\tilde{m} = 3$), the sorption variance is two. This implies that, in normal situations, there will be two coherent "ion-exchange waves" (variations resulting from ion exchange) in the column, where the only type of sorption is ion exchange. In addition, since there is an inactive coion Na^+ in the solution, the total variance is three. This means that, if one changes the sodium concentration by changing the total solution concentration at the column entrance, there will be a

Table A1. Species, Reactions, Moieties, and Reaction Matrices of Example Anion-Exchange System

Classification		Indices of Species	Number
Sorbable		(1)$C\ell^-$, (2)$CO_3^=$, (3)HCO_3^-, (4)OH^-	$\tilde{n} = 4$
Reactive	Nonsorbable	(5)H_2CO_3, (6)H^+	$n = 6$
	Fixed	none	$\bar{n} = 4$
Inactive	Nonsorbable	(0)Na^+	
	Fixed	(0)[quarternary amine]$^+$	

Solution Phase

	Species	$C\ell^-$	$CO_3^=$	HCO_3^-	OH^-	H_2CO_3	H^+
Moiety/Reaction	k/ℓ i	1	2	3	4	5	6
$C\ell$	1	1	0	0	0	0	0
CO_3	2	0	1	1	0	1	0
H	3	0	0	1	−1	2	1
$H_2O \rightleftharpoons H^+ + OH^-$	4	0	0	0	1	0	1
$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$	5	0	0	1	0	−1	1
$HCO_3^- \rightleftharpoons CO_3^= + H^+$	6	0	1	−1	0	0	1

Exchanger Phase

	Species	$C\ell^-$	$CO_3^=$	HCO_3^-	OH^-
Moiety/Reaction	k/ℓ i	1	2	3	4
$C\ell$	1	1	0	0	0
CO_3	2	0	1	1	0
H	3	0	0	1	−1
$HCO_3^- + OH^- \rightleftharpoons CO_3^= + H_2O$	4	0	1	−1	−1

"salinity wave" (Helfferich and Bennett, 1984a,b) traveling without any retardation by ion exchange.

Ion-exchange equilibria

For this bivariant system, one should write two independent ion-exchange equilibrium relations. Assuming constant separation factors for the pairs of the three monovalent counterions, $C\ell^-$, HCO_3^-, and OH^-, one has:

$$x_3y_1/x_1y_3 = \alpha_{13} \quad x_4y_1/x_1y_4 = \alpha_{14} \tag{A1}$$

To fit into the form of Eqs. 24, these relations can be rearranged as follows:

$$\left.\begin{aligned} g_1(\{y_i\}) &= y_1/y_3 = \alpha_{13}x_1/x_3 = f_1(\{x_i\}) \\ g_2(\{y_i\}) &= y_1/y_4 = \alpha_{14}x_1/x_4 = f_2(\{x_i\}) \end{aligned}\right\} \tag{A2}$$

Eigenvalue problem at coherence

Among the three sorbable moieties $C\ell$, CO_3, and H (H is sorbable although H^+ is a nonsorbable species), choose the first two as independent ones. Then, one can write the eigenvalue problem (Eq. 29) specifically for this system as follows:

$$\begin{vmatrix} \partial q_1/\partial s_1 - \lambda & \partial q_1/\partial s_2 \\ \partial q_2/\partial s_1 & \partial q_2/\partial s_2 - \lambda \end{vmatrix} = 0 \tag{A3}$$

To formulate the Jacobian matrix, $\{\partial q_h/\partial s_k\}_{2\times 2}$, one can use Eqs. 32 and 33, where the two matrices associated with the ion-exchange equilibria (Eq. A2) can be written as:

$$\{\partial f_h/\partial x_i\}_{2\times 6} = \begin{bmatrix} \alpha_{13}/x_3 & 0 & -\alpha_{13}x_1/x_3^2 & 0 & 0 & 0 \\ \alpha_{14}/x_4 & 0 & 0 & -\alpha_{14}x_1/x_4^2 & 0 & 0 \end{bmatrix} \tag{A4}$$

$$\{\partial g_h/\partial y_i\}_{2\times 4} = \begin{bmatrix} 1/y_3 & 0 & -y_1/y_3^2 & 0 \\ 1/y_4 & 0 & 0 & -y_1/y_4^2 \end{bmatrix} \tag{A5}$$

To relate the concentrations of the species to those of the two independent sorbable moieties, one can use Eqs. 30, 31 and 34, and an exchanger-phase form of Eqs. 34.

