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A GENERAL MODEL OF LIQUID-SOLID CHROMATOGRAPHY WITH MIXED MOBILE PHASES INVOLVING CONCURRENT ADSORPTION AND PARTITION EFFECTS

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SUMMARY

Liquid-solid chromatography (LSC) with mixed mobile phases is discussed in terms of classical thermodynamics. It is shown that a rigorous consideration of solute and solvent competitive adsorption in systems with a non-ideal mobile (bulk) phase and a surface-influenced non-ideal stationary phase leads to a new general equation for the distribution coefficient of a solute involving concurrent adsorption and partition effects. For special sets of parameters this equation reduces to familiar limiting expressions describing either adsorption or partition effects. A detailed discussion is presented for LSC systems with binary phases, in which bulk and surface solutions are assumed to be regular ones.

INTRODUCTION

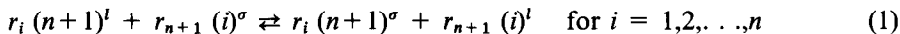
Two limiting models are usually employed to describe the experimental data of liquid-solid chromatography (LSC) with mixed mobile phases. One of them, widely known in the chromatographic literature as the displacement model, was proposed in the 1960's by Snyder¹. According to this model a solute is distributed between a surface phase, usually assumed to be monolayer, and a mobile phase as a result of a competitive solute and solvent adsorption. In adsorption from solutions on solids and similarly in LSC with mixed mobile phases this competitive adsorption is represented by suitable phase-exchange reactions¹⁻⁷. Experimental and theoretical studies of many authors have shown that solute and solvent competitive adsorption plays an important role in the process of solute distribution between the two phases, especially in LSC systems in the normal-phase mode⁴⁻¹⁰. There is a great number of theoretical papers starting with the original displacement model and incorporating additional details such as surface heterogeneity^{11,12}, non-specific interactions in both phases¹³⁻¹⁵, solvation and solvent association in both phases¹⁶⁻¹⁸ and other factors^{19,20}.

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The second limiting model of the LSC process is that assuming distribution of a solute between two phases as a consequence of classical partitioning²¹⁻²⁴. Equations describing partitioning of a solute between a surface-influenced stationary phase and mobile phase are quite analogous to those used in gas-liquid and liquid-liquid chromatography. Ościk²⁵ was the first to derive an equation for LSC with mixed mobile phases, which, as our recent studies have shown^{26,27}, reflects partition effects in the chromatographic process. These effects are dominant in the typical reversed-phase chromatographic systems with chemically bonded phases²¹⁻²³. If the models involving classical partitioning give a good representation of the LSC process in many of the systems in question, there is a great number of systems, in which adsorption and partition phenomena give comparable contributions to the total solute retention. In contrast to the simple approaches describing the above-mentioned limiting models^{6,7,21,24,27}, there is no simple model involving concurrent adsorption and partition effects. Although the unified statistico-thermodynamical description of LSC with mixed mobile phases due to Martire and Boehn^{24,28,29} automatically incorporates the competitive character of solute and solvent adsorption and all contributions from solution nonideality, the final expressions resulting from this description are quite complicated and frequently inconvenient for practical applications. Therefore, in this paper a simple model involving concurrent adsorption and partition effects is proposed and formulated in terms of classical thermodynamics. This formulation makes possible a clear and rigorous definition of adsorption and partition phenomena in LSC with mixed mobile phases and leads to a new general equation describing dependence of the distribution coefficient of a solute upon mobile phase composition. All familiar limiting equations, having rigorous thermodynamical foundations, may be deduced from this general expression.

ADSORPTION FROM MULTICOMPONENT SOLUTIONS ON SOLID SURFACES

This section is devoted to adsorption from multicomponent liquid mixtures on solid surfaces, which is a natural basis to formulate a theory of LSC with mixed mobile phases. Let us consider a $(n + 1)$ -component liquid mixture contacting with a homogeneous solid surface. The liquid mixture contains only nonelectrolytes and its deviation from ideality is described in terms of the activity coefficients. In general, a $(n + 1)$ -component solution contains molecules of different sizes; this means that a molecule of the i -th component contains r_i segments. The adsorption occurs as a consequence of an exchange of the different molecules between two phases, bulk phase and surface phase. The latter phase is assumed to be an autonomous phase, in which molecules lie parallel to the solid surface. The adsorption process may be represented by a series of the following phase-exchange reactions³:



where $(i)^\rho$ denotes a molecule of the i -th component in the ρ -th phase and $\rho = l$ (bulk phase) and σ (surface phase). Although the phase-exchange reaction given by eqn. 1 suggests a monolayer character of adsorption, the recent statistico-thermodynamical studies of Dabrowski *et al.*³⁰ showed that the above reaction may be used to represent the adsorption process for surface phases of greater thickness than the monolayer thickness but showing a special ordering of adsorbed molecules.

