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MODELS OF SOLUTE AND SOLVENT DISTRIBUTION FOR DESCRIBING RETENTION IN LIQUID CHROMATOGRAPHY

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SUMMARY

Models of solute and solvent distribution between the mobile phase and surface-influenced stationary phase are presented and defined in terms of classical thermodynamics. Combination of these models makes possible formulation of models describing solute retention in liquid chromatography. This approach enables the possibility for classification of the majority of known models of solute retention and reveals, in many cases, their thermodynamic foundations.

INTRODUCTION

Retention in liquid chromatography (LC) is determined by many factors and therefore its theoretical description is still incomplete (see reviews[1–7] and references therein). Statistical thermodynamics provides the best possibility to formulate an unified theory of retention[8–11], which automatically incorporates the competitive character of solute and solvent adsorption and all contributions from solution non-ideality, but the final expressions which result are quite complicated and frequently inconvenient for practical applications[12]. Therefore, many attempts have been made to propose simple models of a retention mechanism, which involve only some factors determining the chromatographic process, *e.g.*, models starting with the original displacement mechanism (competitive adsorption of solute and solvents)[1,7,13–15] and incorporating additional details such as adsorbent heterogeneity[16–19], non-specific interactions in both phases[19–25], solvation and solvent association in both phases[26–29], phase composition[15–22,24–29] and other factors[30,31]; models assuming a partition mechanism of solute distribution between two phases[12,32–35] and other models involving the phase composition in solute distribution and solute–solvent interactions[36–38]. Although these simple models have proved to be useful for interpreting specific sets of LC retention data, their wider application for predicting solute retention and optimizing the LC process is often limited because they take into account

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only some factors determining the LC process and simultaneously ignore other important factors.

These models may be roughly divided into two groups. The first group, the most popular in LC theory, contains models of solute retention based on the competitive character of solute and solvent adsorption (displacement mechanism of solute retention) together with other factors determining the LC process (see reviews[1,7] and references therein). However, the second group of LC models invokes an alternative description of solute retention, *i.e.*, a partitioning mechanism, which regards solute retention as a consequence of differences in solute–solvent interactions in the mobile and surface phases[34]. In other words, these alternative approaches assume a dominating role of either adsorption or partitioning effects. Up to now, the adsorption and partitioning mechanisms of solute retention have been considered separately, although in many LC systems both these mechanisms may occur simultaneously.

A general model of LC with mixed mobile phases, involving concurrent adsorption and partition effects, has recently been proposed[12]. Under special conditions this general model reduces to the limiting models based on pure displacement or pure partitioning. In the present paper this idea is developed by defining models of solute and solvent distribution between the mobile and surface phases, in terms of classical thermodynamics. The global LC process may then be represented by different models, which are combinations of the solute and solvent distribution models. This simple approach gives a clear picture of the LC process on the molecular level, leading to a general expression describing solute retention, which under special conditions reduces to familiar limiting equations.

GENERAL CONSIDERATIONS

Let us consider transfer of a component (solute or solvent) from a bulk-liquid mobile phase consisting of a solute and *n* solvents to a surface-influenced (stationary) liquid layer (phase). In the case of LC the mobile and stationary phases usually contain the same components but in different concentrations. An exception is reversed-phase liquid chromatography (RPLC) with chemically bonded phases (CBPs), in which the bonded phase is a component of the surface phase not appearing in the mobile phase. (Another possible exception is liquid–liquid chromatography, in which the stationary phase is a liquid covering a solid surface and is virtually immiscible with the liquid forming the mobile phase.) Since the bonded phase is essentially not removable, the quantity of the component bonded to the solid surface is constant during the LC process. However, the concentrations of components appearing in both phases are established according to the conditions of thermodynamic equilibrium.

