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Nonlinear theory of multicomponent sorption dynamics and chromatography

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Abstract. The results of studies on the nonlinear theory of sorption dynamics and chromatography under conditions of interdependent sorption of the components are surveyed and treated systematically. The principal properties of multicomponent dynamic sorption systems and of the results arising from the nonlinear character of the mass balance equations are analysed in detail. These nonlinear equations describe the propagation and interaction of the multicomponent concentration waves generated in the sorption column during the chromatographic process for a multicomponent mixture of the substances being sorbed. A series of solutions (including those making allowance for dispersion factors in the sorption process), describing the multicomponent concentration waves during their propagation nonlinear multicomponent dynamic sorption systems, are considered. The bibliography includes 224 references.

I. Introduction

Chromatography describes a dynamic process in which at least two phases (one of which is continuous and the other disperse) move relative to one another and mass and/or heat exchange takes place between their interfaces. The general term filtration or percolation processes is frequently applied abroad to such processes.[1] There are phenomenological concepts,[1] potentially common to all filtration processes, which can also be extended to a whole series of other migration phenomena such as sedimentation,[2] electrophoresis,[3] and others.[1,4–6]

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The increased loadings applied to apparatus and columns in connection with the tendency to intensify modern technological processes leads to the need to separate mixtures of substances at high concentrations (including sorption separations).[7–19] As a result, in the analysis of percolation processes it is necessary to take into account their nonlinearity and nonstationary nature and also the multicomponent nature of the dynamic systems considered.

Even in one-component sorption systems, the effects of nonlinearity play a major role, since they are responsible for the tendency of the concentration wave generated in the column to be stabilised or, conversely, to undergo progressive spreading.[20] If the substances sorbed do not interact in the column, the multicomponent system reduces to a one-component system. This special case makes it possible to regard a multicomponent system as a superposition of independent one-component systems. The hypothesis that there is no sorption interaction between the components usually holds in the case of analytical separations at low concentrations and for small loadings applied to the sorbent or in the elution version where the chromatographic peaks move apart rapidly. For preparative separations, where at high concentrations of the molecules the latter compete for a limited number of accessible sorption centres, this hypothesis becomes inapplicable.

When molecules or ions compete for sorption centres, one may speak of the sorption interaction of species in the disperse phase, i.e. of the mutual influence of the components during the sorption process. This effect has been relevantly called the 'interference of species' in the monograph by Helfferich and Klein [21] (see also Helfferich's review [22]). The same term is used in the thermodynamics of irreversible processes [23] to characterise the mutual influence of coexisting processes — the so-called 'cross effects'.[24]

There exists yet another aspect of the interference of substances — the interference of concentration waves propagating at different wave velocities during their generation, collision, and interaction in the course of the sorption processes.[21,22]

process is completely analogous to the processes considered in fluid mechanics and in gas dynamics.

In the general case, the interference of substances in a dynamic sorption process can arise as a consequence of various types or forms of interaction. Each of the mixture components may affect the equilibrium interphase distribution of other substances (static interference effects) and also the time required for the establishment of equilibrium between the concentrations in the disperse and continuous phases (kinetic interference effects). The molecules of the substances may be transformed to another state as a result of a chemical reaction (for example, on complex formation) and under these conditions both static and kinetic interference effects may arise.[21,22]

The static interference effects can be considered on the basis of the ideal equilibrium model of the sorption system. Numerous studies have been considered by the nonlinear theory of isothermal multicomponent sorption dynamics and chromatography involving the application of the ideal model (see, for example, Refs 20–22 and 25–73). In particular, the results of mathematical investigations included the theory of systems of quasi-linear equations in terms of partial derivatives have been used in such studies.[4,39,46,47,74–79]

At the present time, the ideal model has been used successfully for a qualitative explanation of a number of characteristics of the behaviour of multicomponent sorption systems and in many cases also for a quantitative prediction of the results. A further increase in the complexity of the behaviour of multicomponent nonlinear sorption systems is associated with the operation of interference effects together with nonideality factors (a finite rate of establishment of an equilibrium interphase distribution of substances, longitudinal dispersion, etc.). The operation of the static interference effects is fundamentally nonlinear and plays the main role in the behaviour of multicomponent concentration waves generated in the column. The additivity of the factors is impossible under these conditions because of the fundamentally nonlinear character of the multicomponent sorption systems.

The equilibrium properties of sorption systems determine the static interference effects and also sequence, types, forms, and propagation velocities of multicomponent concentration waves. The kinetic and dynamic nonideality factors introduce second-order changes under these conditions into the behaviour of concentration waves. The equilibrium properties of sorption systems determine the first statistical moment of the concentration waves, whereas the nonideality factors determine the second and higher statistical moments.[21]

The successful solution of the problem of the interference of substances and concentration waves together with the description of the behaviour of multicomponent sorption systems in terms of the propagating concentration waves became possible after the introduction of the concept of 'coherence'.[21,22,35,36] This concept was developed by Helfferich[22,35,36,80,81] to facilitate the qualitative understanding and quantitative calculations in the theory of multicomponent nonlinear chromatography under arbitrary initial and boundary conditions. This general concept is fundamental and is applicable to a large class of percolation processes of similar nature.

For a compound multicomponent wave in a nonlinear sorption system, the state of coherence means that the concentration waves for each individual component move jointly without 'splitting', and this implies that their velocities are the same at each point. This leads to the problem of the determination of the eigenvalues and eigenvectors in the mass balance equations for the components.[22,25–31,39,46,47,74–79] The problems of the determination of the eigenvalues for the wave velocities in the theory of multicomponent chromatography, in the fluids and gases mechanic and in nonequilibrium thermodynamics are closely related.

The coherence condition determines the response of the multicomponent system to its perturbation and denotes the state to which it tends. A closed system tends in exactly the same way to attain a state of equilibrium, while an open system with fixed boundaries and constant conditions imposed on them tends to attain a stationary dynamic state.[22,81]

Preparative displacement chromatography, which deals with large concentrations and a strong influence of interference, makes it possible to achieve simultaneously enhancement of concentration and purification of substances. In preparative multicomponent sorption and chromatographic separations, the large loadings applied to the columns and the high concentrations of the components to be separated are responsible for the specific features of the multicomponent dynamic sorption process. These specific features are associated with the interference of the species, which is particularly significant for frontal, displacement, elution, and vacancy versions.[8,9,16]

Nonlinear preparative chromatography, which makes it possible to achieve good results in the separation of substances, has undergone a fresh development recently. It has been applied particularly vigorously in biotechnology.[7,10–12,13,15,17–19] Despite the relatively high cost of the separation, it is more than worthwhile because the final bioproduct is more expensive.[10,11,13]

The aim of the present review is to present the state of the art in the field of the theory of multicomponent nonlinear sorption dynamics and chromatography and also to consider the fundamental theoretical features of the behaviour of dynamic sorption systems in the separation of interfering species. In studies on such systems, it is possible to distinguish three main aspects: statics, kinetics, and dynamics of sorption.

II. Sorption statics

The statics of sorption processes is the study of the equilibrium relations between the concentrations of substances in the continuous and disperse phases. Under isothermal conditions, the interaction of the mixture of sorbable species in the continuous phase with the disperse phase determines the sorption isotherms of the components. The sorption isotherms of the mixture characterise the fundamental thermodynamic properties of the system and permit the calculation of the concentration distributions on the basis of the solution of the mass-balance equations.

The chromatographic separation is based on the difference between the equilibrium relations for the mixture of sorbable components. The greater this difference the more effective the separation of the components, other conditions being equal. In the competition of different molecules for available free sites in the sorbent, one may refer to the 'interaction' of the substances in the disperse phase or to their interference,[21,22] i.e. to the mutual influence of the substances on one another's sorption.

Interference presupposes that the concentration of any component i in the disperse phase (a_i) depends not only on the concentration of this substance in the continuous phase (c_i), as happens in systems without interference, but also on the concentrations (c_j) of all other substances, i.e.

$$a_i = f_i(c_1, ..., c_m), \quad i, j = 1, 2, ..., m . \tag{1}$$

Thus the sorption isotherms for the mixture represent the dependences of the concentrations of the substances in the disperse phase on the mixture composition $\{c_1, ..., c_j, ..., c_m\}$ at a constant temperature.

The number of multicomponent concentration waves arising in the column is determined by the parameter which is called the variance of the multicomponent sorption system.[50,82] The variance (m), the value of which is determined by the Gibbs phase rule,[83–86] characterises the number of degrees of freedom of the multicomponent system under isothermal conditions, i.e. it characterises the minimum number of concentration variables which determine the composition of the mixture at equilibrium. In order to calculate the concentration distributions in the sorption system with a variance m, it is necessary to specify m isotherms, each isotherm f_i representing a surface in a multidimensional concentration space $\{c_1, ..., c_j, ..., c_m\}$.

Using the concentration distribution ratio a_i/c_i, it is easy to determine the sequence of affinities of the substances for the sorbent or, in other words, the 'affinity sequence' of the components: 1, 2, ..., n. The component i has a greater affinity than the component j provided that the inequality $a_i/c_i > a_j/c_j$ holds. Here it is assumed that $i < j$ for the affinity sequence. The separation factor α_{ij} is defined as the ratio

$$\alpha_{ij} = \frac{a_i/c_i}{a_j/c_j}, \quad i,j = 1,...,n, \tag{2}$$

where $\alpha_{ii} = 1$, $\alpha_{ij} = 1/\alpha_{ji}$, and $\alpha_{ij}\alpha_{jk} = \alpha_{ik}$.

In the affinity sequence 1, 2, ..., i, ..., j, ..., n, the components are arranged in the order of decreasing affinity.

When the mixture composition is varied, the positions of the components in the affinity sequence may remain unchanged (we have the so-called 'invariant' affinity sequence[21]) or it may vary. The change in the affinity sequence is called 'inversion'[33,87] or selectivity reversal.[52,88,89] It is remarkable that in certain cases the components do not change positions in the affinity sequence for a univariant system (when the mixture composition changes in the binary i/j exchange of heterovalent ions), but in multicomponent systems (for example, in the exchange of more than three ions) inversion is possible.[21,38]

An even more complex variant of the inversion arises in nonlinear ion-exchange systems, where the equilibria are complicated by the occurrence of chemical reactions, in particular by complex formation. In such cases, inversion is possible even in systems with a variance $m = 1$, i.e. in two-component i/j systems. Combined concentration waves, in which one region of the wave tends to become sharper whilst the other undergoes progressive spreading, may then be generated in the column.

The equivalence (stoichiometry) conditions

$$\sum_i a_i = a_0, \qquad \sum_i c_i = c_0$$

or

$$\sum_i Y_i = 1, \qquad \sum_i X_i = 1, \quad i = 1,...,n, \tag{3}$$

where $Y_i = a_i/a_0$ and $X_i = c_i/c_0$ are dimensionless (normalised) concentrations, are usually valid for ion exchange. When these conditions are taken into account, the variance m of a stoichiometric system in which n ions undergo exchange, is $n-1$ and the system must be regarded as an m-component system.

The relations

$$\left(\frac{\partial a_i}{\partial c_k}\right)_{c_s} < 0, \quad j \neq k; \qquad \left(\frac{\partial a_j}{\partial c_k}\right)_{c_s} > 0, \tag{4}$$

where s, j, $k = 1,...,m$, hold for the sorption of competing substances. Thus, as a result of the competition of the components for available sorption sites, an increase in the concentration c_k leads to a decrease in the concentration a_j for all $j \neq k$. The greater the affinity of the kth component for the sorbent, the stronger this effect.

$$\left(\frac{\partial a_j}{\partial c_k}\right)_{c_s} < \left(\frac{\partial a_j}{\partial c_l}\right)_{c_s} < 0, \quad \text{when } \alpha_{kl} < 1 \tag{5}$$

If the sign of the effect is reversed, then the sorption of substances is called synergistic.

$$\left(\frac{\partial a_j}{\partial c_k}\right)_{c_s} > 0, \quad j \neq k \tag{6}$$

An increase in the sorbability of one component (j) with increase in the concentration of another (k) may arise when the molecules of these substances tend to form complexes or aggregates in the stationary phase.

Having expressed a_j in terms of c_j with the aid of the Law of Mass Action (LMA) [Eqn (2)] and having substituted this value in Eqn (3), we obtain the Langmuir relations for mixture isotherms reflecting the interference of substances in the m-component system:[21]

$$a_i = f_i(c) = \frac{a_0 c_i}{\sum_j \alpha_{ji} c_j}$$

or

$$Y_i = \frac{X_i}{\sum_j \alpha_{ji} X_j}, \quad i,j = 1,...,n. \tag{7}$$

The model of an ideal localised monolayer was introduced by Langmuir[90] for a single component, but the simplicity of the analytical expression (7) for a mixture of substances[91] makes it possible to employ it widely for calculations in the nonlinear theory of multicomponent sorption dynamics and chromatography (see, for example, Refs 92–132).

The Langmuir relations (7) for physical sorption are written in the form

$$a_i = \frac{(a_0/c_0)\alpha_{ik} c_i}{1 + \sum_j b_j c_j}$$

or

$$Y_i = \frac{\alpha_{ik} X_i}{1 + \sum_j (\alpha_{jk} - 1) X_j}, \quad i,j = 1,...,m. \tag{8}$$

Langmuir's adsorption theory[133] can be extended to the adsorption of gaseous mixtures[134,135] if it is supposed that the molecules are adsorbed at specific sites and do not interact with one another. These equations are referred to as the Langmuir equations for the adsorption of a mixture of gases. Similar equations have also been obtained in other studies[136,137] employing the Law of Mass Action.

