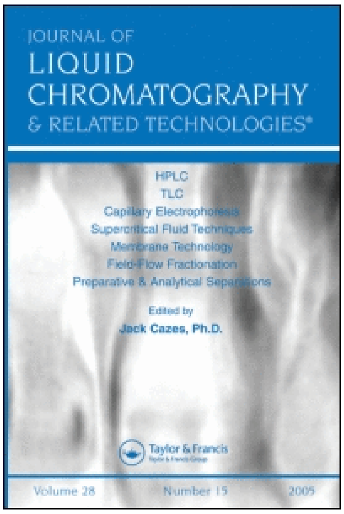

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DESCRIPTION OF NON-SPECIFIC AND SPECIFIC SOLUTE-SOLVENT INTERACTIONS IN LIQUID CHROMATOGRAPHY WITH MIXED ELUENTS

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ABSTRACT

A new description of solute retention in liquid chromatography with mixed eluents is proposed. This description involves non-specific solute-solvent and solvent-solvent interactions in the mobile and surface phases as well as association equilibria occuring in these phases. The general equation derived for the distribution coefficient is discussed with respect to the displacement and partition mechanisms of solute distribution between the mobile and surface phases.

INTRODUCTION

Many attempts have been made to describe solute retention in liquid chromatography (LC) with mixed eluents [see reviews (1-7), papers (8-12) and references therein]. Usually, the

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solute retention models are formulated in terms of classical thermodynamics (1,2) by considering only some factors governing the chromatographic process. Since this process is determined by many factors, such as: the competitive character of solute and solvent adsorption, non-specific and specific solute-solvent and solvent-solvent interactions in the mobile and stationary phases, multilayer nature of the surface phase and its structure involving different orientations of solute and solvent molecules, differences in molecular sizes of solute and solvents, surface and structural heterogeneity of the adsorbents, etc., it is impossible to formulate a simple model of solute retention taking into account all the factors listed above. Up to now, theoretical studies of the LC process have focused on models involving the competitive character of solute and solvent adsorption (2,6,13-15), non-specific (2,7-10,12) and specific (1,16-20) interactions in the mobile and surface phases, and adsorbent heterogeneity (21-24). It follows from these studies that the competitive character of solute and solvent adsorption and solute-solvent and solvent-solvent interactions in both phases play a dominant role in solute retention. While the role of competitive adsorption in the solute retention process is well recognized (2,4,6-10,13), our knowledge about the role of solute-solvent and solvent-solvent interactions in the LC process is less complete. A full description of solute-solvent and solvent-solvent interactions in the LC process is very difficult and leads to complicated equations, which are of limited use for interpreting experimental data.

Several treatments have been proposed to derive equations for the solute distribution coefficient involving non-specific (2,7-10,12) and specific (1,16-20) interactions between solute and solvent molecules in the mobile and surface phases. The non-specific interactions were described in terms of solute and solvent activity coefficients derived from a lattice model of solutions (10,25), as well as in terms of statistical thermodynamics (8,9,26). The specific interactions were represented by suitable quasi-chemical reactions occuring in the mobile and surface phases and leading to formation of solute-solvent and solvent-solvent complexes (associates) (1,16-20). Especially simple equations have been derived for association models assuming formation of 1:1 pure and mixed complexes in the mobile phase (1,18). It follows from these model studies (20) that the assumption of an association model with 1:1 complexes is already sufficient for quantitative estimation of the effects connected with specific solute-solvent and solvent-solvent interactions. This indicates that LC models assuming formation of 1:1 complexes should be useful for evaluating association effects in solute retention. Experimental verification of these models have confirmed their utility for interpreting LC data (27-30).