The distribution of a component between the mobile and stationary phases defined above is due to differences between the adsorption potentials of this component and other components forming the surface-influenced liquid phase, and to differences in the interaction energies of this component with other components appearing in the mobile and stationary phases. Thus, it is a consequence of two molecular processes. The first, typical for liquid–solid chromatography in the normal-phase mode, is competitive adsorption of the solute and solvent (displacement mechanism), which in the case of the solute determines its distribution between the mobile and stationary phases, and in the case of solvents, determines the composition of the surface phase. The second process, typical for liquid–liquid chromatography and RPLC with chemically bonded phases, is analogous to what we usually understand by classical partitioning[12]; this process is due to differences in molecular interactions in the bulk-liquid mobile phase and surface-influenced stationary liquid phase. In the case of liquid–liquid chromatography and RPLC-CBP with exclusion of molecules of solvent, the distribution of a solute occurs between two immiscible phases and is quite analogous to liquid–liquid partition although the stationary layer generally cannot be identified with a bulk liquid. When both phases contain the same solvents, the properties of the stationary phase differ from the bulk one because the solid surface influences the various molecular interactions in the stationary phase and, hence, sets the composition variables in that phase. This difference in molecular interactions also governs the transfer of the solute and solvent from the mobile phase to the stationary phase and the physical nature of this process is analogous to classical partitioning. Therefore, we use the term "partition" to define the contribution to solute and solvent distribution arising from differences in molecular interactions in the bulk phase and the surface-influenced stationary phase.

The above considerations, explaining the terms "displacement" and "partition", enable definition of the models of solute and solvent distribution between two phases and, accordingly, models of the LC process.

MODELS OF SOLUTE DISTRIBUTION

Let us consider the sth solute and solvents 1, 2, ..., n. To analyse the distribution of the sth solute between two phases consisting of the same n solvents, we should consider the competitive adsorption of this solute with respect to all solvents and the different solute–solvent interactions in both phases. In the general case, when both competitive adsorption of solute with respect to the ith solvent (displacement mechanism) as well as different solute–solvent interactions in both phases (partition mechanism) determine the solute distribution, we infer a mixed mechanism of solute transfer from the mobile phase to the stationary one. The displacement and partition model of solute distribution between two phases are the limiting cases of this mixed (general) model. A quantitative characterization of these models will be given later on the basis of theoretical considerations presented in our previous paper[12]. Equations defining the distribution coefficient of the sth solute in a n-component eluent will be derived by using the ith solvent as a reference solvent.

In the case of LC the solute concentration in both phases is infinitely low, *i.e.*

$$\varphi_s^\rho \to 0 \text{ for } \rho = \sigma, l \tag{1}$$

where φ_s^ρ is the volume fraction of the sth solute in the ρth phase and the superscripts σ and l refer to the surface-influenced stationary phase and the mobile phase, respectively. Because of eqn. 1, the volume fractions of the solvents 1, 2, ..., n fulfil the following condition:

$$\sum_{i=1}^{n} \varphi_i^\rho = 1 \text{ for } \rho = \sigma, l \tag{2}$$

To express the compositions of the mobile and stationary phases, we use the volume fractions because, in general, these phases contain molecules of different sizes; this means that a molecule of the ith component contains r_i segments.

The distribution coefficient of the sth solute in a n-component eluent is defined as follows[12]:

$$k_s = \lim_{\varphi_s^l \to 0} (\varphi_s^\rho/\varphi_s^l) \tag{3}$$

This coefficient is dependent on the compositions of the mobile and stationary phases and parameters characterizing the competitive adsorption of the solute and the solute–solvent interactions in both phases. Expressions defining k_s for the three different models of solute distribution are given below; they result directly from theoretical considerations presented elsewhere[12].

Mixed model of solute distribution (MS)

In general, the solute distribution is described[12] by

$$k_s = K_{si} (\gamma_s^l/\gamma_s^\sigma) [(\varphi_i^\sigma \gamma_i^\sigma)/(\varphi_i^l \gamma_i^l)]^{r_s/r_i} \tag{4}$$

where K_{si} is the equilibrium constant for the phase-exchange reaction between molecules of the sth solute and ith solvent, which represents the competitive adsorption of the sth solute with respect to the ith solvent (displacement mechanism); γ_s^ρ and γ_i^ρ are the activity coefficients of the sth solute and the ith solvent in the ρth phase at infinitely low concentration of the sth solute, *i.e.*, $\varphi_s^\rho \to 0$ for $\rho = \sigma$ and l.

The equilibrium constant, K_{si}, is defined by means of the adsorption energies of the sth solute and the ith solvent, ε_s and ε_i, and a pre-exponential factor, K_{si}^0 (entropy factor), *i.e.*[39,40]

$$K_{si} = K_{si}^0 (T) \cdot \exp [(\varepsilon_s - r_s\varepsilon_i/r_i)/(k_B T)] \tag{5}$$

where k_B and T have their usual meanings.