For constant separation factors α_{jk}, the Langmuir relations (8) for an m-component system with nonstoichiometric sorption can be formally reduced to the Langmuir relations for a stoichiometric system with $m + 1$ components. For this purpose, it is necessary to introduce a kth dummy species with a concentration c_k and one must put[21]

$$\Gamma_i = \frac{a_0}{c_o}\alpha_{ik}, \quad V_i \equiv b_i c_i = (\alpha_{ik} - 1)X_i, \quad i = 1, 2, ..., k-1,$$

$$\Gamma_j = \frac{a_0}{c_o}\alpha_{j+1k}, \quad V_j \equiv b_j c_j = (\alpha_{j+1k} - 1)X_{j+1}, \quad j = k, ..., m. \tag{9}$$

Thus the stoichiometric system described by Eqns (2) and (3) for the exchange of n equal-valence ions may be reduced to the Langmuir sorption of a mixture of m components (where $m = n-1$). The Langmuir equilibrium relations for a mixture have been discussed in detail in a monograph.[138] Various properties of the mixture isotherms, obtained with the aid of derivatives of types (4) and (5), have been described.[26] The Langmuir relations (7) or (8) for the mixture isotherms satisfy all the properties described in the above study.[26]

Several dynamic methods for the construction of isotherms on the basis of column output curves have been developed for one-component sorption systems, among which the elution[139,140] and frontal analysis[141,142] methods are the most popular. These methods were updated later for the measurement of isotherms

for binary and multicomponent mixtures.[62,143–146] However the frontal chromatographic method is fairly laborious, since it requires a large number of measurements, pure substances, and takes a long time. This method has been compared with one based on the nonlinear wave effects involving a transformation of a hodograph and the optimum experimental conditions for the applicability of both methods have been determined.[147]

Analytical expressions for mixtures isotherms which could be derived by the methods of statistical physics are lacking. Phenomenological equations for the mixture isotherms, based on the Law of Mass Action, are most widely used.

We shall consider systems in which sorption is stoichiometric [i.e. Eqns (3) hold]. Any composition of a mixture of species can be represented by a point in the 'composition space' $\{c_i\}$ or $\{a_i\}$. This term is applied[21] to an m-dimensional (n-dimensional for a stoichiometric system) space, along the axes of which the concentrations of the mixture components X_i or Y_i are plotted, as shown in Fig. 1*a* for a three-dimensional ($n = 3$) space.

For the normalised concentrations X_i or Y_i, the space of the possible changes in concentrations is a cube for $n = 3$ and a hypercube for $n > 3$, since the inequalities $1 \geqslant Y_i$ and $X_i \geqslant 0$ hold. Eqn (3), defining the stoichiometry of the exchange, reduces the dimensionality of the space of the possible changes in concentration to a hyperplane (for $n > 3$) $P_1 \ldots P_n$, where, as can be seen from Fig. 1*a*, at the points P_i the concentration $X_i(P_i) = 1$, while the concentrations of the remaining components are zero. This hyperplane is usually referred to as a 'simplex'.[21] Figs 1*a* and 2 present examples of simplexes for a stoichiometric

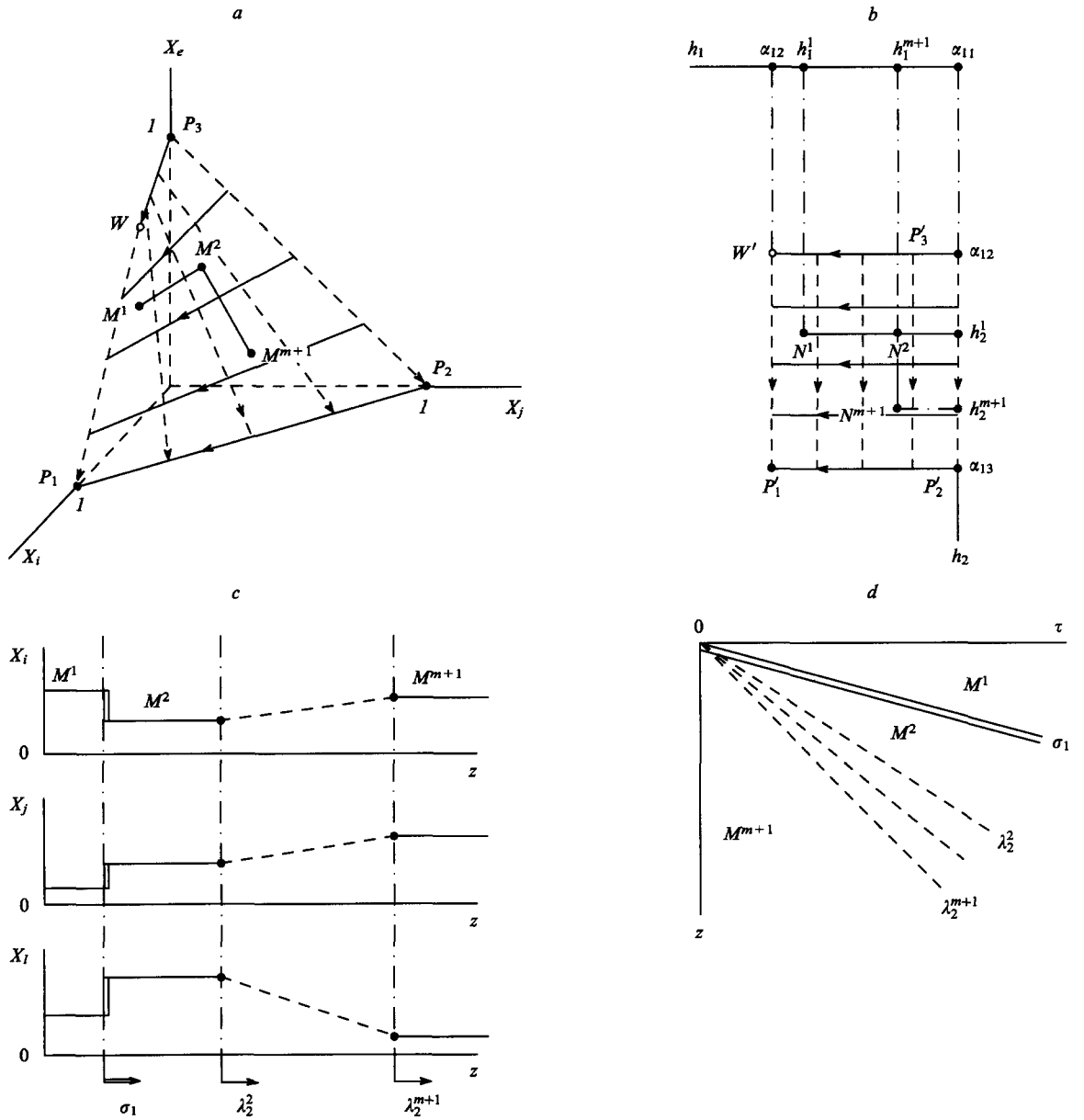


Figure 1. Representations of the characteristics of a three-component stoichiometric system in the composition space and in the physical plane. (*a*) the simplex $P_1P_2P_3$ for a two-component Langmuir system and the characteristic Γ^k paths corresponding to simple k-waves; (*b*) the Riemann invariants space $\{h_k\}$ and the h-transformation of the composition space $\{X_i\}$ (*a*) into the Riemann invariants space $\{h_k\}$ (*b*). Points M^s represent the concentration plateau in the k-wave; points $N^s\{h_k^s\}$ in the invariants space $\{h_k\}$ correspond to points M^s in the concentration space $\{X_i\}$ in Fig. 1*a*; the arrows denote the directions in which the invariants h_k increase along the k-wave; the condition $X_i(P_i) = 1$ holds at points P_i, whilst the condition $h_i = \alpha_{li+1}$ is valid at points P_i'; (*c*) the concentration profiles in the shock k-wave M^1M^2 ($k = 1$) and in the spreading k-wave M^2M^{m+1} ($k = 2$) corresponding to the $M^1M^2M^{m+1}$ route in Fig. 1*a*; σ_1 is the velocity of the first shock wave and $\lambda_2^2, \ldots, \lambda_2^{m+1}$ are the velocities of the second spreading wave; (*d*) is the image on the physical plane (z,τ) of the propagation of the multicomponent concentration k-waves ($k = 1, 2$).

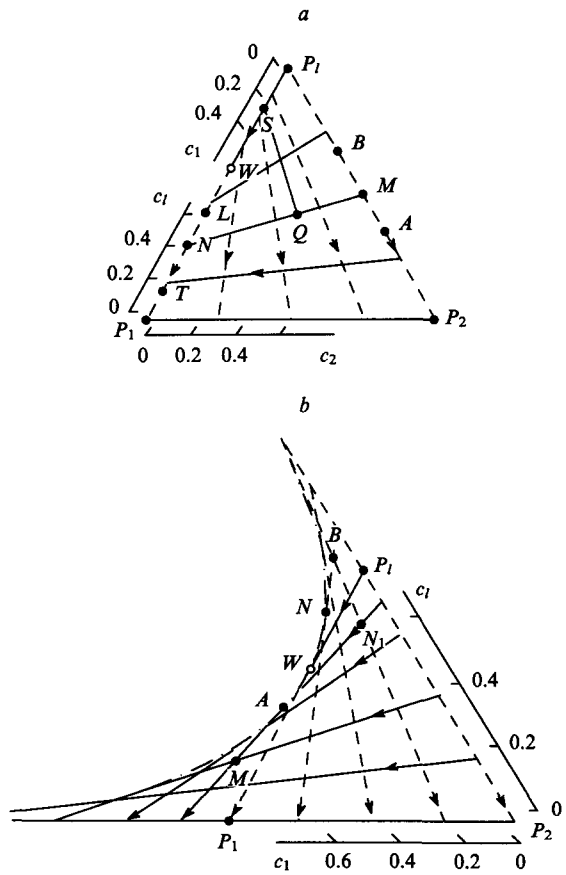


Figure 2. Hodographs for Langmuir two-component sorption systems (8) $\{c_i\}$ and for the equivalent stoichiometric three-component systems (9) $\{X_i\}$. (*a*) For the competitive sorption of the components (b_i, $b_j > 0$); (*b*) for the synergistic sorption of the components ($b_i > 0$, $b_j < 0$). The concentration points *A*, *M*, *N*, etc. correspond to different mixture compositions in the chromatographic process (see text).

Figs 1*a* and 2 present examples of simplexes for a stoichiometric three-component ($n = 3$) system with a variance of two ($m = 2$). Fig. 2 presents in the same region simplexes for a Langmuir two-component system, which is equivalent [see Eqn (9)] to a stoichiometric three-component system.[21]

The most frequently employed Langmuir multicomponent model lacks thermodynamic rigour, since Eqns (8) expressed in a general form do not satisfy the Gibbs–Duhem relations. Furthermore, the Langmuir model (8) does not yield exact predictions in calculations for elution chromatographic processes involving large loadings[62, 148] and does not take into account adequately the experimental data for competitive adsorption.[89, 145, 146] Nevertheless, in many special cases the Langmuir isotherm for a two-component mixture describes experimental data satisfactorily.[89]

Phenomenological bi-Langmuir models for mixture isotherms, represented by the sum of two Langmuir relations, have been proposed:[121, 149]

$$a_i = \frac{k_{i1}c_i}{1+\sum_j b_{j1}c_j} + \frac{k_{i2}c_i}{1+\sum_j b_{j2}c_j}, \quad i,j = 1, 2, ..., m, \qquad (10)$$

where the subscripts *i*1 and *i*2 refer to different adsorption sites[121] or to two different states of the molecules in the sorbent phase (when complex formation takes place in the sorbent phase).[149] Phenomenological equations of the mixture isotherms in the form of the bi-Langmuir relations (10) are frequently used in numerical calculations of concentration distributions.[66] It has been shown[121] that type (10) relations describe the sorption isotherms for mixtures of enantiomers, the first term corresponding to selective chiral interactions and the second to nonselective molecular interactions between the enantiomers and the stationary phase.

Generalised phenomenological equations, including Langmuir and Freundlich relations as special cases, have been proposed:[52, 53]

$$a_i = \frac{k_i c_i^{v_i}}{1+\sum_j b_j c_j^{v_j}}, \quad i,j = 1, ..., m. \qquad (11)$$

In order to eliminate the thermodynamic inconsistency mentioned above, the Langmuir multicomponent model (8) has been supplemented by the theory of an ideally adsorbed solution proposed by Myers and Prausnitz.[151] A thermodynamically consistent model of the competitive adsorption of components has been proposed by LeVan and Vermeulen.[150] The authors introduced into equations (8) of isotherms for two-component systems additional terms taking into account the difference between the column capacities for each component. To a first approximation, subject to the condition that the sorption capacities are the same for both components, the equations which they obtained for the isotherms reduce to the Langmuir equations (8). If the capacities for each component are different, then the LeVan–Vermeulen isotherm[150] can be represented by a rapidly converging series. In practical cases, this series can be restricted to the first two terms

$$a_i = \frac{wb_ic_i}{V} + \left(\frac{a_i}{b_i} - \frac{a_{3-i}}{b_{3-i}}\right) b_1b_2c_1c_2\ln(V),$$

$$V = 1 + b_1c_1 + b_2c_2; \qquad w = \frac{a_1c_1 + a_2c_2}{V-1}; \qquad i = 1, 2. \qquad (12)$$

When two one-component isotherms (for each individual component) are different, then the theory of the ideally adsorbed solution yields a numerical procedure for the determination of the isotherms for the competing components. This approach is based on the normalisation of the spreading pressure.[151] It has been shown[152] that the LeVan–Vermeulen model is consistent with the Gibbs adsorption theory. Numerical calculation of two chromatographic peaks with the aid of expansion (12) demonstrates a stronger displacement effect than could be predicted on the basis of the traditional Langmuir adsorption isotherms. For certain experimental systems, the application of isotherms (12) yields a satisfactory approximation.[89]

Analysis of two-component models based on the method of statistical thermodynamics shows that the equations of the isotherms represent the ratio of two polynomials of the same degree.[153, 154] In the special case of the Langmuir isotherm (8), this is the ratio of first degree polynomials. In another model based on statistical thermodynamics, which yields satisfactory results, the equation of the isotherm has been represented by the ratio of quadratic polynomials of the type.[148, 153]

$$a_i = \frac{k_ic_i + k_{i(3-i)}c_1c_2}{1 + b_1c_1 + b_2c_2 + b_{i(3-i)}c_1c_2}, \quad \text{when } i = 1, 2, \qquad (13)$$

where $k_{12} = k_{21}$ and the coefficients of this equation are the same as in the equation of a one-component isotherm for an individual *i*th component. The coefficients k_{ij} and b_{ij} must be determined from experiments on the adsorption of a binary mixture.

Fowler's isotherm

$$\frac{\theta_i}{c_i(1-\theta_1-\theta_2)} = b_0\exp[\chi_i(\theta_1+\theta_2)], \quad \text{when } i = 1, 2, \qquad (14)$$

where θ_i is the ratio of the concentration of the component in the disperse phase to the sorbent capacity and χ_i are numerical coefficients, may be applied to the description of two-component adsorption [135] taking into account the competitive adsorption of the mixture components. This isotherm is an example of an implicit concentration dependence. The description of the adsorption of a binary mixture with the aid of Eqn (14) requires five parameters: a_{01}, a_{02}, χ_1, χ_2, and b_0.