Composition path grid

For demonstration of the composition path grid, consider a column operated at temperature 25°C with an exchanger of capacity 1.97 meq/mL in contact with a buffer solution of constant Na^+ concentration 0.05 meq/mL. The two concentrations were chosen as the references ($\bar{c}$ and c) for the two phases, respectively. With the assumption of unit activity coefficients in the solution phase, the ionization constant of H_2O and the dissociation constants of H_2CO_3 and HCO_3^- at 25°C were obtained from handbooks. Also, with the same assumption imposed on the intraexchanger pores, the reaction constant in the exchanger phase was calculated (see Helfferich and Bennett, 1984a) with the above solution-phase constants and the fractional water content in the exchanger (0.6 was used). These constants were then normalized; the values are listed below:

Solution:

$$K_4 = 4.0 \times 10^{-12} \quad K_5 = 9.2 \times 10^{-6} \quad K_6 = 8.8 \times 10^{-10}$$

Exchanger:

$$\bar{K}_4 = 1.4 \times 10^4$$

The values of separation factors employed are experimental values for $C\ell^-$ to HCO_3^- (Helfferich and Bennett, 1984a) and for $C\ell^-$ to OH^- (Kunin and Vassiliou, 1964):

$$\alpha_{13} = 2.00 \quad \alpha_{14} = 7.39$$

With these data, a grid of composition paths was constructed by the proposed numerical techniques, Figure A1. The paths associated with the greater eigenvalue λ_1 (and thus smaller wave velocity) are called "slow paths"; those associated with the smaller eigenvalue λ_2, called "fast paths." On each composition path, the direction in which the associated eigenvalue increases is indicated by an arrow. Local maxima and minima of eigenvalues as well as watershed points are also marked in the path grid.

Column experiment

For test of the composition path grid and demonstration of its usage, a simple column experiment was carried out with an anion-exchanger bed of 31.5 mL packed in a glass tube of 1 cm^2 cross-sectional area. The fractional void volume (ϵ) of the bed was estimated as 0.4 (accordingly, $\gamma = 59.1$). A sodium chloride/carbonate buffer solution was fed at a constant flow rate 22.5 mL/min ($v^o = 0.94$ cm/s) to the exchanger bed which had

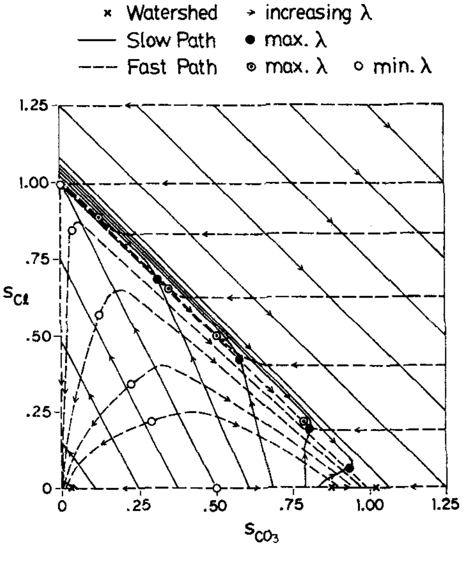

Figure A1. Composition path grid for chloride/carbonate buffer system with strong-base anion exchanger.

been presaturated with another buffer solution of different concentrations of $C\ell^-$ and total CO_3 but the same concentration of Na^+ (0.05 meq/mL). The effluent history was recorded by determining the effluent concentrations of $C\ell^-$ and total CO_3 with chloride and carbon-dioxide electrodes, respectively.

Composition route

The performance of such a column experiment can be predicted by using the composition path grid given in Figure A1 along with the integral coherence condition (Eq. 28). The predicted composition route is shown in Figure A2. The compositions of the feed and the presaturant are denoted by points F and P, respectively. According to the equilibrium theory, the step change FP is resolved into two coherent waves, which can be expressed by composition routes in the composition space. The composition route of the slower wave lies on the slow path FI even if it is a shock wave since this path is linear. The variation of the eigenvalue λ_1 along FI reveals that this wave is indeed a shock wave associated with an eigenvalue Λ_1. In contrast, the composition route of the faster wave would follow the fast path INMP only if it were a diffuse wave. Unfortunately, this wave turns out to be a composite wave containing a shock portion owing to the local minimum and maximum of the eigenvalue λ_2 at points N and M, respectively. The shock portion should correspond to a straight subroute with one end point on the path IN and the other on the path MP. This pair of composition points must satisfy not only the integral coherence condition (Eq. 28) but also an equal-velocity condition requiring λ_2 at both compositions to be equal to the shock-wave eigenvalue Λ_2. These conditions lead to a straight subroute IJ. Accordingly, the faster wave is a composite wave consisting of a shock and a diffuse portion represented by subroutes IJ and JP, respectively.