The activity coefficients γ_s^ρ and γ_i^ρ are formulated[12] as

$$\ln \gamma_s^\rho = \sum_{i=1}^{n} (1 - r_s/r_i)\varphi_i^\rho + r_s \sum_{i=1}^{n} \chi_{is}^\rho \varphi_i^\rho - r_s \sum_{\substack{i,j=1 \\ j>i}}^{n} \chi_{ij}^\rho \varphi_i^\rho \varphi_j^\rho \tag{6}$$

for $\rho = \sigma$, l, and

$$\ln \gamma_i^\rho = \sum_{j=1}^{n} (1 - r_i/r_j)\varphi_j^\rho + r_i \sum_{j=1}^{n} \chi_{ji}^\rho \varphi_j^\rho (1 - \varphi_i^\rho) - r_i \sum_{\substack{j,k=1 \\ j,k \neq 1 \\ k>j}}^{n} \chi_{jk}^\rho \varphi_j^\rho \varphi_k^\rho \tag{7}$$

for $i = 1, 2, ..., n$ and $\rho = \sigma, l$; χ_{ij}^ρ is the usual interaction parameter defined as

$$\chi_{ij}^\rho = (z^\rho/k_B T) [\omega_{ij}^\rho - 0.5 (\omega_{ii}^\rho + \omega_{jj}^\rho)] \tag{8}$$

for $\rho = \sigma, l$, where ω_{ij}^ρ is a segmental energy for the interaction between the ith and jth components in the ρth phase, z^ρ is the lattice coordination number for the ρth phase and r_i denotes the number of segments in a molecule of the ith component. As $\varphi_i^\rho \to 1$, eqns. 6 and 7 give

$$\lim_{\varphi_s^\rho \to 0} \ln \gamma_s^\rho = \ln \gamma_{s(i)}^\rho = (1 - r_s/r_i) + r_s\chi_{is}^\rho \tag{9}$$

and

$$\lim_{\varphi_i^\rho \to 1} \ln \gamma_i^\rho = 1 \tag{10}$$

for $\rho = \sigma, l$. Combining eqns. 6 and 9, we can write $\ln \gamma_s^\rho$ in a slightly different form

$$\ln \gamma_s^\rho = \sum_{i=1}^{n} \varphi_i^\rho \ln \gamma_{s(i)}^\rho - r_s \sum_{\substack{i,j=1 \\ j>i}}^{n} \chi_{ij}^\rho \varphi_i^\rho \varphi_j^\rho \tag{11}$$

for $\rho = \sigma$, 1, where $\gamma_{s(i)}^\rho$ denotes the activity coefficient of the sth solute in the ith pure solvent.

In the mixed model of solute distribution between two phases

$$r_i\varepsilon_s \neq r_s\varepsilon_i \Rightarrow K_{si} \neq 1 \tag{12a}$$

for $i = 1, 2, ..., n$ and

$$\chi_{si}^\rho \neq 0 \Rightarrow \gamma_s^\rho \neq 1 \tag{12b}$$

for $i = 1, 2, ..., n$ and $\rho = \sigma, l$. Eqn. 12a has been written by assuming that the related entropy effects are negligible; this is true for nearly ideal solutions. Generally, the adsorption term gives a contribution to the distribution coefficient, k_s, if $K_{si} \neq 1$; then, $r_i\varepsilon_s \neq r_s\varepsilon_i$ or $K_{si}^0 \neq 1$, both of these conditions are fulfilled simultaneously.

Displacement model of solute distribution (DS)

When competitive adsorption fully controls solute distribution then k_s is expressed as follows[12]:

$$k_s = K_{si}(\varphi_i^\sigma/\varphi_i^l)^{r_s/r_i} \tag{13}$$

Eqn. 13 may be obtained from eqn. 4, then

$$(\gamma_s^l/\gamma_s^\sigma)\ (\gamma_i^\sigma/\gamma_i^l)^{r_s/r_i} = 1 \tag{14}$$

for $i = 1, 2, ..., n$. It has been shown previously[12] that eqn. 14 is fulfilled when all interaction parameters are equal to zero, *i.e.*

$$\chi_{ij}^\rho = 0 \tag{15}$$

for $i, j = 1, 2, ..., n, s$; $i \neq j$ and $\rho = \sigma, l$. Although for solutions containing molecules of different molecular sizes and satisfying eqn. 15 the activity coefficients differ from unity, their ratio is equal to unity because the terms containing $(r_s/r_n - r_s/r_j)$ cancel[12]. Thus, the solute is distributed according to the displacement model when $K_{si} \neq 1$ and all interaction parameters are equal to zero, but there is no limitation concerning the molecular sizes of the solute and solvent molecules.