The equilibrium constant $K_{n+1,i}^*$ relating to the reaction given by eqn. 1 is defined as follows:

$$K_{n+1,i}^* = (a_{n+1}^\sigma/a_{n+1}^l)^{r_i} (a_i^l/a_i^\sigma)^{r_{n+1}} \quad \text{for } i = 1, 2, \dots, n \quad (2)$$

where

$$K_{n+1,i}^* = \alpha_{n+1,i} \exp[(r_i \varepsilon_{n+1} - r_{n+1} \varepsilon_i)/(k_B T)] \quad \text{for } i = 1, 2, \dots, n \quad (3)$$

In the above, a_i^ρ is the activity of the i -th component in the ρ -th phase, ε_i is the adsorption energy of the i -th component and $\alpha_{n+1,i}$ is the factor connected with partition functions of isolated molecules of the i -th and $(n+1)$ -th components in both phases³. The activity a_i^ρ is defined in a standard way, *i.e.*,

$$a_i^\rho = \varphi_i^\rho \gamma_i^\rho \quad \text{for } i = 1, 2, \dots, n+1 \text{ and } \rho = l, \sigma \quad (4)$$

where φ_i^ρ and γ_i^ρ denote the volume fraction and activity coefficient of the i -th component in the ρ -th phase, respectively, where $\gamma_i^\rho \rightarrow 1$ as $\varphi_i^\rho \rightarrow 1$. According to the theory of regular solutions the activity coefficient γ_i^ρ is expressed as follows:

$$\ln \gamma_i^\rho = \sum_{j=1}^{n+1} (1 - r_i/r_j) \varphi_j^\rho + r_i \sum_{\substack{j=1 \\ j \neq i}}^{n+1} \chi_{ji}^\rho \varphi_j^\rho (1 - \varphi_i^\rho) - r_i \sum_{\substack{j,k=1 \\ j,k \neq i \\ k > j}}^{n+1} \chi_{jk}^\rho \varphi_j^\rho \varphi_k^\rho \quad (5)$$

for $i = 1, 2, \dots, n+1$ and $\rho = l, \sigma$. In the above, the interaction parameter χ_{ij}^ρ is defined by the following equation:

$$\chi_{ij}^\rho = [z^\rho/(k_B T)] [\omega_{ij}^\rho - 0.5(\omega_{ii}^\rho + \omega_{jj}^\rho)] \quad (6)$$

for $ij = 1, 2, \dots, n+1$, $i \neq j$, $\rho = l, \sigma$ and $\chi_{ij}^\rho = \chi_{ji}^\rho$

The symbol ω_{ij}^ρ denotes the interaction energy between two segments of the i -th and j -th molecules in the ρ -th phase, z^ρ is the lattice coordination number in the ρ -th phase. Distinguishing the parameters ω_{ij}^l and ω_{ij}^σ , we assume that the interaction energies in the surface solution are perturbed by the potential field of the adsorbent and as a consequence of this, they differ from those in the bulk solution.

Eqns. 2, 4 and 5 make possible calculation of the volume fractions of all components in the surface phase for a given composition of the bulk phase. In other words, these equations describe adsorption from $(n+1)$ -component regular solutions on a homogeneous solid surface in the whole concentration region.

The equilibrium constant $K_{n+1,i}^*$ may be rewritten in a slightly different form:

$$K_{n+1,i}^* = (K_{n+1,i}^*)^{1/r_i} = (\alpha_{n+1,i})^{1/r_i} \exp[(\varepsilon_{n+1} - r_{n+1} \varepsilon_i/r_i)/(k_B T)] \quad (7)$$

for $i = 1, 2, \dots, n$. Then, eqn. 2 becomes

$$K_{n+1,i} = [(\varphi_{n+1}^\sigma \gamma_{n+1}^\sigma) / (\varphi_{n+1}^l \gamma_{n+1}^l)] [(\varphi_i^l \gamma_i^l) / (\varphi_i^\sigma \gamma_i^\sigma)]^{r_{n+1}/r_i} \quad \text{for } i = 1, 2, \dots, n \quad (8)$$

Eqn. 8 is more convenient to formulate equations describing LSC with mixed mobile phases.

FUNDAMENTAL EQUATIONS DESCRIBING LSC WITH MIXED MOBILE PHASES

Let us consider an adsorption system described by eqns. 5 and 8 but at infinitely low concentration of the $(n + 1)$ -th component (solute), *i.e.*,

$$\varphi_s^\rho \rightarrow 0 \quad \text{for } s = n + 1 \text{ and } \rho = l, \sigma. \quad (9)$$

The subscript “ s ” denotes the $(n + 1)$ -th component at infinitely low concentration in the mobile (bulk) phase, and then its concentration in the surface phase is also infinitely low. The volume fractions of the remaining components (solvents) $1, 2, \dots, n$ fulfill the following condition:

$$\sum_{i=1}^n \varphi_i^\rho = 1 \quad \text{for } \rho = l, \sigma \quad (10)$$