Effluent history

With the eigenvalues along the overall composition route FIJP (Λ_1 of FI, Λ_2 of IJ, and λ_2 along JP) as well as the values of γ and v^o, the wave velocities were calculated with Eqs. 25 and 26, and then the effluent history was predicted as shown in Figure A3. For comparison, the observed effluent history is included in Figure A3 and the corresponding composition points are marked in Figure A2. These figures demonstrate that the equilibrium theory provides a good prediction of the wave velocities and the composition (I) of the intermediate zone. The dissipation of the slower wave (FI) as evident in Figure A3 may be attributed to nonequilibrium since the flow rate here is relatively high with respect to the ion-exchange rate on the Amberlite IRA-400 resin beads of 16–50 mesh.

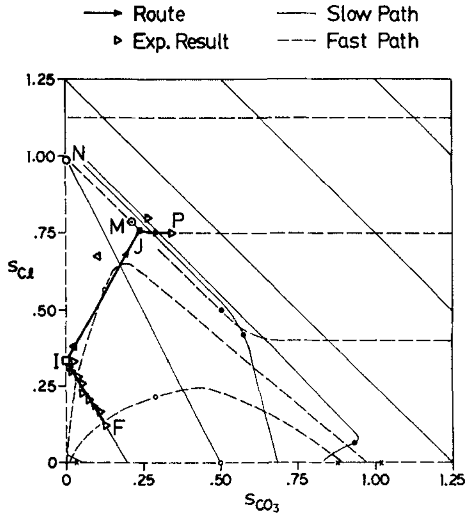

Figure A2. Composition route for column experiment of chloride/carbonate buffer system with strong-base anion exchanger.

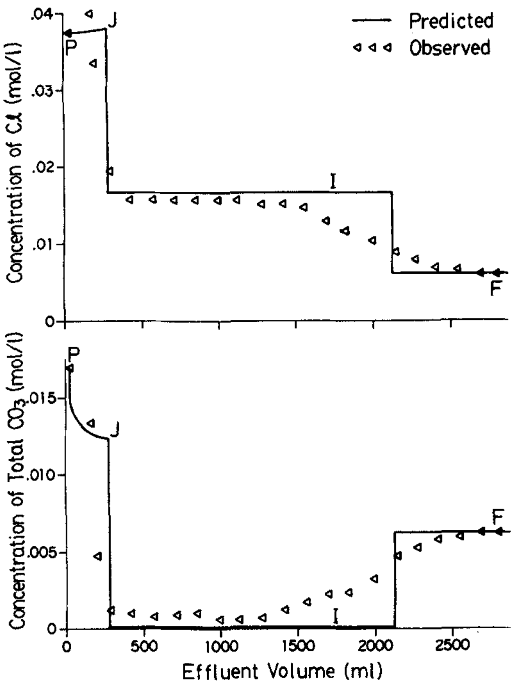

Figure A3. Predicted and observed effluent histories for column experiment of chloride/carbonate buffer system with strong-base anion exchanger.

Notation

A_i = species i
c = reference concentration of solution phase, mmol/ml
$\bar{c}$ = reference concentration of exchanger phase, mmol/ml
c_i = concentration of species i in solution, mmol/ml
$\bar{c}_i$ = concentration of species i in exchanger, mmol/ml
D = square matrix defined in Eqs. 33
E = square matrix defined in Eqs. 33
F = Jacobian matrix associated with sorption equilibria in terms of species concentrations
f_k = function of solution-phase concentrations to specify sorption equilibria
G = Jacobian matrix associated with sorption equilibria in terms of sorbable-moiety concentrations
g_k = function of exchanger-phase concentrations to specify sorption equilibria
I = identity matrix
K_ℓ = normalized equilibrium constant for reaction ℓ in solution
$\bar{K}_\ell$ = normalized equilibrium constant for reaction ℓ in exchanger
m = number of moieties in solution
$\bar{m}$ = number of moieties in exchanger
$\hat{m}$ = number of sorbable moieties
n = number of species in solution
$\bar{n}$ = number of species in exchanger