Partition model of solute distribution (PS)

Neglecting adsorption effects in solute distribution ($K_{si} = 1$), we obtain[12] from eqn. 4 the very simple expression

$$k_s = \gamma_s^l/\gamma_s^\sigma \tag{16}$$

where γ_s^l and γ_s^σ are defined by eqn. 11. The distribution coefficient, k_s, is now determined by differences in the interaction parameters characterizing the solute–solvent interactions in both phases. When the displacement between the solute and solvent molecules is ignored ($K_{si} = 1$) the following condition is also satisfied:

$$(\varphi_i^\sigma \gamma_i^\sigma)/(\varphi_i^l \gamma_i^l) = 1 \tag{17}$$

Thus, eqn. 17 and $K_{si} = 1$ determine the conditions for the partition model of solute distribution.

MODELS OF SOLVENT DISTRIBUTION

Eqn. 4 and its special cases, eqns, 13 and 16, describe the distribution coefficient for the sth solute but provide no information on how to determine the composition of the surface-influenced stationary phase, which, in general, may contain n solvents. The composition of this phase is established according to the conditions characterizing the thermodynamic equilibrium between the mobile and stationary phases. Similarly, as in the case of solute distribution between the mobile and stationary phases, we can also distinguish three mechanisms of solvent distribution assuring thermodynamic equilibrium between these two phases.

Mixed model of solvent distribution (ME)

Equilibrium between the ith and jth solvents contained in the mobile phase and surface-influenced stationary phase is described by the following general expression[40]

$$K_{ij} = [(\varphi_i^\sigma \gamma_i^\sigma)/(\varphi_i^l \gamma_i^l)]\ [(\varphi_j^l \gamma_j^l)/(\varphi_j^\sigma \gamma_j^\sigma)]^{r_i/r_j} \tag{18}$$

for $i, j = 1, 2, ..., n$ and $i \neq j$. The activity coefficients γ_i^σ and γ_i^l are defined by eqn. 7. Then, both adsorption and non-ideality effects determine this equilibrium, and $K_{ij} \neq 1$ and $\gamma_i^\rho \neq 1$ for $i = 1, 2, ..., n$ and $\rho = \sigma$, l. The surface phase compostion ($\varphi_1^\sigma, \varphi_2^\sigma, ..., \varphi_n^\sigma$) may be evaluated by solving $n-1$ equations defining the equilibrium constants K_{ij}, *e.g.*, for $i = 1, 2, ..., n-1$ and $j = n$, together with eqn. 2.

Displacement model of solvent distribution (DE)

Analogous to the DS model, assuming that the interaction parameters for all solvents are equal to zero, *i.e.*

$$\chi_{ij}^{\sigma} = 0 \tag{19}$$

for $i, j, = 1, 2, ..., n, i \neq j$ and $\rho = \sigma, l$, we have

$$K_{ij} = (\varphi_i^{\sigma}/\varphi_i^{l})\,(\varphi_j^{l}/\varphi_j^{\sigma})^{r_i/r_j} \tag{20}$$

where $K_{ij} \neq 1$ denotes the equilibrium constant characterizing the phase-exchange reaction between molecules of the *i*th and *j*th solvents. In this case, the surface phase composition is determined only by competitive solvent adsorption and may be calculated by solving $n-1$ equations defining the constants K_{ij}, *e.g.*, $i = 1, 2, ..., n-1$ and $j = n$, together with eqn. 2.

Partition model of solvent distribution (PE)

Assuming $K_{ij} = 1$ (no displacement between molecules of the *i*th and *j*th solvents), eqn. 18 gives

$$(\varphi_i^{\sigma}\gamma_i^{\sigma})/(\varphi_j^{l}\gamma_j^{l}) = 1 \tag{21}$$

for $i = 1, 2, ..., n$. In this case the solvent interaction parameters $\chi_{ij}^{\sigma} \neq \chi_{ij}^{l} \neq 0$ for $i, j = 1, 2, ..., n$ and $i \neq j$. The composition of the surface-influenced stationary phase is determined by eqns. 21 and 2.

MODELS OF SOLUTE RETENTION IN LC

The models of solute retention may be formulated by combining the models of solvent distribution (ME, DE and PE) with the models of solute distribution (MS, DS and PS). The first of these lead to expressions defining the composition of the surface-influenced stationary phase, whereas the others define the distribution coefficient, k_s.