A binary isotherm model, based on the ion-exchange formalism, has been proposed.[155]

Certain models of isotherms for a two-component mixture have been used in the frontal analysis of the output curves for two components [156–158] for the determination of the constants in the corresponding equations. The simplest model is described by the two-component Langmuir relations (8) (for $i = 1, 2$). In a number of cases, especially when the sorbent capacities are the same for each component, this equation fits satisfactorily the mixture isotherms,[158] but it is more often inconsistent with experimental data.[146, 157] The binary isotherms have been determined and a comparative study of the four models (presented above) for the description of the sorption of phenylethanols on ODS silica gel has been made with the aid of the two-component frontal analysis of the output curves.[157]

We may note that one of the principal problems in the theory of the adsorption of mixtures — the prediction of mixture isotherms based on statistical data obtained for individual isotherms — has still not been solved.

In stoichiometric n-component systems, for which any i/j binary exchange obeys the Law of Mass Action in the form

$$\frac{(Y_i/X_i)^{\nu_i}}{(Y_j/X_j)^{\nu_j}} = K_{ij}, \quad \text{when } i, j = 1, ..., n, \tag{15}$$

(K_{ij} is a concentration constant), the relation between the concentrations Y_i and $\{X_1 ... X_n\}$ cannot be obtained in an explicit form. The equations of the mixture isotherms can be specified by implicit relations, for example, Eqn (14) or by the combination of Eqns (3) and (15). For systems involving the exchange of heterovalent ions, the quantity $1/\nu_i$ defines the valence of the ith ion. In nonideal systems obeying the Law of Mass Action, the concentration constants depend on the ratios of the concentrations of the substances undergoing exchange.

The form of the sorption isotherm has a decisive influence on the behaviour of the concentration waves in sorption columns. The criterion of the convexity of the binary i/j exchange isotherm, derived by Samsonov,[159] makes it possible to determine whether a stationary concentration front for the i/j exchange of the components may be established in the column. It is noteworthy that in a binary system, where the equilibrium is described by Eqns (15), the components do not change positions in the affinity sequence [i.e. the $f_{i/j}$ binary isotherm is either concave (unfavourable) or convex (favourable)]. In multicomponent systems ($n > 3$) of type (15), there is a possibility of the inversion of the components.[37, 38]

Inversion takes place also in chromatographic systems with complex formation.[48, 66, 82] In this case, the selectivity reversal may occur even in a binary system. In other words, the $f_{i/j}$ binary isotherm for components i and j can be S-shaped or σ-shaped (with an inflection and an intersection of the diagonal). An inversion of this type influences significantly the form of the chromatograms owing to the appearance of combined concentration waves — partly stationary and partly spreading waves. The occurrence of inversion also influences the form of the chromatographic fronts also in adiabatic sorption columns, where the heat changes may alter the relative affinities of the components for the sorbent. This results in the appearance of combined (stationary-spreading) concentration waves. Their formation may be regarded as the manifestation of 'cross' effects, which are considered in the thermodynamics of nonequilibrium processes.[23, 24]

III. Theory of nonlinear multicomponent sorption dynamics and chromatography, concentration waves, and velocities

Below we shall speak of the systems investigated as chromatographic systems, emphasising thereby that the behaviour of dynamic systems is considered, although the entire description refers both to multicomponent sorption dynamics and to chromatography.

The nature of the motion, interaction, and spreading of multicomponent concentration waves generated when a mixture of sorbable substances moves through a disperse medium (and hence also the separation of the substances in the mixture) depend on the form of the sorption isotherms for the mixture and on the nonideality factors of the chromatographic process. Such factors include a finite rate of mass exchange between the mixture components in the continuous and disperse phases (kinetic inhibition) and the longitudinal dispersion (usually characterised by the effective dispersion coefficient D_l) of the substances in the continuous phase arising due to various irregularities of the flow in the porous medium of the sorbent (dynamic factor).

In the absence of nonideality factors, when the motion of the mixture of substances is determined solely by the properties of the sorption isotherms for the mixture, the nonlinear theory of sorption dynamics and chromatography is described within the framework of the so-called 'ideal model'.[1, 20–22, 25–73, 80, 81]

In the general case, the theoretical solution of the problem of the sorption separation of a mixture of interfering substances requires the solution of a system of equations in terms of partial derivatives of concentration functions — a system of nonlinear material balance equations.

Many investigations have been based on a computer-assisted numerical solution of such problems.[95–103, 106–132, 160–179] An analytical formulation of the mixture isotherms in the form of the Langmuir relations (8) is usually employed in such cases. In these investigations, the numerical simulation of various chromatographic regimes was based on mass balance equations.

Special mention should be made of the theoretical and experimental studies carried out under the overall guidance by Professor Guiochon, which were devoted mainly to the modelling of chromatographic elution regimes for binary mixtures.[106–122, 156–158, 167–173] In these studies, the numerical calculation was based on the so-called 'semi-ideal model' of sorption dynamics and chromatography in which all the spreading effects are described by a single effective parameter characterising the column (the space integration increment †).[180, 181]

Theoretical studies based on numerical calculations have shown [106] and experiments have confirmed [111, 146, 184–187] that two new effects (which do not exist in the linear model of chromatography) arise in nonlinear elution chromatography—displacement and 'tag-along' effects.

Both effects are a consequence of the static effects of the competition between the sorbable molecules of two elutable components for available sorption sites. The displacement effect results in a component with small affinity being 'forced out' ahead, whilst the more effectively sorbed component remains behind. The rear boundary of the first peak on the chromatogram assumes the characteristic L-shape under these conditions.[60] The second effect is manifested in the form of a plateau of the second component, which arises at the outlet from the column after the completion of the output of the first component (the tag-along effect). It has been shown [58] that the experimental conditions under which the second effect is significant lead to a decrease in the displacement effect and conversely.[60] It has been shown on the

† Previously a numerical calculation of this type, employing the space integration increment, was described in the Russian literature and was better known under the name 'layer-by-layer calculation'.[182, 183] This method can be applied only when all the mixture components have the same nonideal parameters.

basis of the ideal model using the Langmuir equation for a two-component mixture[115] that the intensities of both effects are determined by the ratios of the loadings factors for each component.‡

In the case of mixtures with large amounts of components having different properties, the numerical calculation is performed by the method of finite differences.[95-103,131,132,168,174-179]

Following the ideas of Helfferich and Klein,[21] we shall consider the propagation of concentration waves and dynamic sorption processes in the sorption column. The velocity of the ith species u_i is the average velocity of the propagation of the molecules of this species in the direction of the flow:

$$u_i = \frac{u_0}{\varepsilon + (1-\varepsilon)a_i/c_i},$$

or in the dimensionless form

$$U_i = \frac{X_i}{Y_i}. \tag{16}$$

The species velocity u_i is lower than the flow rate u_0, since the molecules of the ith species, having spent some time in the sorbent, are retarded relative to the flow. As can be seen from Eqn (16), the species velocity is determined solely by the equilibrium properties of the sorption system.

The concentration velocity — the velocity of the kth wave (λ_k) — has a physical significance only in the case where the concentration variables $\{X_i\}$ have a gradient with respect to the column length z (or with respect to the time t when the output curve is considered). Similarly the velocity of the (shock) sth wave σ_s may be determined if the corresponding concentration distributions have a discontinuity which is retained during the propagation along the column. The relations between the concentration velocities λ_k and species velocities are derived from the material balance equations.[21,188]

$$\lambda_k = U_k + Y_k \frac{\partial U_k}{\partial Y_k}, \quad k = 1, 2, \ldots m. \tag{17}$$

Eqn (17) represents the formulation of the material balance equations in terms of the velocities. It is completely analogous to the relation known in fluid mechanics.[4,189] This expression relates the rate of propagation of a given density to the particle velocity and density. Velocities of the wave (λ_k) and the particle (U_k) have always been distinguished in fluid mechanics and the same difference exists also in the theory of chromatography and sorption dynamics.[1,21]

According to Eqns (17), the velocities of the wave and the substances differ both in their significance and in magnitude. Thus the sorbable molecules (or ions) may spread with a velocity U_k greater (or smaller) than the velocity of the wave λ_k moving from the larger to the smaller concentrations or conversely. In conformity with the requirement of continuity of flow, the velocity of the molecules then increases (or diminishes) relative to the velocity in the concentration profile along the wave. This leads to sharpening or spreading effects in the concentration waves, to the instability and abolition of the shock waves (or, conversely to their stabilisation and conservation), and to the accumulation (or depletion) of the species in the region of the concentration plateau.[21]

‡ The loading factor is the ratio of the volume of the injected mixture to the column capacity.[61,115]

IV. A model of ideal equilibrium sorption dynamics and chromatography

Within the framework of the ideal model of nonlinear equilibrium sorption dynamics and chromatography (in the absence of kinetic and dynamic effects of nonideality), the principal parameters determining the behaviour of multicomponent concentration waves are the sorption isotherms of the mixture components. Interference of the substances leads to nonlinear effects on the concentration waves. The ideal model has been developed by numerous investigators.[1,20-22,25-73]

The operation of the nonideality factors (kinetic retardation and longitudinal dispersion) leads to the smoothing of the nonlinear effects and to the asymptotic establishment of a stable ('coherent')[21,22] stake in the system. For example, instead of the shock concentration waves, diffuse stationary waves are formed at the asymptotic stage. However, the nonideality factors cannot alter the fundamentally nonlinear influence of the static effects due to the interference of substances.§

In general mathematical terms, multicomponent nonlinear chromatographic systems are described by a system of nonlinear equations in partial derivatives with respect to functions (concentrations in sorption dynamics and chromatography) which depend on two or more independent variables (time and distance in sorption dynamics and chromatography). The assembly of functions describing the behaviour of the system cannot be obtained by the superposition of the solutions of individual equations in the system for each function separately. Any disturbances in the initial conditions generates a complex response in the system, which is described best on the basis of the theory of propagating multicomponent concentration waves.[4,21,22,46,47,50-73,80,81] The term 'wave' is defined for sorption systems as the variation of concentration functions.[77,193]

V. Concentration waves in multicomponent chromatographic systems

In terms of the approximation of the ideal equilibrium model, the system of material balance equations for the components being sorbed under isothermal conditions assumes the following form in the case of a stationary disperse phase:[1,20-22,25-74]

$$(1-\varepsilon)\frac{\partial a_i}{\partial t} + \varepsilon\frac{\partial c_i}{\partial t} + u_0\frac{\partial c_i}{\partial z} = 0, \quad i = 1, 2, \ldots, m. \tag{18}$$

For the adjusted time $\tau = c_0(u_0 t - z)$ and the normalised concentrations $X_i = c_i/c_0$ and $Y_i = a_i/a_0$, these equations are written in the form.[21,22]

$$\frac{\partial Y_i}{\partial \tau} + \frac{\partial X_i}{\partial z} = 0. \tag{19}$$

Here ε is the porosity of the bed and u_0 the linear flow rate.

Allowance for the interference of the substances requires the simultaneous solution of Eqns (18) [or (19)], which constitute a system of quasi-linear partial differential equations. The characteristic paths or concentration velocities $\lambda_k = (dz/d\tau)_k$ play a decisive role in the solution of such systems of equations.

§ After the introduction of kinetic equations of specific type or abnormal static relations for multicomponent systems with subsequent solution of characteristic equations, complex values have been obtained[190-192] for the wave velocities λ_k. This leads to variable-amplitude concentration oscillations within the waves. In practice, however, such theoretical regimes have not been observed hitherto. Furthermore, it has been shown,[50] on the basis of thermodynamic considerations, that only concentration waves with different wave velocities (the characteristic values of λ_k are real and different) can theoretically be generated in chromatographic systems.

The characteristic equation of system (19), which defines these paths, assumes the form[21,74-79]

$$|A-\lambda I| = 0\,, \tag{20}$$

where $|A|$ is a matrix of the type $|A| = |\partial X_i/\partial Y_j|$ and $|I|$ is a unit matrix. The characteristic values (or eigenvalues) λ_k ($k = 1, ..., m$) are solutions of Eqn (20). A multicomponent wave of the kth kind, which will henceforth be designated as the k-wave, corresponds to each eigenvalue of the concentration velocity λ_k. In the general case, the number of characteristic paths (λ_k) is equal to the variance (m) of the chromatographic nonlinear system.

The dynamic behaviour of such nonlinear multicomponent sorption systems is determined by the topology of the characteristic paths in the composition space. These topologies for different nonlinear systems with a variance $m = 2$ are presented as clear examples in Figs 1–4 and will be discussed below.

For multicomponent Langmuir sorption systems (8) [or the equivalent ion exchange system (2), (3)], the characteristic equation corresponding to Eqns (19) has the simple form.[21,35,39]

$$H(h, X) = \sum_i \frac{X_i}{h - \alpha_{1i}} = 0\,, \quad \text{where } i = 1, ..., n\,. \tag{21}$$

The function H describes the transition from the composition space $\{X_i\}$ (Fig. 1*a*) to the functions space $\{h_i\}$ (Fig. 1*b*) — the Riemann invariants.[21] It has been shown[21] that the reverse transition from the invariants space $\{h_i\}$ to the composition space $\{X_i\}$ or $\{Y_i\}$ is described by the relations

$$X_j = \frac{\prod_i (h_i - \alpha_{1j})}{\prod_i (\alpha_{1i} - \alpha_{1j})}\,,$$

$$Y_j = \frac{\prod_i (1/h_i - 1/\alpha_{1j})}{\prod_i (1/\alpha_{1i} - 1/\alpha_{1j})}\,, \quad i, j = 1, 2, ..., n\,, \tag{22}$$

where the symbol $\prod_i A_i \equiv A_1 A_2 ... A_n$ denotes the product of all the quantities A_i.

The system of Eqns (18) or (19) is called hyperbolic in a narrow sense — when all the eigenvalues λ_k are real and different:[47]

$$\lambda_1 < \lambda_2 < ... < \lambda_m\,. \tag{23}$$

These values define the multicomponent concentration waves propagating different velocities λ_k (Fig. 1*c*).

