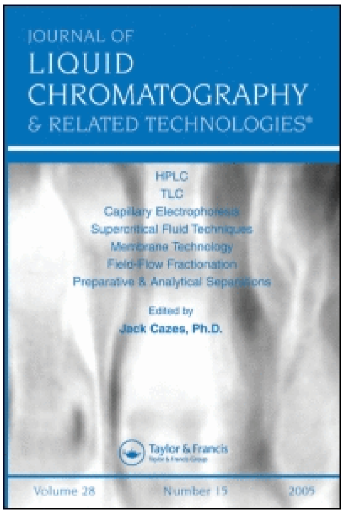

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Simple Models in Liquid Chromatography with Mixed Mobile Phases: Present and Future

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SIMPLE MODELS IN LIQUID CHROMATOGRAPHY WITH MIXED MOBILE PHASES: PRESENT AND FUTURE

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ABSTRACT

This short review presents simple models of solute retention, which involve competitive adsorption of solute and solvents, differences in molecular sizes of solute and solvents, non-specific and specific solute-solvent and solvent-solvent interactions, and adsorbent heterogeneity. According to these models the interactions of solute and solvent molecules with adsorption sites of the solid as well as specific solute-solvent and solvent-solvent interactions are represented by suitable quasi-chemical reactions. Final equations describing solute retention have rigorous foundations in terms of classical thermodynamics, which enable definition of adsorption and partition effects in the chromatographic process.

INTRODUCTION

Although the displacement and partition mechanisms of chromatographic processes were already considered in the first chromatography symposium (1-3), which was held in New York City in 1946, the first theoretical attempts of explanation of their role in the liquid chromatography (LC) process appeared several years after 1946 (4,5). An important role of the displacement mechanism in the LC process was firstly recognized in the 1960's by Snyder (4). The last twenty years have been characterized by dynamic progress in the theoretical studies of the LC process, which starting with the original displacement model incorporated additional factors affecting this process [see reviews (6-12) and references therein]. Parallelly with these studies, another description of the LC process, proposed in 1965 by Ościk (5), was developed and examined by using the TLC data (8). This description involves the partition mechanism of solute distribution between the mobile and surface-influenced stationary phases. The above mentioned studies dealing with the role of displacement and partition mechanisms in the LC process gave theoretical foundations to formulate a general description of LC with mixed mobile phases involving concurrent adsorption and partition effects (13,14). In addition, these studies initiated a series of theoretical papers (15-19) dealing with the statistico-thermodynamical description of LC with mixed mobile phases, which automatically incorporates the competitive character of solute and solvent adsorption and all contributions from solution nonideality. This statistico-thermodynamical description gives rigorous thermodynamical foundations for simple models, which are useful for interpreting the LC data.

The present review gives a brief description of simple models of solute retention in LC with mixed mobile phases and indicates perspectives of their development.

FUNDAMENTAL MODELS OF SOLUTE AND SOLVENT DISTRIBUTION

Let us consider the r-th solute chromatographed in a n-component mobile phase. In the case of LC the mobile and stationary phases usually contain the same components but of different concentrations. An exception is reversedphase liquid chromatography with chemically bonded phases and liquid-liquid chromatography, in which the chemically bonded phase and the stationary liquid form the virtually immiscible surface phase.

From thermodynamic viewpoint the LC process may be represented by series of reversible quasi-chemical reactions, which describe the phase exchange between solute and solvent molecules (20). All possible phase-exchange reactions between solute and solvent molecules may be described by the following reactions:

$$w_n(i)^m + w_i(n)^s \rightleftharpoons w_n(i)^s + w_i(n)^m \quad \text{for } i=1,2,\ldots,n-1 \qquad (1)$$

$$w_1(r)^m + w_r(1)^s \rightleftharpoons w_1(r)^s + w_r(1)^m \qquad (2)$$

where $(j)^\beta$ denotes a molecule of the j-th component in the β-th phase, β = m (mobile phase) and s (stationary phase) and w_j denotes the number of segments in a molecule of the j-th component. The equilibrium constants relating to the reactions 1 and 2 may be written as follows:

$$K_{in} = (a_i^s/a_i^m)(a_n^m/a_n^s)^{w_i/w_n} \quad \text{for } i=1,2,\ldots,n-1 \qquad (3)$$

$$K_{r1} = (a_r^s/a_r^m)(a_1^m/a_1^s)^{w_r/w_1} \qquad (4)$$

where a_j^β ($j=1,2,\ldots,n,r$ and $\beta=m,s$) is the activity of the j-th component in the β-th phase. In the case of different molecular sizes ($w_r \neq w_1 \neq \cdots \neq w_n$) the activity a_j^β is defined by means of the volume fraction y_j^β :

$$a_j^\beta = y_j^\beta f_j^\beta \quad \text{for } j=1,2,\ldots,n,r \text{ and } \beta=m,s \qquad (5)$$

where f_j^β is the activity coefficient of the j-th component in the β-th phase.