The components $1, 2, \dots, n$ are treated as the solvents. The expression defining the activity coefficient of the s -th solute in the ρ -th phase may be obtained from eqn. 5 replacing in it the volume fraction $\varphi_{n+1}^\rho = \varphi_s^\rho$ by zero; finally we have

$$\ln \tilde{\gamma}_s^\rho = \sum_{i=1}^n (1 - r_s/r_i) \varphi_i^\rho + r_s \sum_{i=1}^n \chi_{is}^\rho \varphi_i^\rho - r_s \sum_{\substack{i,j=1 \\ j>i}}^n \chi_{ij}^\rho \varphi_i^\rho \varphi_j^\rho \quad \text{for } \rho = l, \sigma \quad (11)$$

where

$$\tilde{\gamma}_s^\rho = \lim_{\varphi_s^\rho \rightarrow 0} \gamma_s^\rho \quad \text{for } \rho = l, \sigma \quad (12)$$

It is convenient to express the activity coefficient $\tilde{\gamma}_s^\rho$ by means of the activity coefficients $\tilde{\gamma}_{s(i)}^\rho$ for $i = 1, 2, \dots, n$. The symbol $\tilde{\gamma}_{s(i)}^\rho$ denotes the activity coefficient of the s -th solute in the i -th pure solvent, *i.e.*,

$$\tilde{\gamma}_{s(i)}^\rho = \lim_{\varphi_i^\rho \rightarrow 1} \gamma_s^\rho = \lim_{\varphi_i^\rho \rightarrow 1} \tilde{\gamma}_s^\rho \quad \text{for } i = 1, 2, \dots, n \text{ and } \rho = l, \sigma \quad (13)$$

Eqn. 11 gives the following expression for $\ln \tilde{\gamma}_{s(i)}^\rho$:

$$\ln \tilde{\gamma}_{s(i)}^\rho = (1 - r_s/r_i) + r_s \chi_{is}^\rho \quad \text{for } i = 1, 2, \dots, n \text{ and } \rho = l, \sigma \quad (14)$$

Combination of eqns. 11 and 14 gives

$$\ln \tilde{\gamma}_s^\rho = \sum_{i=1}^n \varphi_i^\rho \ln \tilde{\gamma}_{s(i)}^\rho - r_s \sum_{\substack{i,j=1 \\ j>i}}^n \chi_{ij}^\rho \varphi_i^\rho \varphi_j^\rho \quad \text{for } \rho = l, \sigma \quad (15)$$

The activity coefficients $\tilde{\gamma}_i^\rho$ for $i = 1, 2, \dots, n$ at $\varphi_s^\rho \rightarrow 0$ are expressed as follows:

$$\ln \tilde{\gamma}_i^\rho = \lim_{\varphi_s^\rho \rightarrow 0} \ln \gamma_i^\rho = \sum_{j=1}^n (1 - r_i/r_j) \varphi_j^\rho + r_i \sum_{j=1}^n \chi_{ji}^\rho \varphi_j^\rho (1 - \varphi_i^\rho) - r_i \sum_{\substack{j,k=1 \\ j,k \neq i \\ k>j}}^n \chi_{jk}^\rho \varphi_j^\rho \varphi_k^\rho \quad (16)$$

for $i = 1, 2, \dots, n$ and $\rho = l, \sigma$. For $\varphi_i^\rho \rightarrow 1$ eqn. 16 gives

$$\lim_{\varphi_i^\rho \rightarrow 1} \gamma_i^\rho = \lim_{\varphi_i^\rho \rightarrow 1} \tilde{\gamma}_i^\rho = 1 \quad \text{for } \rho = l, \sigma \quad (17)$$

The distribution coefficients of the s -th solute in a n -component eluent and the i -th pure solvent are defined as follows:

$$k_s = \lim_{\varphi_s^l \rightarrow 0} (\varphi_s^\sigma / \varphi_s^l) \quad (18)$$

$$k_{s(i)} = \lim_{\varphi_i^l \rightarrow 1} (\varphi_s^\sigma / \varphi_s^l) \quad \text{for } i = 1, 2, \dots, n \quad (19)$$

Taking into account eqns. 18, 19 in eqn. 8 we obtain

$$\ln k_s = \ln K_{si} + (r_s/r_i) \ln[(\varphi_i^\sigma \tilde{\gamma}_i^\sigma) / (\varphi_i^l \tilde{\gamma}_i^l)] + \ln(\tilde{\gamma}_s^l / \tilde{\gamma}_s^\sigma) \quad (20)$$

$$\ln k_{s(i)} = \ln K_{si} + \ln(\tilde{\gamma}_{s(i)}^l / \tilde{\gamma}_{s(i)}^\sigma) \quad \text{for } i = 1, 2, \dots, n \text{ and } s = n+1 \quad (21)$$