Using the principal ideas of thermodynamics and the stability criteria for thermodynamic multicomponent systems, Kvaalen et al.[50] showed that the roots (eigenvalues) of the characteristic equation (20) are real, positive, and different for physically real sorption systems. The different types of behaviour of multicomponent sorption systems with complex and multiple eigenvalues have been examined theoretically in a number of studies.[103,190-192]

The concentration waves formed in a sorption column will be the subject of further exposition and we shall therefore discuss briefly this concept. There is no unique definition of the waves. A wave has been defined in a monograph[193] as any distinguishable signal propagated from one part of the medium to another at a certain definite velocity. Such a signal may be a perturbation of any kind (for example, a pulse or a step) subject to the condition that the perturbation may be clearly distinguished or its location can be determined at any specified instant. The signal may be distorted or its magnitude may change but it must remain distinguishable. For example, a concentration plateau cannot be a wave. The usual subdivision of waves into two classes — dispersing and hyperbolic waves — is not exhaustive, since there are exceptions which do not correspond to either one of these classes. Mainly hyperbolic concentration waves are formed in the sorption column. There is a clear definition of hyperbolicity[47] associated with the difference between the characteristic values λ_k [see Eqn (23)].

One of the most interesting phenomena in nonlinear sorption systems in the absence of nonideality factors is the shock waves, which represent sharp discontinuities (jumps) in concentrations (for example, the M^1M^2 wave in Fig 1*a*). Shock waves arise in nonlinear systems when waves 'overlap'[4,21,47,193] or, in other words, when the characteristics intersect on the physical plane (z,τ). Shock waves may appear and be propagated even when they are not induced by an initial discontinuity. After the appearance of a discontinuity, the shock waves in nonlinear systems are not disrupted on further propagation, except under certain stability conditions.[21,39,74,78,79] For essentially nonlinear systems of the hyperbolic type, such conditions have been introduced[193] and called the entropy conditions. The term 'Lax's conditions' is frequently used in the mathematical literature.[79] These conditions have a simple physical significance — a shock wave is stable if

(a) the s-wave 'overlaps', i.e. the characteristics of the same sth kind intersect on the physical plane (z,t), forming a discontinuity line or a shock line σ (see Fig. 1*d*) and

(b) the $(s-1)$-wave cannot catch up with the given s-wave, which in its turn cannot catch up with the next (faster) $(s+1)$-wave (Figs 1*c* and 1*d*).

When applied to sorption dynamics and chromatography, Lax's conditions are sometimes referred to as 'convexity conditions' for the isotherms[98-103,163-165] by analogy with a univariant ($m = 1$) system in which a shock sorption boundary of one component arises for a convex $f(c)$ isotherm.[20]

Chromatographic systems where the equilibrium is described by the Langmuir relations (8) are an example of hyperbolic, truly nonlinear systems. For more complex nonlinear systems, having linearly degenerate regions, the stability conditions are subject to a greater number of limitations.[78,79,98,99] In these systems, there is a possibility of the appearance of combined concentration waves in which the discontinuity is in contact with a spreading wave of the same family. Contact discontinuities of this type may be formed in chromatographic systems in the presence of regions of selectivity reversals.

On the discontinuity line σ (see Fig. 1*d*), the material balance differential equations are invalid. They must be replaced by a conservation law expressed in an integral form.[47,75,76,79] In the integral form, this law does not lose its significance for discontinuous solutions and gives rise to relations between the concentrations on the plateau to the left (X_i^s, Y_i^s) and to the right (X_i^{s+1}, Y_i^{s+1}) of the discontinuity in the shock s-wave (an example of the concentration plateau is presented in Fig. 1*c*, M^1M^2 wave). These relations are independent of the number (i) of the component, so that for any i and j the following relations are valid:

$$\sigma_s = \frac{\Delta X_i}{\Delta Y_i} = \frac{\Delta X_j}{\Delta Y_j}\,, \tag{24}$$

$$\Delta X_i = X_i^{s+1} - X_i^s, \qquad \Delta Y_i = Y_i^{s+1} - Y_i^s; \quad 1 \leqslant i, j \leqslant m\,,$$

which are called in mathematics the Hugoniot or Rankine–Hugoniot condition,[4,47] whilst in the theory of chromatography they are referred to as the compatibility condition[41,43] or the integral coherence condition.[21] These relations form a system of algebraic equations, with the aid of which it is possible to determine the composition $\{X_i^s\}$ on one side of the discontinuity, provided that the velocity of the shock waves σ_s and the composition $\{X_i^{s+1}\}$ on the other side of the discontinuity are known.

For a deeper understanding of the behaviour of concentration waves in multicomponent systems, analysis of the nonideality effects is necessary.

The shock concentration waves are an idealisation. When account is taken of dispersion effects, the shock waves in nonideal models assume the form of a distribution with a finite width.[194] In such models, a stationary regime in the propagation of the wave corresponds to shock waves at the asymptotic stage.[20, 21, 65, 92–94, 104, 105, 125–128, 195-200]

The special class of solutions, referring to simple waves, is of greatest interest for the solution of the material balance equations (18) or (19) for multicomponent chromatographic systems. Such waves arise in truly nonlinear systems. An example of sorption dynamic systems of this kind is provided by systems with equilibria described by the Langmuir relations (8). The initial and final conditions, corresponding to the frontal-displacement variant of sorption dynamics and chromatography, i.e.

$$X_i(0,z) = X_i^0, 0 \leqslant z; \quad X_i(t,0) = X_{i0}H(t), \quad i = 1, 2, ..., m, \tag{25}$$

[X_i^0 and X_{i0} are constants and $H(t)$ is the Heaviside function] lead to the class of centred simple waves.

The solution of the material balance equations (18) and (19) under these conditions is called the solution of the Riemann problem.[40, 43, 74, 76, 78, 79] In the Russian literature, this problem is called 'splitting of the initial discontinuity'.[47]

In conformity with the criterion of the stability of shock waves,[74, 78, 79] the splitting problem has a unique solution in the class of centred spreading and shock waves.[47, 74, 78] When applied to the theory of sorption dynamics and chromatography, such solutions for different conditions have been considered in a number of studies.[21, 31–34, 37, 39, 40, 43]

In nonlinear m-component chromatographic systems with an invariant affinity sequence, the initial discontinuity is accompanied by the formation of m concentration waves. This number of waves corresponds to the total number of invariants h which are determined by the characteristic equation (21).

In the m-dimensional composition space $\{X_i\}$, the solution $X_i(h)$ describes the Γ curve with the characteristic parameter h, which varies along this curve. The Γ curve is the geometrical image of the solution (see Figs 1*a* and 2–4). Sometimes the composition space is referred to as the hodograph space,[4, 40, 43, 158] although this term is used more frequently in mathematics for the special case with $m = 2$ (Courant and Freidrichs [4]) when the composition space is a plane.

The Γ^k curves have been called the composition paths [21] and the corresponding concentration waves the coherent [21, 22] or simple [46, 47, 77] waves. The term 'coherence' has been defined [21, 22] as the mutual consistency of the concentrations of the components in the concentration k-wave propagating along the sorption column.

Any changes in the compositions along the composition path grid Γ^k are coherent and all other changes are noncoherent. It is important to note that the path grid is determined by the type of the material balance equations and the system parameters — the separation factors in adsorption and ion exchange processes and the relative permeabilities in a multiphase flow in porous media. The topology of the composition path grid is independent of the compositions in the influent and initial flows. Therefore, for given components, the grid of Γ^k paths may be determined and then used to predict the response of the system under arbitrary initial and boundary conditions. The combination of the time–distance diagram with the $M^1M^2M^{m+1}$ route, which corresponds to the composition waves in the composition space, yields a full and compact quantitative description of the behaviour of the system in time and in space. An example of such description is presented in Fig. 1: the $M^1M^2M^{m+1}$ route in Fig. 1*a* and the corresponding $M^1M^2M^{m+1}$ chromatogram in Fig. 1*c* as well as the physical plane distance–time (z,τ) with the M^1M^2 shock and the M^2M^{m+1} spreading wave in Fig. 1*d*. In the presence of the path grid in the composition space, it is easy to predict (at least qualitatively) the response of the multicomponent system to any perturbation.

Any pair of constant compositions in the composition space, the images of which lie on a same Γ^k path, are connected by a simple wave and the solution is given by the one-parameter family $\{X_i(h)\}$. The images of the initial and boundary conditions are presented by two different points M^1 and M^{m+1} respectively. The image of the solution of the Riemann problem [Eqns (19) and (25)] in the composition space represents the $M^1M^2 \ldots M^{m+1}$ route consisting of sections of the Γ^k paths; each corresponds to the kth wave M^kM^{k+1} of a different $(k = 1, ..., m)$ kind. The route contains the highest values of m for the different sections, which are disposed consecutively from Γ^1 to Γ^m. Each break point M^k on the route (see Figs 1*a* and 1*c*) corresponds to a constant state $\{X_i^k\}$. Thus, together with the terminal points M^1 and M^{m+1}, there are $m+1$ concentration plateaux on a multicomponent chromatogram (see Figs 1*a*, 1*c*, and 1*d*).

The solution represented in the physical plane (z,τ) yields the inverse image of this route (Fig. 1*d*). The physical significance of the picture considered is that the initial discontinuity in the concentrations [Eqn (25)] splits into m concentration waves. The slowest wave corresponds to the characteristic value λ_1 and the fastest to λ_m value. Any of the waves may be of the spreading or shock type. Each wave of the kth kind is separated from the preceding $(k-1)$th wave by the $M^k\{X_i^k\}$ concentration plateau (see Fig. 1*c*). The concentrations $\{X_i^k\}$ on the plateau are independent of the dispersion factors and can therefore be determined by calculations carried out within the framework of the ideal equilibrium model.

VI. Coherence

The coherence conditions define a special regime in the propagation of a multicomponent concentration wave in a chromatographic system in which all the concentrations of the mixture components move synchronously along the k-wave. For a two-component system, this condition has been put forward in the form of a postulate.[29] Later the coherence condition was formulated by Glueckauf [30] in order to obtain a solution in such nonlinear systems. The study of this problem showed [46] that the coherence condition holds along the characteristics.[55]

The concept of coherence describes states of chromatographic systems which they tend to attain similarly to the way that closed systems tend to a state of equilibrium, while open systems with fixed boundaries and constant boundary conditions tend to attain stationary states.[22]

The concept of coherence was developed by Helfferich and Klein.[21, 35, 36, 80] It makes it possible to treat qualitatively and to calculate quantitatively the chromatograms in multicomponent chromatographic systems under arbitrary initial and boundary conditions. This concept was generalised by Helfferich.[22, 81] Subsequently the region of its application was extended to multicomponent multiphase flows in porous media,[195] to multicomponent distillation processes,[196] and to coprecipitation and dissolution processes in multicomponent systems. Up to the present day, the concept of coherence has been justifiably applied to the dynamics of multicomponent nonlinear (sorption) systems.[21, 22, 55, 80]

This global concept [22, 80, 81] indicates the direction in which the development of a multicomponent system develops towards the final coherent state, which may be attained after a finite time in the ideal model or asymptotically in the presence of nonideality factors in the system. The equilibrium and stationary states of the system are then regarded as special cases.

Any multicomponent wave may be regarded as a composite one, consisting of the waves of the individual components, but, in contrast to linear systems, the multicomponent wave can not be presented as their superposition. The determination of the velocity of a multicomponent wave reduces to the calculation of the eigenvalues λ_k [from a type (20) equation]. The value λ_k characterises the velocity of a coherent k-wave, while the eigenvectors define the change in the mixture composition along such a wave.

tions coexisting at such a point in space must move in the same direction and with the same velocity.

However, the concept of coherence has a broader application, since it includes the problem of the propagation of arbitrary perturbations in open systems.[21,80,81] It has been shown[21,22] that coherence may be defined as the state in which all the independent variables (functions) move in a synchronised regime, i.e. without a shift of their (concentration) profiles relative to one another. In mathematics it is known that 'simple waves' behave in this way.[46,47,77] Thus simple waves are coherent by definition.

The principle of coherence reflects the fact that arbitrary perturbations in the system are 'resolved' (splitted) into a series of simple waves. A mathematical proof of this postulate with the aid of the method of characteristics[46] has been given by Helfferich[22,55] for a system of two equations of the hyperbolic type. However, it had been demonstrated previously in a mathematical study[75] that the region adjoining the region of constant states is a simple wave.

If the perturbation at the inlet to the system is smooth, then its 'resolution' into coherent waves does not occur instantaneously even in the ideal model. The time of attainment of the coherent state depends on several factors, among which the most important is the difference between the eigenvalues λ_k ($k = 1, 2, ...$). If the lines for the individual families are almost parallel on the grid of composition paths, the resolution (the transition to the coherent state) requires a longer time interval. Furthermore, when account is taken of the nonideality factors in the system, the state of coherence may be attained only at the asymptotic stage.

VII. Description of the concentration distributions in a multicomponent Langmuir sorption system with the aid of the *h*-transformation

The solution of the Riemann problem is simplified if certain special functions have been found: the Riemann invariants (designated here by h)[25,43] or the generalised Riemann vector-invariants.[39,40,43,65] Such functions have been found for the Langmuir sorption systems (8) or for the equivalent systems (9) involving the exchange of ions with equal valences.[21,39,40,43]

The following equation is valid for the invariant h_k changing along the Γ^k path:

$$\frac{\partial h_k}{\partial \tau} + \frac{dX_i}{dY_i}\frac{\partial h_k}{\partial z} = 0 \quad \text{for all } i, j = 1, 2, ..., m, \tag{26}$$

$$\lambda = \frac{\partial z}{\partial \tau} = \frac{dX_i}{dY_i} = \frac{dX_j}{dY_j} \quad \text{for any component } i, \tag{26a}$$

where d is the symbol of the total differential.

Eqn (26) is the fundamental differential equation of the Riemann problem.[40,43,65] It describes the 'conservation law' from which follows the principal property of these invariants, which facilitates significantly the solution of the problem: only the kth Riemann invariant h_k changes along the shock or spreading wave of the kth kind, while all the remaining invariants h_i ($i \neq k$) are constant. In the monograph of Helfferich and Klein,[21] Eqn (26a) was called the differential coherence condition.

The solution of the differential equation (26) yields the one-parameter family $X(h)$ or the Γ paths in the m-dimensional composition space $\{X_i\}$ (Fig. 1*a*), as well as a broken curves in the invariants space $\{h_k\}$ (Fig. 1*b*).

The relations for the characteristic velocities of the shock sth wave (σ_s) and the spreading kth wave (λ_k) have been derived theoretically[21] with the aid of the concept of coherence:

$$\sigma_s = h_s^1 h_s^{m+1} Q\left(\prod_{i\neq k} h_i\right),$$

$$\lambda_k = (h_k)^2 Q\left(\prod_{i\neq k} h_i\right), \quad Q \equiv \left(\prod_i \alpha_{i1}\right), \tag{27}$$

where h_s^1 and h_s^{m+1} are the values of the invariant h_s, diminishing along the sth wave, to the left and to the right of the shock sth wave respectively (see, for example, the M^1M^2 wave in Fig. 1*a* as well as its image — the N^1N^2 wave in Fig. 1*b*), $\prod_{i\neq k} h_i$ is the product of all the cofactors h_i except h_k, h_k are the values of the invariants h_k increasing along the spreading kth wave (see, for example, the M^2M^{m+1} spreading wave in Fig. 1*a* and also its image — the N^2N^{m+1} wave in Fig. 1*b*), and $\prod_i \alpha_{i1}$ is the product of all the cofactors α_{i1} ($i = 1, 2, ..., n$).