$\tilde{n}$ = number of sorbable species
q_k = normalized concentration of sorbable moiety k in exchanger
R_i = normalized reaction term (generation) of species i in solution
$\overline{R}_i$ = normalized reaction term (generation) of species i in exchanger
r_k = normalized concentration of nonsorbable moiety k in solution
$\overline{r}_k$ = normalized concentration of fixed moiety k in exchanger
S_k = moiety k, conserved with respect to reactions
s_k = normalized concentration of sorbable moiety k in solution
t = time, s
v^o = bulk-flow velocity of solution, cm/s
v_{sk} = wave velocity in terms of solution-phase concentration of moiety k, cm/s
v_{xi} = wave velocity in terms of solution-phase concentration of species i, cm/s
$v_{\Delta sk}$ = shock wave velocity in terms of concentration of moiety k, cm/s
$v_{\Delta xi}$ = shock wave velocity in terms of concentration of species i, cm/s
x_i = normalized concentration of species i in solution, $x_i \equiv c_i/c$
y_i = normalized concentration of species i in exchanger, $y_i \equiv \overline{c}_i/\overline{c}$
z = distance from column entry, cm
z_i = valence of species i in solution
$\overline{z}_i$ = valence of species i in exchanger

Greek letters

α_{ij} = separation factor of counterion i relative to counterion j
γ = ratio of reference concentrations with adjustment of volume bases, $\gamma \equiv (1 - \epsilon)\overline{c}/(\epsilon c)$
Δ = difference across a shock wave
δ_{hk} = Kronecker delta, $\delta_{hk} = 1$ if $h = k$, $\delta_{hk} = 0$ otherwise
ϵ = fractional void volume of column
Λ = eigenvalue for coherent shock wave
λ = eigenvalue for coherent wave
μ_{ki} = reaction-coupling factor of species i with respect to moiety k in solution
$\overline{\mu}_{ki}$ = reaction-coupling factor of species i with respect to moiety k in exchanger
$\nu_{\ell i}$ = stoichiometric coefficient of species i for reaction ℓ in solution
$\overline{\nu}_{\ell i}$ = stoichiometric coefficient of species i for reaction ℓ in exchanger
ω = charge sign of coions and fixed ionic groups

Subscripts

i, j = species index
h,k = moiety index
ℓ = reaction index

Literature Cited

Aris, R., *Introduction to the Analysis of Chemical Reactors,* Ch. 2, Prentice-Hall, Englewood Cliffs, NJ (1965).

Bryant, S. L., R. S. Schechter, and L. W. Lake, "Interactions of Precipitation/Dissolution Waves and Ion Exchange in Flow Through Permeable Media," *AIChE J.,* **32,** 751 (1986).

Bunge, A. L., and C. J. Radke, "Pulse Chromatography of Adsorbing and Reacting Chemicals," *AIChE Symp. Ser.,* **78**(219), 3 (1975).

Carnahan, B., H. A. Luther, and J. O. Wilkes, *Applied Numerical Methods,* Chs. 4 and 5, Wiley, New York (1969).

Clifford, D. A., and W. J. Weber, "Nitrate Removal from Water Supplies by Ion Exchange," EPA-600/2-78-052, U.S. EPA (1978).

Clifford, D. A., "Multicomponent Ion-Exchange Calculations for Selected Ion Separations," *Ind. Eng. Chem. Fund.,* **21,** 141 (1982).

Collins, C. G., and H. A. Deans, "Direct Chromatographic Equilibrium Studies in Chemically Reactive Gas-Solid Systems," *AIChE J.,* **14,** 25 (1968).

Deans, H. A., F. J. M. Horn, and G. Klauser, "Perturbation Chromatography in Chemically Reactive Systems," *AIChE J.,* **16,** 426 (1970).

DeVault, D., "The Theory of Chromatography," *J. Am. Chem. Soc.,* **65,** 532 (1943).

Glückauf, E., "Contributions to the Theory of Chromatography," *Proc. Roy. Soc. (London),* **A186,** 35 (1946).

Golden, F. M., K. I. Shiloh, G. Klein, and T. Vermeulen, "Theory of Ion-Complexing Effects in Ion-Exchange Column Performance," *J. Phys. Chem.,* **78,** 926 (1974).