The most general expression for solute retention is obtained by combining the models ME and MS; then the LC process is described by eqns. 4 and 18, which were discussed in our previous paper[12]. These equations may be reduced, under special conditions, to the expressions derived by Slaats *et al.*[23] (ideality of the surface phase and its constant composition defined by $\varphi_i^{\sigma} = 1$ and $\varphi_j^{\sigma} = 0$ for $j \neq i$) and Jaroniec *et al.*[20] (identical molecular sizes of all solvents and the surface composition determined according to eqn. 20 for $r_1 = r_2 = ... = r_n$). Jaroniec *et al.*[20] also considered the situation where both phases are non-ideal (all activity coefficients in eqns. 4 and 18 differ from unity) and where there is a constant composition of the surface phase defined as $\varphi_i^{\sigma} = 1$ and $\varphi_j^{\sigma} = 0$ for $i \neq j$ and $j = 1, 2, ..., n$.

The next important models, studied by many workers (see reviews[1–7] and references therein), define pure displacement (DE + DS) and pure partition (PE + PS) in LC with mixed mobile phases. These models were discussed in our previous paper[12] although we did not explicitly consider the process of solvent distribution, which finally determines the composition of the surface phase. It is noteworthy that in the majority of papers dealing with solute retention models the problem of the formation of the surface-influenced stationary phase and its composition is omitted or discussed fragmentarily; *e.g.*, in several papers (see reviews[1,7] and references therein) the surface phase composition is assumed to be independent of changes in the mobile phase composition, *i.e.*, $\varphi_i^\sigma = 1$ and $\varphi_j^\sigma = 0$ for $i \neq j$ and $j = 1, 2, ..., n$.

First, let us consider the pure displacement model (DE + DS); in this case the LC process is described by enqs. 13 and 20. As has been shown previously[12], eqns. 13 and 20 generate several familiar expressions which were proposed elsewhere; *e.g.*, expressions proposed by Jaroniec *et al.*[15,20] (the surface phase composition is determined by eqn. 20 and the molecular sizes of all solvents and the solute are identical, *i.e.*, $r_1 = r_2 = ... = r_n = r_s$), Jaroniec and Martire[18] (molecular sizes of all solvents are identical and they differ from that of the solute; *i.e.*, $r_1 = r_2 = ... = r_n \neq r_s$) and Soczewinski[14] ($r_1 = r_2 = ... = r_n \neq r_s$ and the surface phase composition is defined by $\varphi_i^\sigma = 1$ and $\varphi_j^\sigma = 0$ for $i \neq j$ and $j = 1, 2, ..., n$). Moreover, the relationship proposed by Snyder[13] is also a special case of the model DE + DS because it may be obtained by transforming the expression proposed by Jaroniec *et al.*[15] where both phases are ideal and contain molecules of the solute and solvents of identical dimensions. These special cases of the model DE + DS were discussed in our previous paper[12].

The pure partition model (PE + PS) was also discussed previously[12]. This model is described by eqns. 16 and 21. Martire and Jaroniec[34] showed that the model PE + PS leads to an equation analogous to Ościk's expression[4]. In the case where the solvent interaction parameters $\chi_{ij}^\sigma = \chi_{ij}^l = 0$ $(i, j, = 1, 2, ..., n$ and $i \neq j)$ and solute–solvent interaction parameters $\chi_{si}^\sigma \neq \chi_{si}^l \neq 0$, this equation gives a very simple relationship showing the additivity of $\ln k_{s(i)}$ for $i = 1, 2, ..., n$, where $k_{s(i)}$ is the distribution coefficient of the sth solute in the ith pure solvent. The model PE + PS (pure partition) represents solute retention in liquid–liquid chromatography and RPLC with chemically bonded phases, especially when the solvents are excluded from the bonded phase. However, the model DE + DS (pure displacement) is useful to describe solute retention in liquid–solid chromatography in the normal-phase mode.