For a clear demonstration of the h-transformation, we shall return to the consideration of the geometrical interpretation of the Riemann problem.

The characteristic equation for multicomponent systems (21) involving the exchange of ions of equal valence describes the transition from the composition space $\{X_i\}$ (Fig. 1*a*) to the invariants space $\{h_k\}$ (Fig. 1*b*). The reverse transition is described by Eqn (22).[21,35]

The following criteria for the sharpening or spreading of the concentration kth wave, expressed in terms of the invariants h_k, are obtained from Eqns (27): if the value h_k increases along the concentration k-wave, then the velocity λ_k increases and the k-wave spreads (see the N^2N^{m+1} wave in Fig. 1*b* and the M^2M^{m+1} wave in Figs 1*a*, 1*c*, and 1*d*); if the invariant h_s decreases along the s-wave (even if we assume that it is initially diffuse), then this wave tends to become sharpened, becomes a shock wave, and subsequently moves with a velocity σ_s defined by Eqn (27).

The invariant h_k in Eqn (26), changing along the kth wave, can be found by solving Eqn (21), which relates the composition in the wave to the value of this invariant.

The simplification of the solution of the problem on the basis of the function-invariant h consists in the fact that the $M^1 ... M^m$ in the composition space consisting of sections of the Γ^k paths (see Fig. 1*a*) corresponds in the invariants space $\{h_k\}$ to the $N^1 ... N^{m+1}$, the lines in which are orthogonal (see Fig. 1*b*). Only the invariant h_k out of the assembly $\{h_1 ... h_k ... h_m\}$ changes along the k-wave. The linearity of the Γ^k composition paths in the composition space is the property of the Langmuir m-component systems (or the equivalent systems involving the exchange of ions of equal valence) which permits the orthogonalisation of the space, and this simplifies the consideration of the dymanic behaviour of these nonlinear systems. It is noteworthy that the linearity of the Γ paths in the composition space is retained along the stationary concentration waves for multicomponent Langmuir systems even in the presence of dispersion factors identical for each component.[65,104,105,197–200] This property makes it possible to obtain solutions describing the concentration profiles in the stationary waves for this case.

In the physical plane (z,τ), the region corresponding to the Γ^k path is covered by a set of lines-characteristics λ_k^l (the dashed line in Fig. 1*d*) corresponding to the characteristic value λ_k. The direction of the characteristics of the kth kind in the plane (z,τ) is specified by the quantity λ_k. Since the function h_k is constant along each characteristic λ_k^l, each value of $\{X_{iQ}\}$ is represented by a point on the Γ^k path (for example, point Q on the MN line in Fig. 2). Each characteristic λ_k^Q is then a straight line in the physical plane. The family of such straight lines in the plane (z,τ) represents a simple k-wave (see Fig. 1*d*, the family of the lines $\lambda_2^2 ... \lambda_2^{m+1}$, $k = 2$). If the inequality $d\lambda_k/dz > 0$ holds in the region of the simple wave, then the characteristics diverge and the kth wave spreads as a function of time. Such a wave is referred to as 'spreading'[196,201] or 'nonsharpening'.[21]

It has been noted in a monograph[21] and a state of the art review[22] that in the theory of chromatography the h-transformation (albeit under a different name) was first proposed by Davidson in 1949 for ion exchange but remained unnoticed.[22] This transformation was proposed independently by Zhukhovitskii and coworkers[21,22,202,203] for the theory of the high-concentration gas chromatography, vacancy chromatography, and the chromatography without a carrier gas for constant partition coefficients.

As noted in the above review,[22] the polynomial (h) in Eqn (21) is used in differential geometry, but for the description of the behaviour of multicomponent systems in electrodiffusion, electrophoresis, and distillation, this transformation was discovered anew. The transformation (21), based on the h-invariants, has been widely applied to systems in which the interference of the components takes place without any discrimination, i.e. the substances participating in the separation process compete under the conditions of constant relative strengths in the realisation of the function determining the given process.[22] The role of such a function may be assumed by the parameter characterising the degree of occupancy of the adsorption sites in chromatography, the fraction of the void space in vacancy chromatography (or distillation), the transport of electric current in electrophoresis,[3] etc. Competition between the components in the absence of discrimination then corresponds to constant binary interaction coefficients: the separation factors in chromatography, the relative volatilities in distillation, and the relative electrochemical mobilities in electrophoresis.

A computer program, permitting the calculation of both the h-transformation and of the concentration profiles on the basis of the ideal model, has been developed.[49]

Studies have been performed in which the results obtained in the theory of the chromatography of multicomponent systems have been extended to systems with precipitants and with dissolution of the precipitants.[201,204]

A scheme for the solution of the problem of the multicomponent frontal-displacement sorption dynamics and chromatography follows from the foregoing. On the basis of the solution of the characteristic Eqn (21) using the known coordinates of the points M^1 (influent concentrations) and M^{m+1} (initial concentrations in the column) in the concentrations space, the coordinates of the corresponding points N^1 and N^{m+1} in the invariants space $\{h_k\}$ are calculated.

Next, the coordinates $\{h_k^l\}$ $(l = 1, ..., m)$ of the intermediate points N^k on the plateau between the kth and $(k+1)$th waves are determined in the invariants space. The orthogonality of the representation of the waves in the invariants space is then employed in the calculation. Only one invariant h_k changes (from h_k^1 to h_k^{m+1}) along the kth wave ($N^k N^{k+1}$) in this space [all the remaining invariants h_i $(i \neq k)$ remain constant], while all the k-waves from point N^1 to point N^{m+1} are arranged in order of increasing index $k = 1, ..., j, ..., m$. The coordinates $\{h_k^l\}$ found are then employed to determine the coordinates $\{X_i^k\}$ of points M^k on the concentration plateau between the kth and $(k+1)$th waves with the aid of Eqns (22).

This scheme for the calculation of concentration plateaux is used in combination with the solutions obtained for stationary waves for multicomponent Langmuir systems.[104,105,198,204] The above approach made it possible to demonstrate[105,198,200] how a theoretical calculation can be used to correct and test the operation of numerical schemes for computer calculations[98,99] concerning problems in the theory of multicomponent sorption dynamics and chromatography.

VIII. The equivalence of multicomponent Langmuir systems and multicomponent systems with a nonuniform mobile phase velocity due to the sorption effect

The flow rate u in the material balance equation cannot remain constant if significant composition variations take place in the column, with involving net sorption and desorption steps in the molecules. This effect was first described[205,206] for a single component system. Different aspects of this effect, including the effect in multicomponent systems, have been investigated.[207-218] Two reviews by Guiochon,[213,217] in which the results of the theory of gas chromatography with finite concentrations are discussed, are of great interest. These reviews deal briefly with problems in the solutions of systems of partial differential nonlinear equations by the method of characteristics and discuss the problems of the stability of the shock waves (concentration discontinuities).

In the separation process, net desorption steps at the rear boundary and net sorption steps at the leading boundary of the chromatographic band respectively introduce the molecules of the substance into the mobile phase and remove them from the latter. The flow rate in the region of the chromatographic band is therefore higher of the rear boundary and lower at the leading boundary.

This effect, which is significant for gas chromatography, is sometimes referred to as the 'sorption effect'[216] and its influence on the profile of the sorption band of one substance has been examined in the theory of chromatography without a carrier gas.[203,210,211] The dependence of the flow rate on the concentration of the substance has been found for a one-component system.[215] The importance of the sorption effect in chromatographic separation at high concentrations has been emphasised.[214]

The behaviour of the n-component sorption C system, in which account is taken of the influence of sorption effects, has been examined.[65,69,198,199] In this system the $f_i(c)$ isotherms are linear for each component, while the flow rate u is nonuniform due to the 'sorption effect':

$$f_i(c) = \gamma_i c_i; \quad \sum_i^n c_i = c_0 = \text{const}, \quad i = 1, 2, ..., n. \tag{28}$$

It is postulated that the pressure drop in the column may be neglected and that the ideal gas law holds. The sorption effect is taken into account in gas chromatography, while in liquid chromatography it is usually neglected, although in the latter case condition (28) represents incompressibility with retention of the overall concentration c_0 of all the components. In liquid chromatography, this effect may be neglected because of the smallness of the volume changes in the sorption–desorption steps.

The Langmuir system (8) and the C system are united by one common property: in both systems, the separation factors for the ith and mth components are constant, i.e. $\alpha_{mi} = (a_m/c_m)/(a_i/c_i) = \text{const}$. The mixture components $\{c_i\}$ form the affinity sequence 1, 2, ..., n, in which the substances are numbered (and arranged) in order of decreasing affinities of the components for the sorbent:

$$\gamma_1 > ... > \gamma_i > ... > \gamma_n \quad \text{or} \quad \alpha_{11} < ... < \alpha_{1i} ... < \alpha_{1n},$$

where

$$\alpha_{1i} = \frac{\gamma_1}{\gamma_i}. \tag{29}$$

The existence of the relation (28) makes it possible to eliminate one variable (c_n) from the equations. The system of the mass balance equations then defines only $n-1$ independent functions c_i.

The invariant solutions of the system of quasi-linear material balance equations have been analysed on the basis of the ideal model.[65,69,198] These solutions describe the propagation of the sorption shock and spreading concentration waves at high concentrations of the components in the multicomponent C system.

A relation for a variable flow rate u, reflecting the sorption effect, was derived for the first time for the C system by the present author:[65,200]

$$u = \frac{Q}{H - R/c_0} = \frac{Q}{\mu}; \qquad \frac{u}{1+\gamma_i} = \frac{Q_i}{H - R/c_0};$$

$$Q_i = \frac{Q}{1+\gamma_i}, \tag{30}$$

where H = const, $R = \sum_i^n (f_i)$, and Q is the integration constant determined from the initial conditions.

Eqn (30) thus derived represents the dependence of the flowrate u on the concentrations of a mixture of m components.[65,198,200] When account is taken of Eqn (30), the differential equations for the C system are identical with the mass balance equations describing the multicomponent Langmuir system (8). The relations

$$\frac{ue_i}{1+\gamma_i} = \frac{Q_i e_i}{H - R/c_0},$$

where $e_i = (\gamma_i - \gamma_n)c_i$, play the role of multicomponent inverse Langmuir isotherms $G_i(a) = f_i^{-1}(c)$ in the mass balance equations for the C system [see Eqn (7)].[69,198]

The characteristic equation for the C system is formally identical with the corresponding equation for a multicomponent Langmuir system.[65,69,198,200] The separation factors (γ_m/γ_i) for the components m and i in the C system are completely analogous to the separation factors $\alpha_{mi} = \gamma_m/\gamma_i$ [see Eqn (29)][69,198] used in the multicomponent theory of chromatography.[21] The invariants μ_k/γ_1 have the same properties as the invariants $1/h_k$, where h_k are functions introduced for the Langmuir systems.[21] All the calculations of the chromatograms for the Langmuir system based on the equilibrium model can then be carried out also for the C system using h_k and the ratio $\alpha_{1m} = \gamma_1/\gamma_m$ $(m = 1, 2, ..., n)$, taking into account the agreement between the separation factors for the two multicomponent systems considered. In the Langmuir system (8), the components also form the affinity sequence 1, 2, ..., m, in which they are arranged in order of decreasing affinity for the sorbent, namely $\alpha_{1m} > \alpha_{1i} > 1$ [see Eqn (29), $\alpha_{11} \equiv 1$], where $i < m$.

Only the invariant h_k, as well as the vector-invariant $[J_{kk}]$, varies along the characteristic (Γ^k) k-path (corresponding to a wave of the kth kind), whereas the remaining invariants h_m $(m \neq k)$ and $\{J_{mk}\}$ $(m \neq k)$ do not vary (Fig. 1*b*). The corresponding change in the invariant h_k (increase or decrease) determines the type of multicomponent k-wave (spreading or shock) in the chromatogram (see Fig. 1*b*; decrease of h_1 from h_1^1 to h_1^{m+1} along the M^1M^2 wave and increase of h_2 from h_2^1 to h_2^{m+1} along the M^2M^{m+1} wave).

Relations expressing λ_s (for a spreading wave) or σ_k (for a shock wave) (see Fig. 1*d*) in terms of the product of the Riemann invariants $h_1 ... h_m$ (or $\mu_1 ... \mu_m$) are valid for the characteristic velocities of the multicomponent concentration k-waves in the chromatogram.

For the multicomponent C system, the grid of composition paths in the concentration space has the same properties as for a multicomponent Langmuir system (8). An example for a two-component Langmuir system ($m = 2$) or a system with $n = 3$ is presented in Figs 1*a* and 2 (the concentrations c_i are then expressed in terms of an acute-angle coordinate system). The coupling condition (28) reduces the three-dimensional concentrations space $\{c_i\}$ to the $P_1P_2P_3$ plane, where $c_i(P_i) = c_0$ (see Fig. 1*a*). The shock k-wave (or a stationary wave in the nonideal model) arises in the composition space if the change in the concentrations corresponding to this wave takes place in the direction opposite to that indicated in Figs 1 and 2 (i.e. if the invariant h_k or the corresponding invariant γ_1/μ_k diminishes along the k-wave — see Fig. 1*b*). The velocities of the shock and spreading k-waves are determined by the magnitude of the h_k-invariant in accordance with Eqn (27).[21] A large number of examples of composition path grid for multicomponent (m-component) Langmuir systems (or the equivalent systems involving the exchange of n ions of equal valence, where $n = m + 1$) are quoted in the monograph by Helfferich and Klein.[21] Similar path grids on the $P_1 ... P_n$ simplex may be obtained also for the C system. The distributions of the concentrations of the components along the shock or spreading k-wave and its velocity are then described with the aid of the h_k-invariant. Examples of such calculations have been published.[200]

These data indicate the equivalence of the multicomponent sorption systems: C, where there is a sorption effect, and the Langmuir system (8). Naturally, the main result is the possibility of using for such systems a simple procedure for the calculation of the multicomponent (shock and spreading) concentration waves on the basis of the h-invariants.

