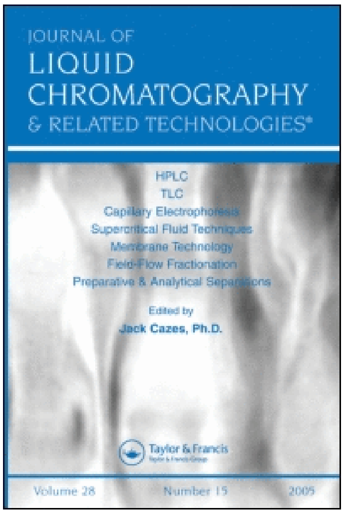

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Surface Heterogeneity Effects in Liquid-Solid Chromatography with Mixed Eluents

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SURFACE HETEROGENEITY EFFECTS IN LIQUID-SOLID CHROMATOGRAPHY WITH MIXED ELUENTS

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ABSTRACT

Equations **describing** liquid-solid chromatography (LSC) systems with ideal surface and bulk phases and heterogeneous adsorbents are derived and discussed. It is shown that for a mixed surface phase formed on a heterogeneous solid surface the dependence of ln k_s on ln x_1^{ℓ} is linear for higher concentrations of the first solvent and its slope is a function of the ratio of molecular sizes of solute and solvents, heterogeneity parameters and equilibrium constants describing phase exchange between solute and solvent molecules. However, for complete coverage of the surface by molecules of the first solvent this linear dependence becomes the Snyder-Soczewiński relationship, in which the slope depends solely on the ratio of molecular sizes of the solute and solvents. These results and an analysis presented herein also demonstrate that a recently proposed interpretation of the Snyder-Soczewiński equation in incorrect.

INTRODUCTION

Energetic heterogeneity of the adsorbent surface plays an important role in liquid-solid (adsorption) chromatography (LSC) with mixed eluents. The effect of surface heterogeneity on LSC retention behavior has been examined in some detail for chromatographic systems containing

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solute and solvent molecules of spherical (1-4) and non-spherical (5,6) shapes. The earliest and simplest description of this problem provides us with the following expression (7-9):

$$k_s = \sum_{q=1}^{Q} f_q \, k_{s,q} \qquad (1)$$

where k_s is the distribution coefficient of the s-th solute referring to the entire heterogeneous surface, $k_{s,q}$ is the distribution coefficient of this solute on the q-th type of adsorption site , Q is the total number of all types of adsorption sites, and f_q is the fraction of the q-th type of adsorption site, subject to the normalization condition:

$$\sum_{q=1}^{Q} f_q = 1 \qquad (2)$$

Equation 1, which is strictly valid only for spherical solute and solvent molecules, has been utilized by Jaroniec et al. (1,2,8) to derive an approximate expression describing the dependence of the distribution coefficient on mobile phase composition for heterogeneous surfaces characterized by a quasi-Gaussian energy distribution.

In spite of the many studies of the role of surface heterogeneity in the LSC process (1-9), this problem requires further elaboration. In particular, there remain unresolved points concerning the influence of this heterogeneity on the dependence of the distribution coefficient upon mobile phase composition.

In this paper surface heterogeneity effects in LSC with mixed mobile phases are discussed in terms of the simple displacement model (7-9). For present purposes, our treatment is limited to chromatographic systems containing only spherical solute and solvent molecules, and ideal stationary (surface) and mobile (bulk) phases. Although, in this case, description of heterogeneity effects would seem to be straightforward, there is apparent conflict concerning the answer to the following question: Is the slope of the Snyder-Soczewiński linear relationship dependent on surface heterogeneity? The popular use of this relationship by practicing chromatographers impels us to resolve this issue.

FUNDAMENTAL EQUATION FOR AN IDEAL DISPLACEMENT MODEL OF LSC

Let us consider a chromatographic system with ideal stationary and mobile phases and containing only spherical solute and solvent molecules. The adsorbent surface is assumed to be heterogeneous. Moreover, let us assume that molecular areas occupied by molecules of different solvents on the solid surface are identical. Let ω denote the area for one isolated solvent molecule and ω_s the area for a molecule of the s-th solute. The ratio of ω_s and ω is denoted by r.