In previous studies concerning interaction effects in solute retention (1,16-20,27-30), non-specific and specific interaction effects were considered separately. While such an approach is fully acceptable for LC systems with negligible specific interactions, it may be inappropriate in the case of LC systems with specific interactions because these systems also show non-specific (dispersive) interactions. Only in the case of strong specific interactions giving a considerably greater contribution to the total interaction effect than that arising from non-specific interactions, may solute retention models involving association and simultaneously neglecting non-specific interactions be used for approximate estimation of the interaction effects in the LC process. In other cases, solute retention models taking into account the specific interactions in both phases should also involve the non-specific interactions between solute and solvent molecules. This is especially important in the case of models involving solute-solvent specific interactions because it gives a usually smaller contribution to the total interaction effect than that arising from solvent-solvent interactions, e.g., strong association of the polar solvent (27-30). Thus, for systems containing 1:1 solute-solvent complexes the contribution arising from dispersive (non-specific) interactions may also be significant in comparison to the association effect. Accordingly, this work represents an attempt at a simple theoretical description of a solute retention model involving both non-specific and specific solute-solvent interactions.

THEORY

General considerations

Let us consider the s-th solute chromatographed in the eluent (1+2), where 1 and 2 denote solvents. The molecular sizes of solute and solvents are different and r_i denotes the number of segments in a molecule of the i-th component (solute or solvent). The non-specific (dispersive) solute-solvent and solvent-solvent interactions in the mobile and surface (stationary) phases will be described in terms of activity coefficients derived from a lattice model of solutions. The specific interactions will be considered in the mobile phase only. With solid surfaces that interact strongly with adsorbate molecules, e.g., a silica surface, the active centres (e.g., silanol groups of the silica surface) can compete with solute-solvent complexes.

Thus, the stronger interactions of solute and solvent molecules with the active centres of the solid surface should preclude formation of molecular complexes in the surface phase (19). To simplify the theoretical considerations we assume that the only 1:1 solute-solvent associates are formed. As was mentioned in the introduction this association model is sufficient (20) to represent the specific solute-solvent interactions in the mobile phase.

According to the above assumptions, the mobile phase contains single molecules of the s-th solute, first and second solvents, and mixed associates consisting of one solute molecule and one molecule of the first solvent. However, the surface phase contains only single molecules of solute and solvents.

Description of non-specific interactions in both phases

From a molecular viewpoint the mobile phase may be considered as a four-component solution containing single molecules of the s-th solute, first and second solvents (three components) and 1:1 solute-solvent complexes (associates) (fourth component). The subscript a is reserved to denote quantities referring to the solute-solvent associates composed of one molecule of the s-th solute and one molecule of the first solvent. Thus, each associate in question has $r_a = r_1+r_s$ segments, where r_s and r_1 denote the numbers of segments in molecules of the s-th solute and first solvent, respectively. Taking into account the considerations presented in the previous papers (10,25), we can express the activity coefficients γ_s^ℓ , γ_1^ℓ , γ_2^ℓ and γ_a^ℓ referring to infinitely low concentration of the solute (then the concentration of the complexes is also infinitely low because they contain solute molecules), as follows:

$$\ell n\ \gamma_s^\ell = (1 - r_s/r_1)\phi_1^\ell + (1 - r_s/r_2)\phi_2^\ell + r_s(\chi_{1s}^\ell\phi_1^\ell + \chi_{2s}^\ell\phi_2^\ell) - r_s\chi_{12}^\ell\phi_1^\ell\phi_2^\ell \quad (1)$$

$$\ell n\ \gamma_a^\ell = (1 - r_a/r_1)\phi_1^\ell + (1 - r_a/r_2)\phi_2^\ell + r_a(\chi_{1a}^\ell\phi_1^\ell + \chi_{2a}^\ell\phi_2^\ell) - r_a\chi_{12}^\ell\phi_1^\ell\phi_2^\ell \quad (2)$$

$$\ell n\ \gamma_1^\ell = (1 - r_1/r_2)\phi_2^\ell + r_1\chi_{12}^\ell\phi_2^\ell(1 - \phi_1^\ell) \quad (3)$$