IX. Multicomponent chromatographic systems with an invariant affinity sequence of the components

The nonlinear theory of sorption dynamics and chromatography may be used also in the calculation for a stoichiometric n-component system consisting of ions with $n = 3$, where all the characteristics lie in one plane (see Fig. 1*a*). In Figures 1–4 the characteristics of the first kind (Γ^1) are represented by continuous lines and those of the second kind (Γ^2) by dashed lines. In this case, the simplex triangle $P_1P_2P_3$ in the space of the Riemann invariants $\{h_k\}$ is transformed into the rectangle $P_1'P_2'W'P_3'$ (see Figs 1*a* and 1*b*).

Points W in Figs 1*a* and 1*b* and in Figs 2–4, at which the characteristic velocities of the k-waves coincide, are referred to as the 'watershed' points.[21,37,38] The coordinates of point W for

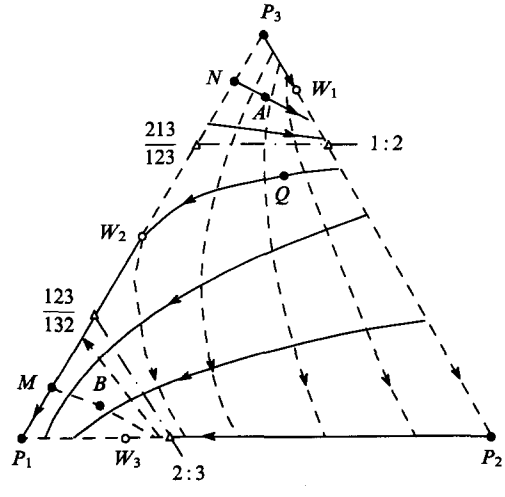


Figure 3. A variant of the hodograph for a stoichiometric three-component system for which the equilibrium relations [of the type of the Law of Mass Action (15) for heterovalent ions] are valid. The ANW_2MB and QW_2MB routes correspond to different variants of the concentration waves (see text).

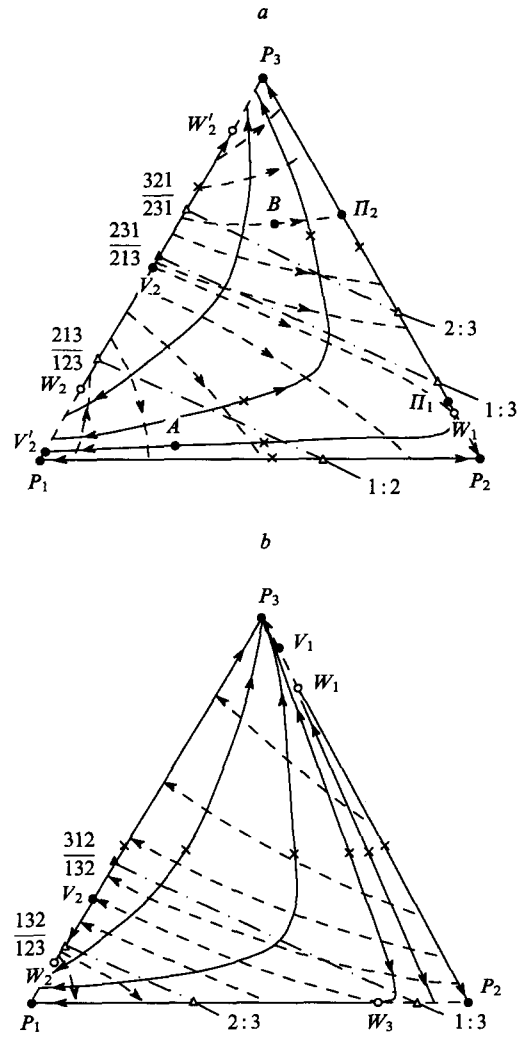


Figure 4. Variants of the hodographs obtained by numerical calculation for a stoichiometric three-component system including selectivity reversals even in a binary exchange (when the binary isotherms f_{ij} are *S*-shaped). (*a*) The presence of the inversion $i:j$ (dash-dot lines) for the 1/2, 1/3, and 2/3 components (the corresponding isotherms f_{ij} are *S*-shaped); (*b*) the presence of the inversion $i:j$ (dash-dot line) for the 1/2 components (the corresponding isotherm $f_{1/2}$ is *S*-shaped); the crosses (×) denote the concentration points at which the wave velocity λ_k on the Γ^k paths is minimal; points V_k correspond to the points of intersection of the borders of the simplex with the Γ^k paths passing (through different watershed points *W*) within the composition region; the $A\Pi_1\Pi_2B$, $P_3V_2W_1P_2$ (*a*), and $P_3V_2W_3P_2$ (*b*) routes correspond to different variants of the concentration waves (see text).

systems with constant separation factors (8) are defined by the relation [21]

$$X_W = \frac{\alpha_{12} - 1}{\alpha_{13} - 1}.$$

The characteristics of the first kind (Γ^1) begin on the P_2P_3 side and terminate on the WP_1 segment. All the characteristics of the second kind (Γ^2) begin on the WP_3 segment and terminate on the P_1P_2 side. Each characteristic of the first kind intersects all the characteristics of the second kind and conversely. As a consequence of this, any two composition points, not located on one characteristic, may be connected by a route which initially follows Γ^1 and then Γ^2 paths, i.e. waves of the first kind and then of the second kind are formed in succession in the corresponding chromatogram. The simplex borders P_1P_2, P_1P_3, and P_2P_3 are also characteristics and only they originate from the P_1, P_2, and P_3 corner points. There are no characteristics originating from these points within the composition region. Thus two substances cannot be absent on one side of the concentration wave and present on the other. In systems with a variable selectivity of the components, such effects may occur (see Section X).

In the case of an *n*-component system, the simplex gives rise to an equilateral *n*-gonal pyramid, but there are no fundamental differences from the case where $n = 3$. [21]

The principal rules governing the behaviour of simple (or coherent) waves may be derived from the compatibility condition (24) (for shock waves) and Eqn (26a) (for spreading waves), and also from properties associated with the continuity of the stream of molecules [see Eqns (16) and (17)]. The same rules may be obtained with the aid of the properties of the Riemann h_i-invariants and Eqn (27). However, these conclusions are valid for systems with constant separation factors α_{ij}. The rules governing the behaviour of simple waves, obtained with the aid of the velocities, are less rigorous: in this, case an invariant selectivity sequence and competitive sorption, reflected by relations (4) and (5), are needed.

In a simple wave, the species velocities u_i differ from the characteristic velocities λ_i, so that the molecules of different species pass through the propagating wave in the direction of flow or in opposition to it. This behaviour gives rise to the following effects. [21]

1. Along the wave the species velocities u_i and the concentrations X_i of all the substances change simultaneously.

2. The existence of the so called 'affinity cut'. This cut subdivides the substances in the affinity sequence $1, ..., j, k, ..., n$ into two groups: the high affinity group $(1, ..., j)$ and the low affinity group $(k, ..., n)$. The cut is designated by $j|k$. The species velocities u_i in the first group are lower and those in the second group are higher than the composition velocity (λ_i for a spreading wave or σ_i for a shock wave). The concentrations of the substances in the wave also vary in the opposite directions (if those of the substances in the first group increase then the species velocities in the second group diminish and conversely).

For an *n*-component (but *m*-variant) stoichiometric system (9), there is a possibility of $n-1$ positions of the affinity cut, namely those ranging from $1|2, ..., n$ to $1, 2, ..., (n-1)|n$, where the cut $k|(k+1)$ corresponds to a simple wave of the *k*th kind with a characteristic velocity λ_k. No concentration can vary abruptly if all others vary smoothly. One of the most important corollaries of the rules under discussion is the fact that only the substances j and k, separated by the cut $j|k$, can be present on one side of the wave and absent on the other. All other components are either present on both sides and within the wave or are altogether absent. However, two substances j and k cannot be absent from the same side of the wave, since their concentrations vary in opposite directions.

The transformation of *m*-component (and *m*-variant) Langmuir systems (9) into stoichiometric *n*-component (but *m*-variant) systems makes it possible to represent hodographs also for Langmuir systems within the space of the simplex. Fig. 2*a* presents a hodograph for a two-component Langmuir system with competitive sorption ($b_1, b_2 > 0$). The concentrations of the components i and j do not exceed unity and are reckoned in an acute-angle coordinate system.

Complications may arise only in the case where some of the coefficients b_i are negative. For example, the hodograph for systems with synergistic sorption, where the corresponding coefficients for one or more susbtances are negative ($b_i < 0$), is illustrated in Fig. 2*b*. As in stoichiometric systems, in such systems the initial discontinuity in concentrations splits into a chain of shock and/or spreading simple waves. Difficulties in the formation of multicomponent waves then arise. Thus Fig. 2*b* shows that the route along the characteristics in order of their increasing indexes, i.e. $B\Gamma^1\Gamma^2M$, is impossible between certain concentration points *B* (composition at the inlet to the column) and *M* (initial

composition in the column). In this case, the solution determining the chromatogram tends to the *BNM* route, passing partly along the envelope indicated in Fig. 2*b* by a dash-dot line. This route does not contain intervening plateaux. Furthermore, routes which may be referred to as metastable (for example, the *ANB* route corresponding to a single, but unstable wave) are likely on this hodograph. Small perturbations lead to the 'switching' of the metastable *ANB* route to the AN_1B route corresponding to two simple waves: a wave of the first kind AN_1 and a wave of the second kind N_1B.[21]

In systems with invariant affinity sequence of the components the topology of the characteristics in the composition space (Fig. 3) is similar to that which occurs in systems with constant separation factors α_{ij} (Figs 1 and 2), but the characteristics are not straight lines (Figs 3, middle part of the hodograph). As a result, in systems with variable separation factors α_{ij} the route corresponding to the shock wave does not coincide with the characteristic, although it passes close to it.[21] The deviations of the shock route are usually small, so that the characteristics may be regarded as a satisfactory approximation also to shock waves.

Problems of frontal and frontal-displacement sorption dynamics in a system with a variance $m = 2$ and with an invariant affinity sequence, in which the first component is always sorbed more effectively than the second, have been examined on the basis of the nonlinear theory of multicomponent sorption dynamics for the ideal model using hodographs with variable factors α_{ij}.[200]

All the variants of the two-component displacement chromatographs [for both convex (favourable) and concave (unfavourable) isotherms] of the components can be readily obtained with the aid of the hodograph presented in Fig. 2. Both shock and spreading waves are then obtained in the displacement chromatograms in the presence of both enhanced concentration and dilution (deconcentration) of the displaced component.

We shall consider initially the variant where both isotherms $f(c)$, of the displacing agent and the displaced component, are convex (see Fig. 2*a*).[200]

1. If the sorbability of the displacing agent is greater than that of the displaced component (i.e. the displacing agent is component *1* and the displaced component is component *2*), then the *NMB* and *NMA* routed on the simplex $P_1P_2P_l$ correspond to the displacement regime. The displacement chromatograms corresponding to these routes have been published.[200]

2. If the sorbability of the displacing agent is lower than that of the displaced component (i.e. the displacing agent is component *2* and the displaced component is component *1*), two displacement regimes, corresponding to the *MNL* and *MQS* routes, are possible. It has been noted[20] that in this case the displaced first component is concentrated on the plateau (C_1^*) in the intervening zone (the *MNL* and *MQS* routes respectively), but the sharp (shock) displacement wave does not arise under these conditions and two-wave displacement regimes occur: the spreading 1-wave *MN* (or *MQ*) and the shock 2-wave *ML* (or *QS*). The case of the spreading wave *NT* is an exception (see Fig. 2*a*, *MNT* route).

The overall character of all the types of chromatograms in the case of concave isotherm $f(c)$ consists in the fact that the concentration of the displaced component diminishes on the plateau between the concentration k-waves ($k = 1, 2$). The concentration waves may be both of the spreading and shock types in conformity with the criteria (26).

The possible variants of the calculation of the concentration waves in the displacement sorption dynamics regime for a two-component Langmuir system with different convex and concave isotherms have been examined.[200] Tsabek[98] carried out a numerical computer calculation of two types of displacement chromatograms for two-component Langmuir isotherms. Comparison of the results with those of the present author[200] showed that the special cases of the regimes examined in the present author's study[200] were obtained in the numerical calculations. For other initial and boundary conditions, it is possible also to obtain other displacement regimes.[200] Thus the results of the numerical calculation do not always yield general conclusions about the behaviour of concentration waves in nonlinear chromatographic systems.

X. Chromatographic systems with regions including selectivity reversals of the components

We shall consider initially a system in which the ion exchange is stoichiometric and is described by the Law of Mass Action. For ideal ion exchange, this variant corresponds to the exchange of heterovalent ions, but in the general case sorption systems can also be assigned to the above systems. The stoichiometric coefficients ν_i and ν_s for which Eqns (15) hold can then be regarded as empirical.

For systems in which the sorption equilibrium is described by Eqns (15), it has been shown[21] that the sorption of all the components, other than the two arbitrarily selected components k and l, diminishes if the concentration of component k with a higher affinity for the sorbent increases as a result of the decrease in the concentration of component l having a lower affinity. Thus the sorption in which the equilibrium is described by Eqns (15) is competitive. The condition of competitiveness, obtained for these systems in the monograph by Helfferich and Klein,[21] refers to differential changes in concentration for a given mixture composition and does not eliminate the selectivity reversals arising in the system, which will be discussed below.