Combining eqns. 14, 15, 16 and 20 we obtain the general expression defining the dependence of $\ln k_s$ upon mobile phase composition:

$$\begin{aligned} \ln k_s = & \ln K_{si} + (r_s/r_i) \ln(\varphi_i^\sigma / \varphi_i^l) + r_s \sum_{j=1}^n (\chi_{js}^l - \chi_{js}^\sigma) \varphi_j^l + \\ & + r_s \sum_{j=1}^{n-1} (\chi_{ns}^\sigma - \chi_{js}^\sigma) (\varphi_j^\sigma - \varphi_j^l) - r_s \sum_{\substack{j=1 \\ j \neq i}}^n \chi_{ji}^l \varphi_j^l + r_s \sum_{\substack{j=1 \\ j \neq i}}^n \chi_{ji}^\sigma \varphi_j^\sigma \end{aligned} \quad (22)$$

This expression may be rewritten in terms of the distribution coefficients of the s -th solute in the pure solvents forming the mixed eluent. For this purpose we express the term $\ln(\tilde{\gamma}_s^l/\tilde{\gamma}_s^\sigma)$ appearing in eqn. 20 by means of $\ln k_{s(i)}$ for $i = 1, 2, \dots, n$; it is

$$\begin{aligned} \ln(\tilde{\gamma}_s^l/\tilde{\gamma}_s^\sigma) = & \sum_{j=1}^n \varphi_j^l \ln k_{s(j)} - \sum_{j=1}^n \varphi_j^l \ln K_{sj} - \sum_{j=1}^n (\varphi_j^\sigma - \varphi_j^l) \ln \tilde{\gamma}_{s(j)}^\sigma + \\ & + r_s \sum_{\substack{j,k=1 \\ k>j}}^n \chi_{jk}^\sigma \varphi_j^\sigma \varphi_k^\sigma - r_s \sum_{\substack{j,k=1 \\ k>j}}^n \chi_{jk}^l \varphi_j^l \varphi_k^l \end{aligned} \quad (23)$$

Substitution of eqns. 23 and 16 into eqn. 20 gives the general expression for the distribution coefficient of the s -th solute in term the distribution coefficients of this solute in the pure solvents; it is

$$\begin{aligned} \ln k_s = & \sum_{\substack{j=1 \\ j \neq i}}^n (r_s/r_j) \varphi_j^l \ln K_{ji} + (r_s/r_i) \ln (\varphi_i^\sigma/\varphi_i^l) + \sum_{j=1}^n \varphi_j^l \ln k_{s(j)} + \\ & + \sum_{j=1}^{n-1} r_s (\chi_{ns}^\sigma - \chi_{js}^\sigma) (\varphi_j^\sigma - \varphi_j^l) + r_s \sum_{\substack{j=1 \\ j \neq i}}^n \chi_{ji}^\sigma \varphi_j^\sigma - r_s \sum_{\substack{j=1 \\ j \neq i}}^n \chi_{ji}^l \varphi_j^l \end{aligned} \quad (24)$$

where $K_{ii} = 1$ and $\chi_{ji}^\sigma = \chi_{ij}^\sigma$. At this point it is worth noting that eqns. 22 and 24 defining the distribution coefficient of the s -th solute in a n -component eluent are equivalent; the first of them is written in terms of the molecular parameters characterizing regular bulk and surface solutions, whereas the second equation is written in terms of the distribution coefficients of the s -th solute in pure solvents forming the mixed eluent. These equations have been obtained from eqn. 20 by replacing the activity coefficients of the s -th solute and the i -th solvent in both phases by analytical expressions resulting from the model of regular solutions. Thus, eqn. 20 is a fundamental relationship in LSC with mixed eluents.

With special assumptions eqns. 20, 22 and 24 yield equations having rigorous thermodynamical foundations, which have been used up to date in LSC with mixed mobile phases. Before discussing this question we consider definitions of adsorption and partition phenomena in LSC.

ADSORPTION AND PARTITION PHENOMENA IN LSC

Let us return to eqn. 21 defining the distribution coefficient of the s -th solute in the i -th pure solvent. Rewriting this equation in a slightly different form we obtain:

$$k_{s(i)} = K_{si} (\tilde{\gamma}_{s(i)}^l/\tilde{\gamma}_{s(i)}^\sigma) \quad \text{for } i = 1, 2, \dots, n \quad (25)$$

A simple analysis of eqn. 25 shows that distribution of the s -th solute between stationary (surface) and mobile (bulk) phases consisting of the i -th pure solvent is determined by two terms: K_{si} (equilibrium constant describing phase-exchange of solute and solvent molecules) and $(\tilde{\gamma}_{s(i)}^l/\tilde{\gamma}_{s(i)}^\sigma)$ (ratio of the activity coefficients of the s -th solute in the bulk and surface phases). The equilibrium constant K_{si} (eqn. 7) contains the pre-exponential entropy factor involving the difference in partition functions of isolated molecules of the s -th solute and i -th solvent in the bulk solution and surface layer, and an exponential factor containing the difference in adsorption energies of the s -th solute and i -th solvent. This exponential term gives the greatest contribution to the constant K_{si} . For the same entropy factor, adsorption of the s -th solute increases with an increasing difference in adsorption energies of the s -th solute and i -th solvent. This difference of energies mainly determines the distribution of the s -th solute between the two one-component phases occurring as a result of the competitive solute and solvent adsorption process, which is represented by the phase-exchange reaction (eqn. 1). Such a mechanism of distribution of the s -th solute between one-component bulk and surface-influenced stationary phases has been described earlier in terms of the displacement model^{1,4-9}.