Helfferich, F. G., "Multicomponent Ion Exchange in Fixed Beds—Generalized Equilibrium Theory for Systems with Constant Separation Factors," *Ind. Eng. Chem. Fund.* **6,** 362 (1967).

Helfferich, F., "Chromatographic Behavior of Interfering Solutes—Conceptual Basis and Outline of a General Theory," *Adv. Chem. Ser.,* **79,** 30 (1968).

Helfferich, F., and G. Klein, *Multicomponent Chromatography—Theory of Interference,* Marcel Dekker, New York (1970).

Helfferich, F. G., and B. J. Bennett, "Weak Electrolytes, Polybasic Acids, and Buffers in Anion Exchange Columns—I. Sodium Acetate and Sodium Carbonate systems," *Reactive Poly.,* **3,** 51 (1984a).

Helfferich, F. G., and B. J. Bennett, "Weak Electrolytes, Polybasic Acids, and Buffers in Anion Exchange Columns—II. Sodium Acetate Chloride Systems," *Solvent Extr. Ion Exch.,* **2,** 1151 (1984b).

Hwang, Y.-L., and F. G. Helfferich, "Generalized Model for Multispecies Ion-Exchange Kinetics Including Fast Reversible Reactions," *Reactive Poly.,* **5,** 237 (1987).

IMSL Inc., *IMSL (International Mathematical and Statistical Library of Subprograms) Library Reference Manual,* 3 vols., IMSL LIB-0008, IMSL Inc., Houston (1980).

Klein, G., D. Tondeur, and T. Vermeulen, "Multicomponent Ion Exchange in Fixed Beds—General Properties of Equilibrium Systems," *Ind. Eng. Chem. Fund.,* **6,** 339 (1967).

Klein, G., "Ion Exchange and Chemical Reaction in Fixed Beds," *Percolation Processes—Theory and Applications,* A. E. Rodrigues and D. Tonduer, eds., Sijthoff & Noordhoff, Alphen aan den Rijn, Netherlands, 363 (1981).

Klein, G., "Fixed-Bed Ion Exchange with Formation or Dissolution of Precipitate," *Ion Exchange: Science and Technology,* A. E. Rodrigues, ed., Martinus Nijhoff Publishers, Dordrecht, Netherlands, 199 (1986).

Kočiřík, M., "A Contribution to the Theory of Chromatography—Linear Nonequilibrium Chromatography with a Chemical Reaction of the First Order," *J. Chromatog.,* **30,** 459 (1967).

Kunin, R., and B. Vassiliou, "New Deionization Techniques Based upon Weak Electrolyte Ion Exchange Resins," *Ind. Eng. Chem. Proc. Des. Dev.,* **3,** 404 (1964).

Magee, E. M., "The Course of a Reaction in a Chromatographic Column," *Ind. Eng. Chem. Fund.,* **2,** 32 (1963).

Rhee, H.-K., R. Aris, and N. R. Amundson, "On the Theory of Multicomponent Chromatography," *Phil. Trans. Roy. Soc.,* **A267,** 419 (1970).

Schweich, D., and J. Villermaux, "The Chromatographic Reactor—A New Theoretical Approach," *Ind. Eng. Chem. Fund.,* **17,** 1 (1978).

Schweich, D., J. Villermaux, and M. Sardin, "An Introduction to the Nonlinear Theory of Adsorptive Reactors," *AIChE J.,* **26,** 477 (1980).

Tondeur, D., and G. Klein, "Multicomponent Ion Exchange in Fixed Beds—Constant-Separation-Factor Equilibrium," *Ind. Eng. Chem. Fund.,* **6,** 351 (1967).

Tondeur, D., "Theory of Ion-Exchange Columns," *Chem. Eng. J.,* **1,** 337 (1970).

Wang, N.-H. L. and S. Huang, "Multicomponent Ion Exchange in Fixed Beds for Selective Removal of Ammonium Carbonate," *AIChE Symp. Ser.,* **79,**(230), 26 (1983).

Weiss, J., "On the Theory of Chromatography," *J. Chem. Soc. (London),* 297 (1943).

Wicke, E., "Empirische und theoretische Untersuchungen der Sorptionsgeschwindigkeit von Gasen an porösen Stoffen—II," *Kolloid Z.,* **86,** 295 (1939).

Wilson, J. N., "A Theory of Chromatography," *J. Am. Chem. Soc.,* **62,** 1583 (1940).

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