The competitive solute and solvent adsorption process on the q-th type of adsorption site may be represented by the following quasi-chemical reaction (8,9):

$$r\,(1)_q^{\sigma} + (s)^{\ell} \rightleftarrows r\,(1)^{\ell} + (s)_q^{\sigma} \qquad (3)$$

where

$$r = \omega_s/\omega \,. \qquad (4)$$

In the above, $(s)^{\ell}$ and $(1)^{\ell}$ denote molecules of the s-th solute and 1-st solvent in the mobile phase (ℓ), and $(s)_q^{\sigma}$ and $(1)_q^{\sigma}$ denote molecules of the s-th solute and 1-st solvent in the surface phase adsorbed on the q-th type of adsorption site. Writing the equilibrium constant $K_{s1,q}$ for the reaction given by equation 3:

$$K_{s1,q} = (x^{\sigma}_{s,q}/x^{\ell}_{s})(x^{\ell}_{1}/x^{\sigma}_{1,q})^{r} \tag{5}$$

and combining it with the equation defining the distribution coefficient of the s-th solute on the q-th type of adsorption site:

$$k_{s,q} = x^{\sigma}_{s,q}/x^{\ell}_{s} \quad , \tag{6}$$

we have

$$k_{s,q} = K_{s1,q}\,(x^{\sigma}_{1,q}/x^{\ell}_{1})^{r} \quad . \tag{7}$$

In the above, x^{ℓ}_{i} is the mole fraction of the i-th component in the mobile phase, $x^{\sigma}_{i,q}$ denotes the mole fraction of this component referring to the q-th type of adsorption site, and the subscript "i" denotes solute (i=s) or solvent (i=1). The distribution coefficient k_s referring to the entire heterogeneous surface may be obtained by combining equations 1 and 7. This combination gives:

$$k_{s} = (x^{\ell}_{1})^{-r} \sum_{q=1}^{Q} f_{q}\, K_{s1,q}\, (x^{\sigma}_{1,q})^{-r} \tag{8}$$

Equation 8 may be rewritten in a slightly different form containing the distribution coefficient of the s-th solute in the (pure) 1-st solvent $k_{s(1),q}$; the subscript "q" denotes that this coefficient refers to the q-th type of adsorption site. For $x^{\ell}_{s} \to 0$ and $x^{\ell}_{1} \to 1$ the equilibrium constant $K_{s1,q}$ given by equation 5 becomes the distribution coefficient $k_{s(1),q}$, i.e.,

$$k_{s(1),q} = K_{s1,q} \tag{9}$$

Taking into account the above equality in equation 8, we have

$$k_{s} = (x^{\ell}_{1})^{-r} \sum_{q=1}^{Q} f_{q}\, k_{s(1),q}\, (x^{\sigma}_{1,q})^{r} \tag{10}$$

Equation 10 defines the distribution coefficient of the s-th solute in a mixed eluent on heterogeneous surfaces possessing a discrete distribution of adsorption sites. This equation is valid for chromatographic systems where both phases are ideal. (An expression analogous to equation 10 may be obtained for systems with nonideal phases, but then additional assumption about the topography of adsorption sites on the surface is required (8,9).) Note that for $Q=1$, equation 10 gives the expression for a homogeneous surface.

SNYDER-SOCZEWINSKI LINEAR RELATIONSHIP

Let us consider a chromatographic systen in which 1-st solvent is very strongly adsorbed in comparison to other solvents of the mixed eluent. Then, for higher concentrations of 1-st solvent we can assume that the mole fractions $x^{\sigma}_{1,q}$ for $q=1,2,...,Q$ are equal to unity. Under this assumption equation 10 gives:

$$\ln k_s = \ln k_{s(1)} - r \ln x^{\ell}_1 \qquad (11)$$

where

$$k_{s(1)} = \sum_{q=1}^{Q} f_q \, k_{s(1),q} \qquad (12)$$

Equation 11 is known in the chromatographic literature (10) as the Snyder-Soczewiński linear relationship. Equation 11 has been obtained from equation 10 derived rigorously for LSC on heterogeneous surfaces. This derivation shows that the slope r is defined by equation 4 and is clearly independent of parameters characterizing the surface heterogeneity. The above result should be self-evident because surface heterogeneity affects only the mole fraction of the 1-st solvent in the surface phase (see equation 10), which is assumed to be equal to unity. Hence, assumption of complete coverage by molecules of the 1-st solvent in a region of its higher concentrations automatically eliminates the dependence of k_s upon heterogeneity parameters.