The second factor determining the distribution of the s -th solute between surface and bulk phases consisting of the i -th pure solvent is the ratio of the activity coefficients $\tilde{\gamma}_{s(i)}^l/\tilde{\gamma}_{s(i)}^\sigma$. This ratio is different from unity for $\chi_{is}^l \neq \chi_{is}^\sigma$, i.e., when we assume different values of the interchange energies of the s -th solute in the i -th solvent forming the bulk and surface-influenced stationary phases. Thus, differences in the interchange energies characterizing solute-solvent interactions in surface and bulk dilute solutions (s, i) may also affect distribution to the s -th solute between the two phases. Such a mechanism of distribution of the s -th solute between the surface and mobile phases consisting of the i -th solvent is quite analogous to that appearing in gas-liquid and liquid-liquid chromatographic systems and has been already described in terms of the so-called partition model²⁴⁻²⁷.

The above discussion enables us to distinguish three main models of the LSC process. In the case of LSC with a one-component eluent, equations defining these models may be obtained on the basis of eqn. 25. They are:

$$k_{s(i)} = K_{si} = (\alpha_{si})^{1/r_i} \exp[(\varepsilon_s - r_s \varepsilon_i / r_i) / (k_B T)] \quad (26)$$

with the condition

$$\tilde{\gamma}_{s(i)}^l / \tilde{\gamma}_{s(i)}^\sigma = 1; \quad i = 1, 2, \dots, n \quad (27)$$

for the displacement model (DM), and

$$k_{s(i)} = \tilde{\gamma}_{s(i)}^l / \tilde{\gamma}_{s(i)}^\sigma = \exp[r_s (\chi_{is}^l - \chi_{is}^\sigma)] \quad (28)$$

with the condition

$$K_{si} = 1 \text{ for } i = 1, 2, \dots, n \quad (29)$$

for the partition model (PM), and

$$K_{si} \neq 1; \gamma_{s(i)}^l / \tilde{\gamma}_{s(i)}^\sigma \neq 1 \text{ for } i = 1, 2, \dots, n \quad (30)$$

for the mixed model (MM).

Similar equations to eqns. 26–29 may be written for the displacement and partition models of LSC with multicomponent eluents. In this case eqn. 20 gives:

$$\ln k_s = \ln K_{si} + (r_s/r_i) \ln (\varphi_i^\sigma / \varphi_i^l) \quad (31)$$

with the condition

$$\ln[(\tilde{\gamma}_s^l / \tilde{\gamma}_s^\sigma)(\tilde{\gamma}_i^l / \tilde{\gamma}_i^\sigma)^{r_s/r_i}] = 0 \text{ for } i = 1, 2, \dots, n \quad (32)$$

for the displacement model, and

$$\ln k_s = \ln (\tilde{\gamma}_s^l / \tilde{\gamma}_s^\sigma) \quad (33)$$

with the condition

$$K_{ij} = 1 \text{ for } i, j = 1, 2, \dots, n, s \quad (34)$$

for the partition model. Eqns. 31 and 33 defining the distribution coefficient of the s -solute between two multicomponent phases by assuming displacement and partition models, respectively, are well known in the chromatographic literature^{4–8, 24–27}. These equations have been obtained from eqn. 20 by assuming special conditions given by eqns. 32 and 34. Discussion of these conditions in terms of our treatment is both interesting and pertinent because it can reveal the physical limitations of the above models.

Let us consider the condition given by eqn. 32. On the basis of eqns. 14–16 we can write:

$$\begin{aligned} (r_s/r_i) \ln(\tilde{\gamma}_i^l / \tilde{\gamma}_i^\sigma) &= \sum_{j=1}^{n-1} (r_s/r_n - r_s/r_j) (\varphi_j^\sigma - \varphi_j^l) + r_s \sum_{j=1}^n [\chi_{ji}^\sigma (\varphi_j^\sigma)^2 - \chi_{ji}^l (\varphi_j^l)^2] + \\ &+ r_s \sum_{\substack{j,k=1 \\ j,k \neq i \\ k > j}}^n (\chi_{ji}^\sigma + \chi_{ki}^\sigma - \chi_{jk}^\sigma) \varphi_j^\sigma \varphi_k^\sigma - r_s \sum_{\substack{j,k=1 \\ j,k \neq i \\ k > j}}^n (\chi_{ji}^l + \chi_{ki}^l - \chi_{jk}^l) \varphi_j^l \varphi_k^l \end{aligned} \quad (35)$$