For many years it has been difficult to rationalize the applicability of Ościk's equation[7], which is quite similar to the expression derived in terms of the pure partition model, for analysing liquid–solid chromatographic systems that also exhibit adsorption effects. On the basis of our considerations, it can readily be shown that the models DE + PS and ME + PS lead to Ościk's classical equation and its extended form, respectively[35]. According to these models we assume that the adsorption properties of the sth solute and the reference solvent, *e.g.*, solvent 1, are very similar; then the equilibrium constant, $K_{s1} = 1$, and the distribution coefficient, k_s, is defined by eqn. 16. The assumption $K_{s1} = 1$ requires that the equilibrium constants K_{si} and K_{1i} for $i = 2, 3, ..., n$ be identical because $K_{1i} = K_{si}/K_{s1}$, *i.e.*

$$K_{si} = K_{1i} \tag{22}$$

for $i = 2, 3, ..., n$. If the constants $K_{1i} = 1$ for $i = 2, 3, ..., n$, then $K_{si} = 1$ and we can obtain the equations for the pure partition model. However, with $K_{si} = K_{1i} \neq$

1 for $i = 2, 3, ..., n$, the surface phase composition is defined by eqn. 18 (ME model) or eqn. 20 (DE model). The equation for the distribution coefficient, k_s, is obtained from eqns. 16, 6 and 22

$$\ln k_s = \sum_{i=1}^{n} \varphi_i^l \ln(\gamma_{s(i)}^l/\gamma_{s(i)}^\sigma) + \sum_{i=1}^{n-1} (\varphi_i^\sigma - \varphi_i^l) \ln(\gamma_{s(n)}^\sigma/\gamma_{s(i)}^\sigma) + \\ + r_s \left(\sum_{\substack{i,j=1 \\ j>i}}^{n} \chi_{ij}^\sigma \varphi_i^\sigma \varphi_j^\sigma - \sum_{\substack{i,j=1 \\ j>i}}^{n} \chi_{ij}^l \varphi_i^l \varphi_j^l \right) \quad (23)$$

where

$$\ln (\gamma_{s(1)}^l/\gamma_{s(1)}^\sigma) = \ln k_{s(1)} \quad (24)$$

and

$$\ln (\gamma_{s(i)}^l/\gamma_{s(i)}^\sigma) = \ln k_{s(i)} - \ln K_{si} = \ln k_{s(i)} - \ln K_{1i} \quad (25)$$

for $i = 2, 3, ..., n$. Eqn. 23 describes k_s in terms of the model ME + PS. In the case of the model DE + PS the last term in eqn. 23 cancels because the solvent interaction parameters $\chi_{ij}^\sigma = \chi_{ij}^l = 0$. In the case of the pure partition model (PE + PS) the constants $K_{si} = K_{1i} = 1$ for $i = 2, 3, ..., n$ and then eqn. 25 gives a form analogous to eqn. 24; moreover, the surface phase composition is determined by eqn. 21.

Another interesting model of solute retention may be formulated by assuming a mixed model of solute distribution (enq. 4) and a displacement model of solvent distribution (eqn. 20). In this case all the equilibrium constants are different from unity, *i.e.*, $K_{si} \neq 1$ and $K_{ij} \neq 1$ for $i \neq j$ and $i = 1, 2, ..., n$, the solvent interaction parameters $\chi_{ij}^\sigma = \chi_{ij}^l = 0$ for $i \neq$ j and $i, j, = 1, 2, ..., n$ and the solute–solvent interaction parameters $\chi_{si}^\sigma \neq \chi_{si}^l \neq 0$ for $i = 1, 2, ..., n$.

From a theoretical point of view, other combinations of solute and solvent distribution models are yet possible but they are hardly realistic from a physical viewpoint and therefore are not pursued here.

CONCLUSIONS

Defining models of solute and solvent distribution between the mobile phase and surface-influenced stationary phase, we have proposed a simple scheme to formulate solute retention models in terms of combinations of the solute and solvent distribution models. In the general case, which is described by eqns. 4 and 18, we assume a mixed model for the solute and solvent distribution which, under special conditions, generates the majority of specialized equations derived previously to describe solute retention in liquid chromatography.

The advantage of this approach is a clearer explanation of solute retention in terms of classical thermodynamics and the possibility of its extension to take account of the adsorbent heterogeneity, specific solute–solvent and solvent–solvent interactions, etc. For example, the extension of this approach to the LC process on heterogeneous surfaces requires new expressions for the activity coefficients defining non-ideality of the surface solution formed on an heterogeneous solid, or determination of the equilibrium constants for each type of adsorption site[12]. Moreover, the present approach may easily be adapted to chromatographic systems in which some components appear only in the surface phase, *e.g.*, RPLC-CBP[12].

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