$$\ell n\ \gamma_2^\ell = (1 - r_2/r_1)\phi_1^\ell + r_2\chi_{12}^\ell\phi_1^\ell(1 - \phi_2^\ell) \quad (4)$$

where ϕ_i^ℓ is the volume fraction of the i-th component (i = s,a,1,2) in the mobile phase, and χ_{ij}^ℓ is the interaction parameter defined by:

$$\chi_{ij}^\ell = (z^\ell/k_BT)[\omega_{ij}^\ell - 0.5(\omega_{ii}^\ell + \omega_{jj}^\ell)]; \quad \chi_{ij}^\ell = \chi_{ji}^\ell \text{ and } i \neq j \quad (5)$$

The symbol ω_{ij}^ℓ denotes the non-specific interaction energy between two segments of the i-th and j-th molecules in the mobile phase, z^ℓ is the lattice coordination number in the mobile phase, and the superscript ℓ denotes the mobile phase. Equations 1-4 define the activity coefficients for solute, solvents and associates by assuming random mixing of molecules in the mobile phase. Although the assumption of association equilibria in this phase perturbs this random mixing, this perturbation is negligible because we assumed only formation of 1:1 solute-solvent complexes, the concentration of which is determined by infinitely low solute concentration. [However, for models assuming solvent-solvent association this perturbation may be significant and the equations should contain corrections for non-random mixing of molecules (31)].

Equation 2 contains the interaction parameters χ_{1a}^{ℓ} and χ_{2a}^{ℓ}. These parameters may be expressed by means of χ_{1s}^{ℓ}, χ_{2s}^{ℓ} and χ_{12}^{ℓ}. To derive the suitable relationships, let us define the interaction energies ω_{aa}^{ℓ}, ω_{as}^{ℓ}, ω_{1a}^{ℓ} and ω_{2a}^{ℓ}; they are (31):

$$\omega_{aa}^{\ell} = f_1^{\,2}\omega_{11}^{\ell} + 2\,f_1 f_s \omega_{1s}^{\ell} + f_s^{\,2}\omega_{ss}^{\ell} \tag{6}$$

$$\omega_{as}^{\ell} = f_s \omega_{ss}^{\ell} + f_1 \omega_{1s}^{\ell} \tag{7}$$

$$\omega_{1a}^{\ell} = f_s \omega_{1s}^{\ell} + f_1 \omega_{11}^{\ell} \tag{8}$$

$$\omega_{2a}^{\ell} = f_s \omega_{2s}^{\ell} + f_1 \omega_{12}^{\ell} \tag{9}$$

where

$$f_1 + f_s = 1 \tag{10}$$

and

$$f_1 = r_1/r_a = r_1/(r_1 + r_s)\ ; \quad f_s = r_s/r_a = r_s/(r_1 + r_s) \tag{11}$$

Taking into account the definition of χ_{ij}^{ℓ} and equations 6-11 we have:

$$\chi_{1a}^{\ell} = f_s^{\,2}\chi_{1s}^{\ell} \tag{12}$$

$$\chi_{2a}^{\ell} = f_s \chi_{2s}^{\ell} + f_1 \chi_{12}^{\ell} - f_1 f_s \chi_{1s}^{\ell} \tag{13}$$

Thus, the parameters χ_{1a}^{ℓ} and χ_{2a}^{ℓ} appearing in equation 2 may be replaced by equations 12 and 13, respectively. Then, equation 2 may be rewritten as follows:

$$\ell n\ \gamma_a^{\ell} = \ell n\ \gamma_s^{\ell} + \ell n\ \gamma_1^{\ell} - 1 - f_1 r_s \chi_{1s}^{\ell} \tag{14}$$