and

$$\begin{aligned} \ln(\tilde{\gamma}_s^l / \tilde{\gamma}_s^\sigma) &= - \sum_{j=1}^n (r_s/r_n - r_s/r_j) (\varphi_j^\sigma - \varphi_j^l) + r_s \sum_{j=1}^n (\chi_{js}^l - \chi_{js}^\sigma) \varphi_j^l + \\ &+ r_s \sum_{j=1}^{n-1} (\chi_{ns}^\sigma - \chi_{js}^\sigma) (\varphi_j^\sigma - \varphi_j^l) + r_s \sum_{\substack{j,k=1 \\ k > j}}^n \chi_{jk}^\sigma \varphi_j^\sigma \varphi_k^\sigma - r_s \sum_{\substack{j,k=1 \\ k > j}}^n \chi_{jk}^l \varphi_j^l \varphi_k^l \end{aligned} \quad (36)$$

Comparing eqns. 35 and 36 according to the condition given by eqn. 32 we can see that terms containing $(r_s/r_n - r_s/r_j)$ cancel out. Thus, eqn. 32 is fulfilled if the parameters χ_{ij}^{ρ} are equal zero, *i.e.*,

$$\chi_{ij}^{\rho} = 0 \text{ for } i,j = 1,2,\dots,n,s, i \neq j \text{ and } \rho = l, \sigma \quad (37)$$

Eqn. 37 defines LSC systems with ideal surface and mobile phases.

Now, we consider eqn. 33 describing dependence of $\ln k_s$ upon mobile phase composition according to the partition model of LSC with mixed eluents. This equation is valid when eqn. 34 is fulfilled. The equilibrium constant K_{ij} describing the phase-exchange reaction for molecules of the i -th and j -th components contained in an infinitely dilute solution with respect to the s -th solute, may be expressed as follows:

$$K_{ij} = [(\varphi_i^{\sigma}\tilde{\gamma}_i^{\sigma})/(\varphi_i^l\tilde{\gamma}_i^l)][(\varphi_j^l\tilde{\gamma}_j^l)/(\varphi_j^{\sigma}\tilde{\gamma}_j^{\sigma})]^{r_i/r_j} \quad \text{for } i,j = 1,2,\dots,n,s \quad (38)$$

Since, for the partition model (eqn. 34) the constants $K_{ij} = 1$ for $i,j = 1,2,\dots,n$, (no displacement process between solute and solvent molecules), eqn. 38 gives

$$(\varphi_i^{\sigma}\tilde{\gamma}_i^{\sigma})/(\varphi_i^l\tilde{\gamma}_i^l) = [(\varphi_j^{\sigma}\tilde{\gamma}_j^{\sigma})/(\varphi_j^l\tilde{\gamma}_j^l)]^{r_i/r_j} \quad \text{for } i,j = 1,2,\dots,n,s \quad (39)$$

For different values of r_i eqn. 39 is fulfilled when³¹

$$(\varphi_i^{\sigma}\tilde{\gamma}_i^{\sigma})/(\varphi_i^l\tilde{\gamma}_i^l) = 1 \text{ for } i = 1,2,\dots,n,s \quad (40)$$

It is easy to see that eqn. 40 for $i = s$ associated with the definition of k_s (see eqn. 18) gives eqn. 33. Moreover, eqn. 20 becomes eqn. 33 when $K_{si} = 1$ and eqn. 40 is fulfilled.

Eqns. 31, 32 and 33, 34 define the so-called pure displacement and partition models, respectively. The pure displacement model of LSC assumes identical interactions between solute and solvent molecules (see eqn. 37). Then distribution of solute and solvent molecules between two phases occurs only as a result of the competitive adsorption. However, the pure partition model of LSC assumes no competitive solute and solvent adsorption. In this case the distribution of a solute between the two phases is a result of differences in its activity coefficients in the mobile and surface-influenced stationary phases. Besides the above "pure" models of LSC, eqn. 20 can describe different mixed models involving concurrent adsorption and partition effects, *e.g.*, models assuming competitive adsorption for solute and one solvent or only competitive solvent adsorption, etc. One of the main advantages of eqn. 20 is its general character; this equation coupled with the expressions defining solute and solvent activity coefficients (eqns. 15 and 16) can also generate the most popular equations derived up to date for displacement and partition models of LSC^{6,7,24,29}.