(Of course, the assumption $x_1^\sigma = 1$ means that the surface phase contains only molecules of the 1-st solvent and an infinitely small number of solute molecules, enabling us to neglect x_s^σ with respect to x_1^σ.)

Recently, Rudziński et al. (4) discussed the Snyder-Soczewiński linear relationship and obtained the surprising result that its slope also depends on a heterogeneity parameter. Detailed analysis of their work reveals that an inconsistency in their theoretical considerations leads to this incorrect conclusion. They analysed an equation defining adsorption for a binary liquid mixture on a heterogeneous surface (equation 27 in Ref. 4) and considered this equation at an infinitely low concentration of one component (their equations 35 and 36). This case relates to LSC with a one-component mobile phase, whereas the Snyder-Soczewiński relationship describes LSC with mixed mobile phases (8,9). Thus, equation 36 in Ref. 4 ultimately describes the distribution coefficient of the second component in the first pure component. Moreover, at infinitely low concentration of the second component this distribution coefficient assumes an unreasonable value (zero). This is a direct consequence of their applying an unsuitable equation for describing the LSC process, in which the solute concentration is infinitely low. The isotherm equations of adsorption from solution, used to formulate the theory of LSC, should follow the proper Henry's law behavior at low concentrations of the component later considered as the solute. It can be readily shown that equation 27 of Ref. 4 does not fulfill Henry's law at low solute concentrations and therefore predicts the zero value for the solute distribution coefficient in the pure solvent.

Also, equation 36 in Ref. 4, which is valid only for low concentrations of the second component, was combined with equation 32 to obtain equation 37, which, if it were correct, could be used only at low concentrations of the second component, which the authors designate as the more efficient eluting solvent. (Please note that it relates to the first component in our notation; see equation 11) The above discussion indicates that their equation 37 has been derived incorrectly and cannot be considered as or compared to the Snyder-Soczewiński relationship.

PRESENTATION OF CHROMATOGRAPHIC DATA IN $\ln k_s - \ln x_1^\ell$ COORDINATES

LSC data are usually plotted in $\ln k_s - \ln x_1^\ell$ coordinates and interpreted according to the Snyder-Soczewiński model (see equation 11). This model gives a reasonable interpretation for LSC systems with ideal surface and mobile phases and homogeneous adsorbents. However, the experimental dependence of $\ln k_s$ on $\ln x_1^\ell$ is linear only in a limited concentration region and for many systems the slope is found to be smaller than r, the ratio of the molecular sizes of solute and solvents. In other words, the linear dependence of $\ln k_s$ on $\ln x_1^\ell$ is an acceptable relationship for describing LSC data over a limited concentration range, but in the case of LSC systems with nonideal phases and heterogeneous adsorbents its physicochemical interpretation is more complex than that resulting from Snyder-Soczewiński model. This problem is illustrated here for LSC systems with heterogeneous adsorbents. The systems in question may be described by equation 10. The mole fraction $x_{1,q}^\sigma$ describing the absolute adsorption of the 1-st solvent on the q-th type of adsorption site may be represented by the following well-known equation (11,12):

$$x_{1,q}^\sigma = K_{12,q}\, x_1^\ell/(x_2^\ell + K_{12,q}\, x_1^\ell) \qquad (13)$$

where $K_{12,q}$ is the equilibrium constant describing the phase-exchange between molecules of 1-st and 2-nd solvent occuring on the q-th type of adsorption site. This constant is defined as follows:

$$K_{12,q} = \alpha_{12}\exp[(\varepsilon_{1,q} - \varepsilon_{2,q})/(RT)] \qquad (14)$$

where α_{12} is the pre-exponential factor connected with the partition functions of isolated molecules of the 1-st and 2-nd solvents in the surface and bulk phases, respectively, and $\varepsilon_{i,q}$ (i=1,2) is the adsorption energy of the i-th solvent on the q-th type of adsorption site.