or

$$\gamma_a^{\ell} = \gamma_s^{\ell}\gamma_1^{\ell}/A^{\ell} \tag{15}$$

where

$$A^{\ell} = \exp[1 + r_1 r_s \chi_{1s}^{\ell}/(r_1+r_s)] \tag{16}$$

The surface activity coefficients will be presented only for solute and solvents, because according to our earlier assumption the surface phase does not contain associates. They are expressed by analogous equations to those defining the bulk activity coefficients:

$$\ell n\ \gamma_s^{\sigma} = (1 - r_s/r_1)\phi_1^{\sigma} + (1 - r_s/r_2)\phi_2^{\sigma} + r_s(\chi_{1s}^{\sigma}\phi_1^{\sigma} + \chi_{2s}^{\sigma}\phi_2^{\sigma}) - r_s\chi_{12}^{\sigma}\phi_1^{\sigma}\phi_2^{\sigma} \tag{17}$$

$$\ell n\ \gamma_1^{\sigma} = (1 - r_1/r_2)\phi_2^{\sigma} + r_1\chi_{12}^{\sigma}\phi_2^{\sigma}(1 - \phi_1^{\sigma}) \tag{18}$$

$$\ell n\ \gamma_2^{\sigma} = (1 - r_2/r_1)\phi_1^{\sigma} + r_2\chi_{12}^{\sigma}\phi_1^{\sigma}(1 - \phi_2^{\sigma}) \tag{19}$$

where

$$\chi_{ij}^{\sigma} = (z^{\sigma}/k_B T)[\omega_{ij}^{\sigma} - 0.5(\omega_{ii}^{\sigma} + \omega_{jj}^{\sigma})] \ ; \ \chi_{ij}^{\sigma} = \chi_{ji}^{\sigma} \text{ and } i \neq j \tag{20}$$

The superscript σ refers to the surface (stationary) phase.

Description of solute-solvent specific interactions in the mobile phase

The solute-solvent specific interactions in the mobile phase may be represented by the following quasi-chemical reaction (1):

$$(s)^{\ell} + (1)^{\ell} \rightleftarrows (s1)^{\ell} \tag{21}$$

The equilibrium constant relating to this reaction is defined as follows:

$$C^{\ell} = [\phi_a^{\ell}/(\phi_1^{\ell}\phi_s^{\ell})][\gamma_a^{\ell}/(\gamma_1^{\ell}\gamma_s^{\ell})] \tag{22}$$

where ϕ_a^ℓ denotes the volume fraction of the associates formed according to the reaction 21 , and the activity coefficients γ_a^ℓ, γ_1^ℓ and γ_s^ℓ are defined by equations 14, 3 and 1, respectively.

Description of solute distribution between the mobile and stationary phases

The solute can transfer from the mobile phase to the stationary phase according to the displacement or partition models, which are described elsewhere (10). This transfer may occur through distribution of single solute molecules and 1:1 solute-solvent complexes between both phases. Since, the solute-solvent complexes interact weakly with the solid surface in comparison to the single solute molecules and their molecular sizes are greater than the solute molecular size, we assume that the solute distribution between both phases is due only to single solute molecules. These energetic and sterical factors favor such a solute distribution mechanism.

In general, the equation describing the distribution mechanism of single solute molecules between two phases may be written as follows (10):

$$K_{s1} = [(\phi_s^\sigma/\phi_s^\ell)(\phi_1^\ell/\phi_1^\sigma)^{r_s/r_1}][(\gamma_s^\sigma/\gamma_s^\ell)(\gamma_1^\ell/\gamma_1^\sigma)^{r_s/r_1}] \qquad (23)$$

where K_{s1} denotes the thermodynamic equilibrium constant connected with the difference of adsorption energies of the solute and first solvent, and the bulk and surface activity coefficients of the s-th solute and first solvent are given by equations 1,3,17,18.