PURE DISPLACEMENT MODEL OF LSC

Eqn. 37 defines the physical condition where only solute and solvent competitive adsorption determines the LSC process. Under this condition the dependence of the distribution coefficient of the s -th solute upon mobile phase composition is given by eqn. 31. This equation may be rewritten in a slightly different form:

$$\ln k_s = \ln k_{s(i)} + v_i \ln (\varphi_i^s / \varphi_i^l) \quad \text{for } v_i = r_s / r_i \text{ and } i = 1, 2, \dots, n \quad (41)$$

In many chromatographic models the eluent is assumed to be a mixture consisting of molecules of identical sizes, then $r_1 = r_2 = \dots = r_n = r$. Hence, the volume fractions of solvents are equivalent to the mole fractions. Taking this into account in eqn. 41, we have

$$\ln k_s = \ln k_{s(i)} + v \ln (x_i^s / x_i^l) \quad \text{for } v = r_s / r \text{ and } i = 1, 2, \dots, n \quad (42)$$

where x_i^s denotes the mole fraction of the i -th solvent in the ρ -th phase. Eqn. 42 has been derived by Jaroniec *et al.*¹³. As $x_i^s \rightarrow 1$ this equation becomes the well-known Snyder–Soczewiński relationship^{4,9}:

$$\ln k_s = \ln k_{s(i)} - v \ln x_i^l \quad (43)$$

A similar relationship to that expressed by eqn. 43 may be obtained from eqn. 41 by assuming $\varphi_i^s \rightarrow 1$:

$$\ln k_s = \ln k_{s(i)} - v \ln \varphi_i^l \quad (44)$$

Eqn. 44 may be used to describe chromatographic data measured for mixed eluents consisting of molecules of different molecular sizes.

An interesting expression may be obtained from eqn. 42 by assuming Everett's equation for x_i^s (refs. 2 and 3):

$$x_i^s = K_{in} x_i^l / \left(x_n^l + \sum_{j=1}^{n-1} K_{jn} x_j^l \right) \quad \text{for } i = 1, 2, \dots, n \quad (45)$$

Eqns. 45 and 42 give

$$k_s = \left\{ \sum_{j=1}^n [x_j^l / (k_{s(j)})^{1/v}] \right\}^{-v} \quad (46)$$

where

$$K_{jn} = [k_{s(n)} / k_{s(j)}]^{1/v} \quad \text{for } j = 1, 2, \dots, n-1 \quad (47)$$

Eqn. 46 has been recently obtained by Borówko³². For $r_s = r$ (identical molecular

sizes of solute and solvent molecules) eqn. 46 becomes the well-known relationship^{28,29,33}:

$$k_s = \left[\sum_{j=1}^n (x_j^l/k_{s(j)}) \right]^{-1} \quad (48)$$

Jaroniec *et al.*³³ showed that eqn. 48 is equivalent to Snyder's fundamental relationship¹:

$$k_s = \sum_{j=1}^n x_j^g k_{s(j)} \quad (49)$$

This problem was also discussed in terms of statistical thermodynamics^{28,29,34}. The equations considered in this section, referring to the pure displacement model, have been discussed in detail in two reviews^{6,7}.

PURE PARTITION MODEL OF LSC

Eqns. 33 and 34 defining the distribution coefficient of the *s*-th solute in terms of the pure partition model, combined with eqn. 23 give:

$$\begin{aligned} \ln k_s = & \sum_{i=1}^n \varphi_i^l \ln k_{s(i)} + \sum_{i=1}^{n-1} [(r_s/r_i - r_s/r_n) + r_s(\chi_{ns}^\sigma - \chi_{is}^\sigma)](\varphi_i^\sigma - \varphi_i^l) + \\ & + r_s \sum_{\substack{i,j=1 \\ j>i}}^n \chi_{ij}^\sigma \varphi_i^\sigma \varphi_j^\sigma - r_s \sum_{\substack{i,j=1 \\ j>i}}^n \chi_{ij}^l \varphi_i^l \varphi_j^l \end{aligned} \quad (50)$$

This equation has been recently derived by Martire and Jaroniec²⁷. Two important special cases may be deduced from this equation. The first case refers to chromatographic systems with nearly ideal eluents containing solvents strongly interacting with solute molecules. Under these assumptions eqn. 50 reduces to Ościk's relationship^{6,25}:

$$\ln k_s = \sum_{i=1}^n \varphi_i^l \ln k_{s(i)} + \sum_{i=1}^{n-1} (\varphi_i^\sigma - \varphi_i^l) \ln \kappa_{s(i)n}^\sigma \quad (51)$$

where

$$\ln \kappa_{s(i)n}^\sigma = (r_s/r_i - r_s/r_n) + r_s (\chi_{ns}^\sigma - \chi_{is}^\sigma) \quad (52)$$

For chromatographic systems showing ideal behaviour the term containing $\ln \kappa_{s(i)n}^\sigma$ becomes zero and then eqn. 51 reduces to the well-known relationship^{7,27}

$$\ln k_s = \sum_{i=1}^n \varphi_i^l \ln k_{s(i)} \quad (53)$$

Eqn. 53 is, besides the Snyder–Soczewiński eqn. 43, one of the most popular relationships used for describing LSC data. This equation represents the linear dependence of the logarithm of the distribution coefficient upon the volume fractions of solvents forming a mixed eluent. Eqn. 53 and other equations presented in this section describe distribution of the s -th solute between the bulk and surface-influenced stationary phases. In other words, these equations describe partition effects in LSC with mixed mobile phases.