The characteristic equation for such systems yields $n-1$ real roots λ_k,[21] which fall within the range $V_k < \lambda_k < V_{k+1}$, where

$$V_k = \frac{X_k}{Y_k}, \quad k = 1, 2, ..., (n-1). \tag{31}$$

As in systems with a invariant affinity sequence, in the system under consideration there is an affinity cut. The condition of sorption competitiveness and the existence of the $(n-1)$th affinity cut for an arbitrary composition does not eliminate the reversal of selectivity. Within each region with an invariant affinity sequence, the properties of the systems (15) are the same as those of the Langmuir systems but with the difference that here the characteristics are not straight lines (see the example of Figs 3 and 4) and cannot be orthogonalised with the aid of the Riemann invariants (by the h-transformation). In this case, the path grid may be found by the numerical integration of the equation relating the concentrations of the components in the wave.[21, 66, 200] The separation factor α_{ij} in these systems is variable and depends on the concentrations. When $\nu_i \neq \nu_j$, the separation factor varies both as a function of the partition ratio of the components and of mixture composition. If the separation factor α_{ij} varies in the range $\alpha_{ij} < 1$ to $\alpha_{ij} > 1$ course of such variation, then the components i and j change places in the sorption series. This phenomenon is in fact referred to as selectivity reversal or inversion. When the inequality $\nu_i < \nu_j$ holds, the separation factor α_{ij} is greater in the concentration range where the partition ratio Y_j/X_j greater, i.e. where there is less competition from the component (i) having a higher affinity for the sorbent. If the composition changes in the direction of a greater proportion of substances with a low affinity, then the affinity of substances with a low stoichiometric coefficient ν_i increases relative to the other substances.[21]

The lines in the composition space on which the inversion of components i and j takes place (i.e. the equality $\alpha_{ij} = 1$ holds on this line) have been called[21,36,37] 'reversals' and in the present review are designated by '$i:j$' (the dash-dot lines in Figs 3 and 4). From the standpoint of the appearance of a possible inversion, the specification of the numbering of the substances in the sorption series has been modified.[21] The substances are numbered in accordance with the rule

$$i < j, \quad \text{if} \quad K_{ij} > 1. \tag{32}$$

In the i/j binary system, for two arbitrary substances, the affinity of the substance with a smaller number is greater. In systems without inversion the definition (32) is equivalent to that

presented above. If inversion takes place in the system, then the composition space is divided by the reversals $i:j$ into regions where $\alpha_{ij} < 1$ and $\alpha_{ij} > 1$ (see Figs 3 and 4). For the systems (15), the reversal $j:k$ in the composition space is described by the equation of a $(n-2)$-dimensional hyperplane parallel to the P_jP_k edge in the simplex $\{Y_i\}$ or $\{X_i\}$ (for $n = 3$, this is a straight line; see the 1 : 2 and 2 : 3 reversal lines in Fig. 3).[21] For any two substances j and k, such a hyperplane exists $v_j \neq v_k$. There is only one hyperplane j/k of this kind, so that multiple reversal of the selectivities of components j and k does not take place. All these rules can be observed in relation to the hodograph illustrated in Fig. 3.

A sufficient condition for the existence of the reversal $j:k$ is

$$(K_{ij})^{v_k} > (K_{ik})^{v_k} \quad \text{when} \quad j < k, \; i \neq j,k\,. \tag{33}$$

The system (15) has at least one reversal $j:k$ or $k:l$ if the coefficients v_i for the three components j, k, and l satisfy the condition

$$v_j, v_l > 2v_k \quad \text{when} \quad j < k < l\,. \tag{34}$$

It has been noted in the monograph by Helfferich and Klein [21] that condition (34) contains no coefficients K_{ij}, so that the widely held view that there is no reversal of selectivity when $K_{1n} > K_{2n} > K_{(n-1)n}$ is erroneous. For example, a three-component system ($n = 3$) with $v_1 = 2$, $v_2 = 1$, and $v_3 = 3$ has at least one reversal regardless of the quantity K_{ij}.[21]

The influence of the reversals on the disposition of the characteristics and hence on the dynamic behaviour of chromatographic systems, described by equilibria of type (15), is not very strong owing to the existence of the following rules, which the reversals obey.

1. All the reversals are such that only neighbouring substances change places in the affinity sequence. Thus, for the reversal $j:k$, the affinity sequence changes as follows: $1, ..., j, k, ..., n \rightarrow 1, ..., k, j, ..., n$ even if j and k do not occupy neighbouring positions.

2. The reversal $j:k$ is not intersected by the characteristic with the cut $j|k$ (for example, the Γ^1 paths in Fig. 3 intersect the reversal 2 : 3, while the Γ^2 paths intersect the reversal 1 : 2). Therefore, along any Γ^k path the compositions of groups with high and low affinities do not change. As a result, all the concentrations in the corresponding concentration wave vary monotonically.

3. Sorption remains competitive despite the reversals, so that within the limits of each region between the reversals the orientation of the characteristics and the qualitative dynamic response of the chromatographic system remain the same as in systems with invariant affinity sequence.

However, new features also appear — there is a greater number of watershed points (points W_1, W_2, and W_3 in Fig. 3*a*). Point W_2 on the P_1P_3 segment is unusual because it includes the Γ^1 and Γ^2 paths, which are tangents to the border P_1P_3 of the simplex. This property was first described by Tondeur.[37] In addition, the postulate that all the paths of one kind intersect all the paths of another kind, applicable to systems without inversions (cf. the hodographs in Figs 2 and 3), now ceases to be invalid.

The hodographs for systems with inversion have paths along which the velocity λ_s is constant. Such paths coincide with the reversal (the path $j|k$ on the reversal $j:k$). For example, on Fig. 3 the reversal 1 : 2 coincides with the Γ^1 path and the reversal 2 : 3 coincides with the Γ^2 path. The concentration changes along the wave corresponding to migration along all these characteristics are not sharpened and do not become diffuse in the ideal model. Evidently, in the presence of dispersion effects in the nonideal model, such waves do become diffuse.

In contrast to systems with invariant affinity sequence in systems where a component participates in more than one reversal (for example, component *2* undergoes inversion in the reversals 1 : 2 and 2 : 3 — see Fig. 3), the initial discontinuity in concentrations may split into a larger number of concentration waves, exceeding the variance of the system (m).

Thus in Fig. 3 the ANW_2MB route from the concentration point A via the watershed point W_2 and extending to point B and intersecting two reversals gives rise to three concentration waves: AN, NW_2M, and MB. The component (in the given instance component *2*) may be present when the column is filled initially (point B) and may be moved to the inlet (point A), but it is absent from the intervening concentration wave NW_2M.[21, 200]

This variant may occur also in the case where the route runs along the Γ path, which is tangential to the border of the simplex at the watershed point W (see the concentration wave QW_2M in Fig. 3; point Q corresponds to the mixture composition at the inlet to the column).

We shall consider the properties of nonlinear chromatographic systems in the presence of static complex-formation effects when the inversion $i:j$ may arise even for the i/j binary exchange of a pair of components i and j. In this case, the binary exchange isotherm $f_{i/j}$ can have the *S*- or σ-shape.[48, 66] A common feature of complex-forming systems in the presence of inversions consists in the fact that the concentration wave may be combined, i.e. may contain both discontinuous and diffuse sections.

Figs 4*a* and 4*b* present certain variants of hodographs (among those obtained by numerical integration) [66] for a system modelling the static complex-formation effects in which the multicomponent isotherms are represented by bi-Langmuir multicomponent isotherms.[149] The nonmonotonic variation of the wave velocity along the wave implies that the corresponding concentration wave may be partly of the shock type and partly of the spreading type — a property which is absent from the sorption systems (9) and (15).

The possible reversals for a three-component system, shown in Fig. 4*a*, are 1 : 2, 1 : 3, and 2 : 3. A hodograph of this type has been presented in a study [48] where the exchange of ions of equal valence in the presence of complex formation was considered. In this case, all three binary exchange isotherms $f_{1/2}$, $f_{1/3}$, and $f_{2/3}$ are *S*-shaped. The same topology of the characteristics, but this time with two reversals, was observed in the above study [48] and obtained in a theoretical investigation.[66] The binary isotherms $f_{1/3}$ and $f_{2/3}$ are then *S*-shaped, while the isotherm $f_{1/2}$ is convex (favourable). Other possible variants of the hodographs for a three-component system in the presence of complex formation have been quoted by the present author.[66] As for the systems (15), the hodographs for the above systems have several watershed points (cf Figs 3 and 4). There are also characteristics along the tangent to the border of the composition triangle within the composition region (cf the Γ^1 paths passing through the watershed points: through point W_1 in Fig. 4*a* and through point W_3 in Fig. 4*b*).

In the previous Section, it was noted that composition lines originating from the corner points of the simplex within the composition region are absent from the hodographs for essentially nonlinear systems. This means that on the chroma-togram two components cannot be absent on one side of the wave and present on the other. For complex-forming stoichiometric systems, chromatograms of this kind are possible. For example, on the chromatogram corresponding to the $P_3V_2P_2$ route (Fig. 4*b*), two components i ($i = 1, 2$) are present only on one (left) side of the shock 2-wave V_2P_2. In the usual stoichiometric systems, component *3* separates components *1* and *2* on the chromatogram, whereas on the chromatogram corresponding to the $P_3V_2P_2$ route, components *1* and *2* cannot be separated from one another (for further details on this topic, see the present author's earlier communication [66]). The inversion of components *1* and *3* on the isotherm $f_{3/1}$ plays a decisive role in the formation of such a chromatogram.[66, 200]

For the *S*-shaped binary isotherm $f_{1/3}$ and the convex (favourable) binary isotherms $f_{1/2}$ and $f_{2/3}$, a study has been made on the basis of qualitative considerations of the possibility of the formation of chromatograms consisting of two shock waves (see Fig. 4*b*):[219] the 1-wave P_3V_2 and the 2-wave V_2P_2. The formation of displacement chromatograms of this type has been demonstrated experimentally.[220]

It was stated above that in the general case $n-1$ concentration waves, separated by $n-2$ intervening plateaux (Π_k), arise in nonlinear chromatographic n-component stoichiometric systems with invariant affinity sequence of the components. Thus, routes with a single intervening plateau Π_1 (for example, the $A\Pi_1V_2$ route in Fig. 4*a*) are possible in three-component stoichiometric systems with complex formation.[66] Under these conditions, the two concentration waves on the chromatogram may be of the shock or spreading types partly of the shock type and partly of the spreading type. However, in the presence of inversion of the components, the route with a single intervening plateau does not always occur in chromatographic systems.

The postulate that each path of one kind intersects all the paths of another kind is invalid for such systems, so that in a number of instances one cannot move from a certain region of the simplex (the region $P_1V_2W_1P_2$ in Fig. 4*a*) to another region via a route including consecutively only two paths (Γ^1 and Γ^2). A variant of the route, which passes through a watershed point and contains three concentration waves and two intervening plateaux, has been proposed for such cases.[38]

A route (for example, the $A\Pi_1\Pi_2B$ route in Fig. 4*a*), corresponding to a chromatogram with three concentration waves $A\Pi_1$, $\Pi_1\Pi_2$, and Π_2B and with two intervening plateaux (Π_1 and Π_2), in which one of the components (component *1*) is present during the initial filling (point *B*) and in the inlet zone (point *A*) of the chromatogram but is absent from the intervening region (segment $\Pi_1\Pi_2$), arises under these conditions. In individual instances (when the route passes along the characteristic $V_2W_3P_2$ — see Fig. 4*b*), the concentration of component *1* may become zero on the shock concentration 2-wave (section W_3P_2).[66]

XI. Interaction of concentration waves in multicomponent chromatographic systems

The initial discontinuity in concentrations (from the influent concentration to the concentration during the initial filling of the column) in the frontal displacement multicomponent dynamic sorption problem splits into m concentration waves separated by concentration plateaux. In cyclic chromatographic processes, the column should be regenerated and for this reason yet another discontinuity concentration is created at the inlet. As a result, a further assemble (k) of concentration waves of different kinds ($k = 1, 2, ...$) arises in the column. Thus there is a possibility of a situation where a fast wave of the kth kind catches up with a slow wave of the sth kind ($k > s$) generated during the preceding break in concentrations, whereupon the interference of two concentration (k, s)-waves of different kinds takes place. In contrast to linear systems, in the interference of waves in nonlinear systems the principle of superposition does not hold, which leads to specific results of the interaction of the waves.

If two waves of different kinds meet, a local noncoherence arises for a time, being resolved by transition to a coherent state, as in the case where a perturbation is introduced into the system. During the interference of waves, the general postulate that the noncoherent state of the wave, defined as a superposition of coherent waves, is resolved during propagation and tends to a coherent state remains valid.[21]

In a calculation for such interaction in ideal systems with constant separation factors, the Riemann invariants have been used.[21] In the case of variable separation factors, in systems with invariant affinity sequence, the characteristics of the interaction of the concentration waves remain the same, but the Γ^k paths on the hodograph are no longer straight, which significantly complicates the quantitative calculation for the interaction of concentration waves.

It has been shown[68] that, for a three-component stoichiometric system with invariant affinity sequence of the components but with variable separation factors, there are two special cases of the interaction of concentration waves. If in the interaction of two waves in a three-component stoichiometric system the boundary concentration plateaux are at the borders of the simplex while one of the interacting waves is of the shock type, the calculation for the interaction is carried out with the aid of only the binary isotherms f_{ij}.[68] This principle has been applied in a calculation, based on the ideal model, for a cyclic four-stage process involving preparative chromatographic multicomponent separation.[67]

XII. Stationary concentration waves in multicomponent nonlinear chromatographic systems including dispersion factors

The conditions governing the appearance of stationary regimes in multicomponent sorption dynamics for Langmuir mixture isotherms (8) have been analysed[21, 39, 40] on the basis of both the general theory of quasi-linear equations of the hyperbolic type[46, 57] and the model of equilibrium ideal sorption dynamics and chromatography. It has been show[39] that, in the case of Langmuir mixture isotherms (8), Lax's stability conditions hold for the shock waves arising under these conditions. Therefore, for certain relations between the assembly of input concentrations and their assembly in the initial stage of the filling of columns in a chromatographic system, various shock S-waves arise (where integral numbers S assume values ranging from 1 to m).

In the presence of dispersion effects in the nonideal models considered, stationary regimes governing the propagation of multicomponent concentration S-waves with a finite width, which depends on the dispersion factors and on the 'curvature' of the multicomponent sorption isotherms, correspond to the shock S-waves.

The conditions governing the attainment of stationary regimes in multicomponent chromatographic systems with invariant affinity sequence of the components are independent of the magnitude of the dispersion factors and are therefore determined on the basis of the ideal model. However, the time required for the attainment of the stationary stage in the propagation of a multicomponent concentration S-wave depends on the values of the nonideality factors. These factors lead to the spreading of the concentration S-wave, the width of which becomes constant after a time. The time needed to establish stationary regimes depends on the height equivalent to the theoretical plate (HETP) and on the 'curvature' of the multicomponent isotherm. The dispersion parameter HETP is well known and is used widely in chromatographic theory and practice. It determines the width of the concentration waves and the effectiveness of the operation of the sorption bed.

After the attainment of the stationary regime (in the asymptotic stage), a multicomponent S-wave with a fixed width propagates at a constant velocity equal to the velocity of the shock wave σ_s. This velocity is independent of dispersion effects and is determined by the concentrations on the plateaux to the left (c_i^S) and to the right (c_i^{S+1}) of the Sth wave.[20, 65, 69, 104, 105, 197–200] The methods for the determination of the concentrations on the plateaux were discussed above and examples of such calculations may be found in a number of communications.[105, 198, 200]

In the presence of dispersion effects, the material balance equations assume the general form

$$\frac{\partial(a_i + c_i)}{\partial t} + \frac{\partial(c_i u)}{\partial z} = D_i \frac{\partial^2 c_i}{\partial z^2}, \quad i = 1, 2, ..., m, \tag{35}$$

where D_i are the effective longitudinal dispersion coefficients for m mixture components.