Evaluation of the surface phase composition

The surface (stationary) phase contains molecules of solute and solvents, i.e.,

$$\phi_1^\sigma + \phi_2^\sigma + \phi_s^\sigma = 1 \tag{24}$$

Since, the solute concentration is infinitely low ($\phi_s^\sigma \rightarrow 0$) we have:

$$\phi_1^\sigma + \phi_2^\sigma \simeq 1 \tag{25}$$

The surface phase composition may be described by an equation analogous to equation 23; it is

$$K_{12} = [(\phi_1^\sigma/\phi_1^\ell)(\phi_2^\ell/\phi_2^\sigma)^{r_1/r_2}][(\gamma_1^\sigma/\gamma_1^\ell)(\gamma_2^\ell/\gamma_2^\sigma)^{r_1/r_2}] \tag{26}$$

where K_{12} denotes the thermodynamic equilibrium constant connected with the difference of adsorption energies of the 1-st and 2-nd solvents, and the bulk and surface activity coefficients of these solvents in both phases are given by equations 3,4,18 and 19.

General expression describing solute retention

First, we calculate the total volume fractions of solute in the mobile and stationary phases (denoted by subscript o); they are:

$$\phi_{o,s}^\ell = \phi_s^\ell + \phi_a^\ell \tag{27}$$

$$\phi_{o,s}^\sigma = \phi_s^\sigma \tag{28}$$

Thus, the distribution coefficient k_s is given by:

$$k_s = \phi_{o,s}^\sigma/\phi_{o,s}^\ell \tag{29}$$

Equations 27 and 22 give:

$$\phi_{o,s}^\ell = \phi_s^\ell(1 + C^\ell\phi_1^\ell\gamma_1^\ell\gamma_s^\ell/\gamma_a^\ell) \tag{30}$$

Combining equations 29, 30 and 23 we have:

$$k_s = K_{s1}\ (\gamma_s^\ell/\gamma_s^\sigma)[(\phi_1^\sigma\gamma_1^\sigma)/(\phi_1^\ell\gamma_1^\ell)]^{r_s/r_1}(1 + C^\ell\phi_1^\ell\gamma_1^\ell\gamma_s^\ell/\gamma_a^\ell)^{-1} \qquad (31)$$

Equation 31 may be considerably simplified by application of equation 15 to express the ratio $\gamma_1^\ell\gamma_s^\ell/\gamma_a^\ell$:

$$k_s = K_{s1}\ (\gamma_s^\ell/\gamma_s^\sigma)[(\phi_1^\sigma\gamma_1^\sigma)/(\phi_1^\ell\gamma_1^\ell)]^{r_s/r_1}(1 + C^\ell A^\ell\phi_1^\ell)^{-1} \qquad (32)$$

Equation 32 describes the distribution coefficient in terms of the assumed chromatographic model. This equation indicates that one must take into account the non-specific interactions in the mobile phase to extract a meaningful equilibrium constant for association (C^ℓ). The volume fraction ϕ_1^σ determining the surface phase composition may be evaluated according to equation 26. The distribution coefficients $k_{s(1)}$ and $k_{s(2)}$ refer to pure solvents 1 and 2, respectively; they are:

$$k_{s(1)} = K_{s1}\ [\gamma^\ell_{s(1)}/\gamma^\sigma_{s(1)}]\ (1 + C^\ell\gamma^\ell_{s(1)}/\gamma^\ell_{a(1)})^{-1} \qquad (33)$$

where for $\phi_2^\ell = \phi_2^\sigma = 0$ we have:

$$\ln\ \gamma^\rho_{s(1)} = 1 - r_s/r_1 + r_s\chi^\rho_{1s} \quad \text{for } \rho = \sigma,\ \ell \qquad (34)$$

$$\ln\ \gamma^\ell_{a(1)} = 1 - r_a/r_1 + r_a\chi^\ell_{1a} = -r_s/r_1 + r_s f_s\chi^\ell_{1s} \qquad (35)$$

$$\ln\ \gamma^\rho_{1(1)} = 1 \quad \text{for } \rho = \sigma,\ \ell \qquad (36)$$