The equilibrium constant $K_{si,q}$ is expressed by an equation similar to equation 14; it is

$$K_{si,q} = \alpha_{si}\ \exp[(\varepsilon_{s,q} - r\ \varepsilon_{i,q})/(RT)] \qquad (15)$$

The constant $K_{12,q}$ may be expressed by means of the constants $K_{s1,q}$ and $K_{s2,q}$; then (13)

$$K_{12,q} = 1/K_{21,q} = (K_{s2,q}/K_{s1,q})^{1/r} \qquad (16)$$

where

$$\alpha_{12} = (\alpha_{s2}/\alpha_{s1})^{1/r} \qquad (17)$$

Taking into account equations 9 and 16 in equation 13, we obtain

$$x^{\sigma}_{1,q} = (x^{\ell}_{1}/k^{1/r}_{s(1),q})/[(x^{\ell}_{1}/k^{1/r}_{s(1),q}) + (x^{\ell}_{2}/k^{1/r}_{s(2),q})] \qquad (18)$$

Combination of equations 10 and 18 gives

$$\ln k_{s} = \ln \sum_{q=1}^{Q} f_{q}[(x^{\ell}_{1}/k^{1/r}_{s(1),q}) + (x^{\ell}_{2}/k^{1/r}_{s(2),q})]^{-r} \qquad (19)$$

Expanding $\ln k_s$ into a Taylor's series about the point $\ln x^{\ell}_{1} = 0$ (then $x^{\ell}_{1} = 1$), we have

$$\ln k_s = \ln k_{s(1)} - [(r/k_{s(1)}) \sum_{q=1}^{Q} f_q\, k_{s(1),q}(1 - K_{21,q})] \ln x_1^{\ell} \quad (20)$$

where $k_{s(1)}$ is defined by equation 12, whereas, $K_{21,q}$ is defined by equation 16. The high-order terms appearing in the series 20 have been neglected. Thus, for LSC systems with a heterogeneous adsorbent equation 20 predicts a linear dependence of $\ln k_s$ vs. $\ln x_1^{\ell}$ in the region of $x_1^{\ell} \to 1$ but its slope is dependent on the ratio of molecular sizes of solute and solvents (r), heterogeneity parameters (f_q for $q = 1,2,\ldots,Q$) and the equilibrium constants $K_{21,q}$ and $K_{s1,q}$. It is worth mentioning that equation 20 has been derived for $x_{1,q}^{\sigma}$ smaller than unity. The mole fraction $x_{1,q}^{\sigma}$ expressed by equation 13 approaches unity when $K_{12,q} \gg 0$, i.e., $K_{21,q} \simeq 0$. For $K_{21,q} \simeq 0$ (then $x_{1,q}^{\sigma} \simeq 1$) equation 20 becomes the Snyder-Soczewiński equation 11. Thus, when we assume complete coverage of the surface by molecules of the 1-st solvent (the Snyder-Soczewiński assumption) equation 20 becomes equation 11, in which the slope depends on the parameter r only, as expected.

The second special case of equation 20 may be obtained by assuming q=1 (a homogeneous surface). Then, we have

$$\ln k_s = \ln k_{s(1)} - [r(1 - K_{21})] \ln x_1^{\ell} \quad (21)$$

In this case the slope of the $\ln k_s$ vs. $\ln x_1^{\ell}$ plot depends on r and K_{21}. When K_{21} approaches zero (then $x_1^{\sigma} = 1$), equation 21 also reduces to the Snyder-Soczewiński relation (equation 11), as expected. In general, since the 1-st solvent is the more efficient eluting solvent, K_{21} may be greater than zero (but smaller than unity) and the slope would then be less than r. This is consistent with the observed experimental behavior of many LSC systems.

In summary, it is now clear that for LSC systems with ideal phases and heterogeneous adsorbents, the slope of the linear regime of plots of ln k_s against ln x_1^ℓ for $x_{1,q}^\sigma = 1$ (the Snyder-Soczewiński case) is determined solely by the ratio of the molecular sizes of solute and solvents, r. However, if there exists a mixed composition of the surface phase ($x_{1,q}^\sigma < 1$), this slope then becomes a function of the heterogeneity parameters, the equilibrium constants describing the phase-exchange reactions between solute and solvent molecules, and r.

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