This system must be supplemented by kinetic sorption effects. A reasonable approximation to the kinetic equations is provided by model phenomenological equations based on the concept of linear driving forces. For intraparticle diffusion control, the kinetic equation proposed by Glueckauf[221, 222] for a one-component system, extended to multicomponent systems, is usually employed:

$$\frac{\partial a_i}{\partial t} = \beta_i[f_i(c) - a_i], \quad i = 1, ..., m. \tag{36}$$

For film diffusion control, analogous phenomenological equations are employed:[223,224]

$$\frac{\partial a_i}{\partial t} = \zeta_i[c_i - \varphi_i(a)], \quad i = 1, 2, ..., m. \tag{37}$$

Here $f_i(c)$ and $\varphi_i(a)$ are sorption isotherms which are reciprocal relative to one another, i.e. $f_i(c) = \varphi_i^{-1}(a)$.

The solution of the systems of differential equations (35) and (36) and (35) and (37), describing the profiles of stationary k-waves for two special types of nonlinear multicomponent chromatographic systems (L and C), has been considered.[65,104,105,197-200]

The L system is a multicomponent sorption Langmuir system (8) with constant separation factors for the components and a uniform velocity of the mobile phase u.

The C system is a system of n sorbable components in the presence of the sorption effect with linear isotherms and nonuniform flow rate u.

It has been shown on the basis of the ideal multicomponent model that the L and C systems are equivalent.[65,69,198,200]

It has been demonstrated for both systems[65,69,104,105,197-200] that, in the case of dispersion factors identical for each component, the relation between the concentrations of the components in the stationary multicomponent S-wave is linear:
for the L system

$$c_i - c_i^S = A_i^S(V - V^S), \quad \text{where} \quad A_i^S = \frac{c_i^{S+1} - c_i^S}{V^{S+1} - V^S}, \tag{38a}$$

and for the C system

$$c_i - c_i^S = B_i^S(R - R^S), \quad \text{where} \quad B_i^S = \frac{c_i^{S+1} - c_i^S}{R^{S+1} - R^S}, \tag{38b}$$

$i = 1, 2, ..., m$.

The linear relations (38) describe the dependence of the concentrations of the components along the multicomponent concentration S-wave at the stationary stage with dispersion factors identical for each component. These relations describe a path grid in the concentration space, which coincides with the grid of the Γ^k paths for the ideal model. For a two-component model, examples of path grids of this kind are presented in Figs 1*a* and 2. The linear relations (38) may serve as reliable tests of the validity, convergence, and accuracy of the numerical schemes developed for the solution of nonlinear problems in multicomponent sorption dynamics (see the examples given in a number of papers[105,198,200]).

In the ideal model, the parameters A_i^S and B_i^S represent the Riemann vector-invariants.[40,43,65,69,198] A large number of examples of path grids Γ^k, including those for multicomponent systems, have been presented in the monograph by Helfferich and Klein.[21]

Accurate analytical solutions, describing the stationary multicomponent concentration waves of the Sth kind for different combinations of the dispersion factors, have been obtained in the case of the L and C systems in a moving coordinate system (c,Z).[65,104,105,198-200]

1. The *L* system [104,105,198,200]

For equilibrium sorption dynamics, one can write

$$D_i = D \text{ and } \frac{1}{\beta_i} = 0 \left(\text{or } \frac{1}{\zeta_i} = 0\right); \quad \text{HETP} = \frac{2D}{u}.$$

For nonequilibrium (intraparticle diffusion) sorption dynamics, without allowance for longitudinal diffusion, we have

$$D_i = 0 \text{ and } \beta_i = \beta; \quad \text{HETP} = \frac{2(1 - \sigma_S/u)\sigma_S}{\beta},$$

$$V^S \ln|E| - V^{S+1}\ln|1 - E| = \frac{2(1 - \sigma_S/u)(V^S - V^{S+1})Z}{\text{HETP}} + K_S,$$

$$V^S = 1 + \sum_i b_i c_i^S, \quad S = 1, 2, ..., \quad Z = z - \sigma_S t. \tag{39}$$

The following expressions are used for the description of nonequilibrium (film diffusion) sorption dynamics without allowance for longitudinal dispersion:

$$D_i = 0 \text{ and } \zeta_i = \zeta; \quad \text{HETP} = \frac{2(1 - \sigma_S/u)^2 u}{\zeta},$$

$$V^{S+1}\ln|E| - V^S\ln|1 - E| = \frac{2(1 - \sigma_S/u)(V^S - V^{S+1})Z}{\text{HETP}} - K_S,$$

$$K_S = V^S - V^{S+1},$$

$$E = E_S = \frac{c_i - c_i^S}{c_i^{S+1} - c_i^S} = \frac{V - V^S}{V^{S+1} - V^S}. \tag{40}$$

Here the distribution of the concentrations E_S along the multicomponent concentration S-wave is independent of the number i of the component ($i = 1, 2, ..., m$) when account is taken of Eqn (38). The distribution of concentrations has been formulated in a dimensionless form and normalised, since the relation $0 \leqslant E \leqslant 1$ is valid.

A widely employed empirical parameter — the effective width Δz_S

$$\Delta z_S = \frac{\text{HETP}(V^S + V^{S+1})}{(V^S - V^{S+1})2(1 - \sigma_S/u)} \ln\left|\frac{1 - \varepsilon}{\varepsilon}\right|, \tag{41}$$

where ε is an arbitrarily selected small dimensionless quantity ($\varepsilon = 0.1$ is usually employed in practice), is applied to the description of the spreading of the wave.

2. The *C* system [65,198-200]

In the case of equilibrium multicomponent sorption dynamics, we have

$$D_i = D \text{ and } \frac{1}{\beta_i} = 0 \left(\text{or } \frac{1}{\zeta_i} = 0\right); \quad \text{HETP} = \frac{2D}{u}$$

$$\ln|E| - \ln|1 - E| = \frac{2(\sigma_S/u)(R^S - R^{S+1})Z}{c_0\text{HETP}}. \tag{42}$$

The following relation is valid for nonequilibrium intraparticle diffusion multicomponent sorption dynamics without allowance for diffusion:

$$D_i = 0 \text{ and } \beta_i = \beta; \quad \text{HETP} = \frac{2(1 - \sigma_S/u)\sigma_S}{\beta},$$

whilst for nonequilibrium film diffusion multicomponent sorption dynamics without allowance for longitudinal dispersion, we have

$$D_i = 0 \text{ and } \zeta_i = \zeta; \quad \text{HETP} = \frac{2(1 - \sigma_S/u)^2 u}{\zeta},$$

$$(u^S - \sigma_S)\ln|E| - (\sigma_S - u^{S+1})\ln|1 - E|$$

$$= \frac{2(1 - \sigma_S/u)(R^S - R^{S+1})\sigma_S Z}{c_0\text{HETP}} + K_S,$$

$$K_S = u^{S+1} - u^S, \tag{43}$$

where u^S is the velocity on the concentration plateaux to the left of the S-wave and u^{S+1} the velocity on the concentration plateaux to the right of the S-wave (for the C system, the velocity u is nonuniform).

Relations for estimating the effective width of the multicomponent stationary S-wave are obtained from the distributions (42) and (43):

$$\Delta z_S = \frac{\mathrm{HETP}c_0(u/\sigma_S)}{(R^{S+1} - R^S)} \ln\left|\frac{1-\varepsilon}{\varepsilon}\right|, \quad (44)$$

$$\Delta z_S = \frac{\mathrm{HETP}c_0[1 - (u^S + u^{S+1})/2\sigma_S]}{(R^{S+1} - R^S)(1 - \sigma_S/u)} \ln\left|\frac{1-\varepsilon}{\varepsilon}\right|. \quad (45)$$

The integration constants K_S in Eqns (39), (40), (42), and (43) have been obtained from the consideration that the centre of gravity of the S-wave is zero in the moving coordinate system with $Z = z - \sigma_S t$.[65, 104, 105, 199, 200]

It follows from Eqns (41), (44), and (45), where the denominator includes the difference $V^{S+1} - V^S$ or $R^{S+1} - R^S$, that the smaller the number of concentration jumps in the S-wave the greater its width and diffuseness.

Analytical solutions of Eqns (38) and (45) can be readily used for the analysis of the stationary stage in two-component displacement sorption dynamics of two components (or for the equivalent system involving the exchange of three ions).[200] It follows from this analysis that the static effects of the interference of components lead to additional spreading of the concentration wave compared with its spreading in a one-component system. This additional spreading occurs in the concentration profiles of both the displacing agent and of the displaced component and is greater the greater the curvature of the sorption isotherms.

For markedly curved Langmuir isotherms for the displacing agent [large values of b_i in Eqn (8)], it has been shown[198, 200] that, in the displacement regime for a two-component system, the additional spreading of the displacing agent wave ($i = 1$) occurs in the region of low concentrations in the 2-wave ($S = 2$) for the intraparticle diffusion kinetic stage and in the region of high concentrations for the film diffusion kinetic stage.

It follows from Eqns (39)–(41) that, in a two-component L system with displacement of component *2* by component *1*, the mutual influence of the components leads (owing to the sorption effect) to additional spreading of the concentration waves of both components compared with a one-component system.[198, 200] In a C system, such operation of the static effect of the interference of substances is analogous to the effect which arises in the Langmuir sorption L systems. This additional spreading is greater the greater the Henry coefficient of the displaced component and the smaller the Henry coefficient of the displacing agent.[199, 200]

XIII. Conclusion

The above analysis of the nonlinear theory of multicomponent sorption and chromatographic systems yields general conclusions about the current state of this field of study and of the trends in its development.

The application of concepts associated with the description of the behaviour of nonlinear multicomponent chromatographic systems within the framework of multicomponent concentration waves, in particular for the determination of the eigenvalues of the wave velocities, is exceptionally fruitful. Here one should employ the advances achieved in the theory of fluid and gas mechanics and also in the mathematical theory of systems of nonlinear equations of the hyperbolic type.

The theory of multicomponent nonlinear sorption dynamics and chromatography based on the ideal model has been well developed for nonlinear Langmuir systems with constant separation factors for the components.

The Riemann invariants, describing the propagation of the multicomponent concentration waves arising during the separation process, have been found. On this basis, the general characteristics of the behaviour of substances in multicomponent chromatographic systems have been obtained with allowance for interference effects. The application of the Riemann invariants on the basis of the ideal model permits not only calculations of multicomponent shock and spreading concentration waves with allowance for the effects of the interference of substances but also calculation for different forms of the interaction of multicomponent concentration waves.

Such results have been obtained with the aid of both the h-transformation and of the concept of coherence, which is of a general character and is applicable to the vast majority of nonlinear multicomponent chromatographic systems. The results have a simple and visual geometrical interpretation, which is based on the properties of the orthogonalisation of the composition space $\{c_i\}$ on transition to the invariants space $\{h_k\}$.

The application of the h-transformation, based on the properties of the Riemann invariants and developed in detail in the monograph by Helfferich and Klein,[21] makes it possible to calculate the concentrations $\{c_i^k\}$ on the concentration plateaux for the distributions corresponding to the multicomponent waves of the $(k-1)$th and kth kinds.

The predictive power of these calculations is based on the fact that the calculated values on the concentration plateaux between multicomponent waves are independent of the dispersion factors (nonideality factors). Using the criterion of the establishment of stationary regimes in concentration k-waves (defined as the decrease in the invariant h_k along such a wave), it is easy to deduce for Langmuir multicomponent systems whether such a regime is attained for the given k-wave under the specified initial and boundary conditions in the chromatography of a mixture of substances.

The concentration profiles calculated on the basis of the postulates of the ideal model are unrealistic, since they do not take into account the dispersion factors in sorption processes (although these factors always operate). Nevertheless, the ideal model yields a satisfactory first approximation, especially for the concentration distributions of spreading k-waves. In such waves, the nonlinearity factors and the factors associated with the static interference of substances, taken into account in the equations for multicomponent mixture isotherms, play the main role in the spreading of the k-waves.[21]

The solutions presented in Section XII of the present review supplement the approach based on the ideal model of the theory of multicomponent sorption dynamics and chromatography. The solutions obtained describe the stationary distributions of concentrations in a multicomponent k-wave of finite width (Δz) with allowance for the nonideality factors in the dynamic sorption process. According to these solutions, the width (Δz) of a stationary k-wave is proportional both to the HETP and the static factors arising from the interference of substances, which are related to the parameters of multicomponent sorption isotherms. The advantage of these simple analytical solutions consists in the possibility of taking into account the joint influence of the nonideality factors and the factors arising from the interference of the sorbable substances in the stationary stage of the propagation of multicomponent sorption k-waves.

More accurate results have been obtained in the numerical integration of the nonlinear multicomponent equations of sorption dynamics. However, in this case too the analytical solutions presented here [especially the linear relations (38)] can serve as reliable tests of the validity, convergence, and accuracy of the numerical schemes developed for the solution of nonlinear problems of multicomponent sorption dynamics.

Furthermore, the results based on the analytical solutions (in contrast to specific numerical solutions) make it possible to obtain general estimates of the influence of the effects of the interference of substances in nonlinear multicomponent dynamic sorption

systems.[198-200] It follows from the analytical solutions presented here that the effects of the interference of substances lead to an additional broadening of the concentration distributions along the sorption multicomponent waves generated in the column.

For multicomponent systems with variable separation factors, especially for systems having regions with selectivity reversals of the components, the theory has not so far been adequately developed. For such systems, there is a possibility of a nontrivial chromatogram in which a specific component is present at the inlet and outlet and is absent within the multicomponent concentration distributions in the wave.

The concept of coherence,[21,22,81] used to take into account the effects of the interference of substances, is fundamental in the description of the behaviour of nonlinear multicomponent dynamic systems and plays a major role in the development of a general theory of multicomponent nonlinear sorption dynamics and chromatography for multicomponent systems of a general kind. This concept facilitates the qualitative description and quantitative calculations for multicomponent systems, especially for arbitrary initial and boundary conditions. The fundamental nature of this concept extends to the description of the behaviour of a wide range of multicomponent nonlinear dynamic mass transfer, heterophase systems, such as multiphase flows in porous media,[195] chromatographic reactors, and nonstationary distillation.[196]

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