Similarly

$$k_{s(2)} = K_{s1}\ [\gamma^\ell_{s(2)}/\gamma^\sigma_{s(2)}]\ [\gamma^\sigma_{1(2)}/\gamma^\ell_{1(2)}]^{r_s/r_1} \qquad (37)$$

where

$$\ln\ \gamma^\rho_{s(2)} = 1 - r_s/r_2 + r_s\chi^\rho_{2s} \quad \text{for } \rho = \sigma,\ \ell \qquad (38)$$

$$\ln\ \gamma^\rho_{1(2)} = 1 - r_1/r_2 + r_1\chi^\rho_{12} \quad \text{for } \rho = \sigma,\ \ell \qquad (39)$$

In the above, $\gamma^{\rho}_{s(1)}$ and $\gamma^{\rho}_{a(1)}$ ($\rho = \sigma, \ell$) denote the activity coefficients γ^{ρ}_{s} and γ^{ρ}_{a} as $\phi^{\rho}_{1} \to 1$; similarly, $\gamma^{\rho}_{s(2)}$ and $\gamma^{\rho}_{1(2)}$ ($\rho = \sigma, \ell$) denote the activity coefficients γ^{ρ}_{s} and γ^{ρ}_{1} as $\phi^{\rho}_{2} \to 1$.

Special cases of equation 31

Now, we consider the special cases of equation 31. If we neglect association in the mobile phase ($C^{\ell} = 0$) equation 31 reduces to the expression discussed in a previous paper (10); it is

$$k_s = K_{s1} \, (\gamma^{\ell}_{s}/\gamma^{\sigma}_{s})[(\phi^{\sigma}_{1}\gamma^{\sigma}_{1})/(\phi^{\ell}_{1}\gamma^{\ell}_{1})]^{r_s/r_1} \tag{40}$$

Then, the surface phase composition is determined according to equation 26.

For the pure displacement model (all interaction parameters are equal to zero) (10), equation 31 reduces to the following form:

$$k_s = K_{s1} \, (\phi^{\sigma}_{1}/\phi^{\ell}_{1})^{r_s/r_1} \, (1 + C^{\ell}\phi^{\ell}_{1})^{-1} \tag{41}$$

where the surface phase composition is defined by the following expression:

$$K_{12} = (\phi^{\sigma}_{1}/\phi^{\ell}_{1})(\phi^{\ell}_{2}/\phi^{\sigma}_{2})^{r_1/r_2} \tag{42}$$

If we assume identical molecular sizes of both solvents ($r_1 = r_2$), then

$$\phi^{\sigma}_{1} = K_{12}\phi^{\ell}_{1}/(\phi^{\ell}_{2} + K_{12}\phi^{\ell}_{1}) \tag{43}$$

An analogous expression to equation 41, but written in terms of the mole fractions, is discussed elsewhere (1,19).

In the case of pure partition model discussed in Ref.(10), equation 31 gives:

$$k_s = (\gamma^{\ell}_{s}/\gamma^{\sigma}_{s})(1 + C^{\ell} \, \phi^{\ell}_{1}\gamma^{\ell}_{1}\gamma^{\ell}_{s}/\gamma^{\ell}_{a})^{-1} \tag{44}$$

Combining this equation with equation 15 we have:

$$k_s = (\gamma_s^{\ell}/\gamma_s^{\sigma})(1 + A^{\ell}C^{\ell}\ \phi_1^{\ell})^{-1} \tag{45}$$

In this case the surface phase composition is determined by:

$$(\phi_i^{\sigma}\gamma_i^{\sigma})/(\phi_i^{\ell}\gamma_i^{\ell}) = 1 \text{ for } i = 1,2 \tag{46}$$

and

$$\phi_1^{\rho} + \phi_2^{\rho} = 1 \quad \text{for } \rho = \sigma,\ \ell. \tag{47}$$

Equation 45 is considerably simpler than equation 32 and may be useful for describing the data measured by reversed-phase liquid chromatography.