Since the concentration of the r-th solute is infinitely low, equation 4 may be rewritten in terms of the distribution coefficient k_r, which is defined by:

$$k_r = \lim_{y_r^m \to 0} (y_r^s/y_r^m) \qquad (6)$$

Then, equations 4, 5 and 6 give:

$$k_r = K_{r1}\ (f_r^m/f_r^s)\ \left(\frac{y_1^s\ f_1^s}{y_1^m\ f_1^m}\right)^{w_r/w_1} \tag{7}$$

Similarly, equations 3 and 5 give:

$$K_{in} = \frac{y_i^s\ f_i^s}{y_i^m\ f_i^m} \cdot \left(\frac{y_n^m\ f_n^m}{y_n^s\ f_n^s}\right)^{w_i/w_n} \quad \text{for } i=1,2,\ldots,n-1 \tag{8}$$

In terms of classical thermodynamics equations 7 and 8 represent the most general description of the LC process. Special cases of these equations may be obtained by assuming different models of the mobile and stationary phases (physicochemical properties of these phases are described by the activity coefficients f_j^m and f_j^s) and different models of solute and solvent distribution between both phases (displacement or partition mechanisms of the solute and solvent distribution).

The activity coefficient f_j^m may be defined in a general form, which comprises different types of molecular interactions (13,21):

$$f_j^m = f_{(d)j}^m\ f_{(s)j}^m \quad \text{for } j=1,2,\ldots,n,r \tag{9}$$

where $f_{(d)j}^m$ and $f_{(s)j}^m$ denote the activity coefficients of the j-th component in the mobile phase reflecting nonideality of the solution due to dispersive (d) and specific (s) interactions. The surface activity coefficient f_j^s for a homogeneous solid is defined analogously as the coefficient f_j^m. However, for an energetically heterogeneous solid its definition may be extended to describe also the nonideality of the surface solution due to the surface heterogeneity. Then

$$f_j^s = f_{(d)j}^s f_{(s)j}^s f_{(h)j}^s \quad \text{for } j=1,2,\ldots,n,r \tag{10}$$

where $f_{(h)j}^s$ reflects nonideality of the solution associated with energetic heterogeneity of the solid; for a homogeneous solid this coefficient is assumed to be equal to unity. Physicochemical interpretation of the activity coefficient $f^s_{(h)j}$ is given elsewhere (22,23).

Equation 7 has been derived by Jaroniec et al. (20). For ideal surface phase ($f^s_r = f^s_1 = 1$) and $y^s_1 = 1$ this equation reduces to the expression derived by Slaats et al. (24), however, for ideal both phases and $y^s_1 = 1$ equation 7 gives Snyder-Soczewiński relationship (7,25). An important special case of equation 7 is the expression describing LC with ideal both phases, i.e.,

$$k_r = K_{r1} \, (y^s_1/y^m_1)^{w_r/w_1} \tag{11}$$

Equation 11 was examined by using the TLC (20,26,27) and HPLC data (28,29). It follows from these studies that the surface phase composition affects strongly the solute retention, especially in the LC systems with solvents of similar properties. Moreover, these studies indicate that the excess adsorption isotherm measured for the eluent-adsorbent system is useful for interpreting the LC data.

MODELS OF SOLUTE RETENTION INVOLVING NON-SPECIFIC INTERACTIONS

A significant progress in interpretation of equation 7 has been done by Jaroniec and Martire (13,14). They assumed the regular solution model to represent nonideality of the bulk and surface phases and considered equation 7 for $f^\beta_{(s)j} = 1$ ($j=r,1$ and $\beta=m,s$) and $f^s_{(h)j} = 1$. Combination of this equation with the activity coefficients for regular bulk and surface solutions gives a general equation for the distribution coefficient k_r , which may be reduced to equation 11 (displacement model) and equation describing partition model (13,14,30,31):

$$k_r = f^m_{(d)r} / f^s_{(d)r} \tag{12}$$

Thus, this general equation involving concurrent adsorption and partition effects gives theoretical foundations for the LC models, which are based on equations 11 and 12.