According to treatments presented elsewhere (32,33) we can consider a mixed model of solute retention; then the solute distribution may be described by equation 45 (partition mechanism for solute distribution) and the surface phase composition may be determined by equation 42 (solvent interaction parameters are equal to zero). Thus, the competitive solvent adsorption is assumed to establish the equilibrium composition of the surface phase. The surface phase composition for a nonideal solvent mixture may be determined by equation 26. When the solute-solvent association is neglected ($C^{\ell} = 0$), equation 45 reduces to a previously discussed equation (32,33):

$$k_s = \gamma_s^{\ell}/\gamma_s^{\sigma} \tag{48}$$

and the surface phase composition is determined by equations 26 or 42. For the pure partition model without association in both phases equation 48 should be used together with equation 46 describing the surface phase composition.

Determination of the surface phase composition from excess adsorption data

The volume fraction ϕ_1^σ appearing in equations defining the distribution coefficient k_s may be evaluated from the excess adsorption data measured for the system: binary eluent + adsorbent (14,24,34). The experimentally measurable adsorption excess is defined as follows:

$$n_1^e = n^\sigma(x_1^\sigma - x_1^\ell) \tag{49}$$

where

$$n^\sigma = n_{o,1}^\sigma/[r + x_1^\sigma(1-r)] \tag{50}$$

and

$$r = r_1/r_2 \tag{51}$$

In the above, x_1^ρ is the mole fraction of the first solvent in the ρ-th phase ($\rho = \sigma, \ell$); $n_{o,1}^\sigma$ is the surface phase capacity with respect to the pure component 1. Since

$$x_1^\rho = r\phi_1^\rho/(r\phi_1^\rho - \phi_1^\rho + 1) \text{ for } \rho = \sigma, \ell \tag{52}$$

we can express the volume fraction ϕ_1^σ by means of n_1^e as follows:

$$\phi_1^\sigma = n_1^e(r\phi_1^\ell + 1 - \phi_1^\ell)/n_{o,1}^\sigma + \phi_1^\ell \tag{53}$$

Thus, equation 49 may be utilized to evaluate the volume fraction ϕ_1^σ appearing in equations defining the distribution coefficient k_s. This equation assumes a simple form for $r_1 = r_2$ (then $r = 1$; identical molecular sizes of solvents); it is

$$x_1^\sigma = n_1^e/n^\sigma + x_1^\ell \tag{54}$$

and

$$n^{\sigma} = n^{\sigma}_{o,1} = n^{\sigma}_{o,2} \tag{55}$$

Equation 54 has been obtained from equation 53; for r = 1 the volume fractions are identical to the mole fractions. Determination of the parameters $n^{\sigma}_{o,1}$ or n^{σ}, needed to evaluate ϕ^{σ}_{1}, is described in the literature dealing with adsorption from solutions (35,36). In general, these quantities may be determined from the excess adsorption data as well as from the single-vapor adsorption data (36).

Solute retention model with association in the surface phase

Association effects in the stationary phase are generally weaker than those in the mobile phase but they may be significant in chromatographic systems in which the solute-adsorbent interactions are comparable to the solute-solvent interactions, e.g., reversed-phase liquid chromatography. If we assume formation of 1:1 solute-solvent complexes in the stationary phase, then we should write an additional equation for γ^{σ}_{a} ; it is

$$\begin{aligned}\ell n\ \gamma^{\sigma}_{a} = {} & (1 - r_a/r_1)\phi^{\sigma}_{1} + (1 - r_a/r_2)\phi^{\sigma}_{2} + r_a(\chi^{\sigma}_{1a}\phi^{\sigma}_{1} + \chi^{\sigma}_{2a}\phi^{\sigma}_{2}) \\ & - r_a\chi^{\sigma}_{12}\phi^{\sigma}_{1}\phi^{\sigma}_{2}\end{aligned} \tag{56}$$