It has been shown in the papers (13,14) that equation 12 combined with the activity coefficients for the regular bulk and surface solutions gives Ościk-type equation (5,8). Physical interpretation of this equation is presented elsewhere (30,31). This interpretation showed that although Ościk's equation is better suited for describing partition effects in LC, after small modification it may be used to describe systems, in which partition and adsorption phenomena occur simultaneously (mixed model of solute retention). In light of this mixed model the solute is distributed according to partition model, whereas, the solvent composition in the surface phase is established according to the adsorption equilibrium.

MODELS OF SOLUTE RETENTION INVOLVING SPECIFIC INTERACTIONS

If the activity coefficients $f^m_{(s)j}$ and $f^s_{(s)j}$ [see equations 9 and 10] are known, then equations 7 and 8 may be directly used to describe the LC systems with specific solute-solvent interactions. Although this description seems to be promising for studying association effects in the LC process, as yet it has not been utilized. An alternative treatment has been proposed to derive equations involving specific interactions in the LC process (11,32-37). According to this treatment these interactions are represented by suitable quasi-chemical reactions, which lead to formation of solute-solvent and solvent-solvent complexes (associates) in the mobile and surface phases. Especially simple equations have been derived for association models assuming formation of double pure and mixed complexes (7,32,33). For example, formation of double solute-solvent associates in the mobile phase may be represented as follows (32):

$$(r)^m + (1)^m \rightleftharpoons (r1)^m \tag{13}$$

where the equilibrium constant C^m is defined by:

$$C^m = y^m_{r1}/(y^m_r\, y^m_1) \tag{14}$$

Combination of equation 14 with equation 7 leads to an expression for the distribution coefficient, which involves solute-solvent association in the mobile phase. This approach has been recently extended by Jaroniec and Martire (37). They derived equations for the distribution coefficient, which involves non-specific and specific solute-solvent interactions in both phases. The above treatment may be easily extended for different models of association (models assuming formation of multimolecular associates) but final expressions are complicated and frequently inconvenient for practical applications.

One of the main advantage of this treatment is its simplicitly. An analogous description may be also used to study dissociation effects in LC(38).

MODELS OF SOLUTE RETENTION INVOLVING ADSORBENT HETEROGENEITY

Equations 7 and 8 may be also used to describe LC on heterogeneous solid surfaces but then expressions defining the surface activity coefficients should contain the coefficient $f^s_{(h)j}$ reflecting nonideality of the surface solution due to the adsorbent heterogeneity (21). Another possibility of description of adsorbent heterogeneity effects in the LC process was initiated by Snyder (4) and developed by Jaroniec et al. (39-42). This description is based on the theory of physical adsorption on heterogeneous solid surfaces (43-45). According to this treatment the phase-exchange reactions 1 and 2 occur on different types of adsorption sites; the equilibrium constants depend on the adsorption energies characterizing these adsorption sites. The fundamental relationship, which is utilized to derive expressions for the distribution coefficient, assumes that the total distribution coefficient $k_{r,t}$ is given by the following sum:

$$k_{r,t} = \sum_{l=1}^{L} g_l \, k_{r,l} \tag{15}$$

where $k_{r,l}$ denotes the distribution coefficient for the l-th type of adsorption sites, g_l is the fraction of adsorption sites of the l-th type, and L is the total number of all types of adsorption sites. Equation 15 combined with special cases of equation 7 leads to the expressions, which were discussed elsewhere (39-42).

CONCLUDING REMARKS

A brief review of simple models used in LC with mixed mobile phases shows further possibilities of their extension and application for interpreting the LC data. It has been shown in the papers (13,14,37) that these models leads to a general description of the LC process, which has rigorous foundations in terms of classical and statistical thermodynamics.

Representation of different types of interactions in the LC process [see reactions 1,2 and 13] creates a new possibility for studying liquid chromatography. In this case the method of numerical stochastic simulation (46) seems to be a very attractive and efficient way for studying the chromatographic systems, in which the kinetic effects play a significant role. This method was successfully utilized to study the adsorption kinetics (46) and therefore it seems to be promising for modeling the LC process on the molecular level.

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