or

$$\ell n\ \gamma^{\sigma}_{a} = \ell n\ \gamma^{\sigma}_{s} + \ell n\ \gamma^{\sigma}_{1} - 1 - f_1 r_s \chi^{\sigma}_{1s} \tag{57}$$

where

$$\chi^{\sigma}_{1a} = f_s^{2}\chi^{\sigma}_{1s} \tag{58}$$

$$\chi^{\sigma}_{2a} = f_s\chi^{\sigma}_{2s} + f_1\chi^{\sigma}_{12} + f_s f_1\chi^{\sigma}_{1s} \tag{59}$$

Similarly as in the mobile phase, the equilibrium constant describing association in the surface phase is equal to:

$$C^{\sigma} = [\phi_a^{\sigma}/(\phi_1^{\sigma}\phi_s^{\sigma})][\gamma_a^{\sigma}/(\gamma_1^{\sigma}\gamma_s^{\sigma})] \tag{60}$$

where ϕ_a^{σ} denotes the volume fraction of 1:1 solute-solvent complexes in the surface phase. Thus, the total volume fraction $\phi_{o,s}^{\sigma}$ is:

$$\phi_{o,s}^{\sigma} = \phi_s^{\sigma}(1 + C^{\sigma}\ \phi_1^{\sigma}\gamma_s^{\sigma}\gamma_1^{\sigma}/\gamma_a^{\sigma}) \tag{61}$$

Equations 29, 30, 23 and 61 give:

$$k_s = K_{s1}\ (\gamma_s^{\ell}/\gamma_s^{\sigma}) \left(\frac{\phi_1^{\sigma}\ \gamma_1^{\sigma}}{\phi_1^{\ell}\ \gamma_1^{\ell}}\right)^{r_s/r_1} \left(\frac{1 + C^{\sigma}\phi_1^{\sigma}\gamma_1^{\sigma}\gamma_s^{\sigma}/\gamma_a^{\sigma}}{1 + C^{\ell}\phi_1^{\ell}\gamma_1^{\ell}\gamma_s^{\ell}/\gamma_a^{\ell}}\right) \tag{62}$$

Equation 62 may be rewritten as follows:

$$k_s = K_{s1}\ (\gamma_s^{\ell}/\gamma_s^{\sigma})\ [(\phi_1^{\sigma}\gamma_1^{\sigma})/(\phi_1^{\ell}\gamma_1^{\ell})]^{r_s/r_1}\ [(1+A^{\sigma}C^{\sigma}\phi_1^{\sigma})/(1+A^{\ell}C^{\ell}\phi_1^{\ell})] \tag{63}$$

where

$$A^{\sigma} = \exp\ [1 + r_1r_s\chi_{1s}^{\sigma}/(r_1+r_s)] \tag{64}$$

and γ_1^{ℓ} , γ_1^{σ} are defined by equations 3 and 18, respectively; the surface phase composition is defined by equation 26. Similarly as in the case of equation 32, a meaningful extraction of the equilibrium constants C^{ℓ} and C^{σ} requires taking into account the non-specific interactions in the mobile and surface phases. It is readily seen that for $C^{\sigma} = 0$ (no association in the surface phase), equation 63 becomes equation 32 describing the solute retention model with 1:1 solute-solvent complexes in the mobile phase.

CONCLUDING REMARKS

Our previous description of the LC process (10) gives a general equation for the distribution coefficient, which involves competitive solute and solvent adsorption as well as non-specific solute-solvent and solvent-solvent interactions in both phases. In the present paper this approach has been extended to a solute retention model involving additionally simple association equilibria in the mobile and surface phases. Of course, these considerations may be easily extended to the solute retention models involving more complex association equilibria in both phases but the final equations are even more complicated and of limited use for practical applications.

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