LSC WITH BINARY ELUENTS

In this section we present a short discussion of equations describing LSC with binary eluents. A general equation for binary eluents may be obtained from eqn. 24 for $n = 2$; it is

$$\begin{aligned} \ln k_s = & (r_s/r_2)\varphi_2^l \ln K_{21} + (r_s/r_1) \ln (\varphi_1^\sigma/\varphi_1^l) + \varphi_1^l \ln k_{s(1)} + \varphi_2^l \ln k_{s(2)} + \\ & + r_s(\chi_{2s}^\sigma - \chi_{1s}^\sigma) (\varphi_1^\sigma - \varphi_1^l) + r_s \chi_{12}^\sigma \varphi_2^\sigma - r_s \chi_{12}^l \varphi_2^l \quad (54) \end{aligned}$$

Eqn. 54 may be also obtained from eqn. 20, in which the subscript “ i ” is replaced by “1” and γ_s^ρ and γ_1^ρ ($\rho = l, \sigma$) are replaced by suitable equations defining activity coefficients of the s -th solute and 1-st solvent in an infinitely dilute regular solution ($s, 1, 2$) with respect to the s -th solute. It is difficult to obtain special cases of eqn. 54 relating to the pure displacement and partition models because some terms appearing in the expressions $\ln(\tilde{\gamma}_s^l/\tilde{\gamma}_s^\sigma)$ and $\ln(\tilde{\gamma}_1^\sigma/\tilde{\gamma}_1^l)$ have cancelled out. However, these equations may be easily obtained from eqns. 46 and 50 when $n = 2$. In the case of the displacement model we have:

$$k_s = [x_1^l/(k_{s(1)})^{1/\nu} + x_2^l/(k_{s(2)})^{1/\nu}]^{-\nu} \quad (55)$$

The Snyder–Soczewiński relationship is valid for chromatographic systems with binary eluents, which contain solvents showing a great difference in elution strengths, then $k_{s(2)} \gg k_{s(1)}$ where the subscript “1” denotes the more efficient eluting solvent^{6,7}. Under this condition eqn. 55 becomes the Snyder–Soczewiński relationship:

$$\ln k_s = \ln k_{s(1)} - \nu \ln x_1^l \quad (56)$$

In the case of the partition model, eqn. 50 for $n = 2$ gives an extended form of Ościk’s equation²⁷:

$$\begin{aligned} \ln k_s = & \varphi_1^l \ln k_{s(1)} + \varphi_2^l \ln k_{s(2)} + (\varphi_1^\sigma - \varphi_1^l) \ln \kappa_{s(12)}^\sigma - \\ & r_s \chi_{12}^l \varphi_1^l \varphi_2^l + r_s \chi_{12}^\sigma \varphi_1^\sigma \varphi_2^\sigma \quad (57) \end{aligned}$$

Let us return to the general eqn. 54. It is interesting to consider this equation for ideal binary eluents ($\chi_{12}^\sigma = \chi_{12}^l = 0$ and $r_1 = r_2 = r$). If, in addition, the solute

molecules have comparable interactions with molecules of the 1-st and 2-nd solvents and they are not perturbed by the solid surface, then

$$\chi_{1s}^{\sigma} = \chi_{1s}^{\prime} = \chi_{2s}^{\sigma} = \chi_{2s}^{\prime} \quad (58)$$

Under these conditions eqn. 54 gives eqn. 55, which has been derived for the pure displacement model. This indicates that Ościk's equation should contain terms referring to solvent-solvent interactions in both phases because for systems with strong solvent-solvent interactions partition effects should be dominant and this enables us to neglect the effects connected with the displacement process.

CONCLUDING REMARKS

Eqn. 20 contains activity coefficients of the solute and a reference solvent. These activity coefficients may be expressed in an analytical form when we assume a definite molecular model for the bulk and surface solutions. This paper presents equations for the distribution coefficient by taking the model of regular solutions for the mobile and surface-influenced stationary phases, where the surface layer has been formed on an energetically homogeneous solid. This model is based on random mixing and, hence, involves primarily dispersive interactions between the molecules. However, according to Dubinin *et al.*³⁵ it is possible to express the total activity coefficient of the j -th component in the mobile and surface phases as follows:

$$\tilde{\gamma}_j^{\sigma} = \tilde{\gamma}_{j,d}^{\sigma} \tilde{\gamma}_{j,s}^{\sigma} \tilde{\gamma}_{j,h}^{\sigma} \quad (59)$$

and

$$\tilde{\gamma}_j^{\prime} = \tilde{\gamma}_{j,d}^{\prime} \tilde{\gamma}_{j,s}^{\prime} \quad \text{for } j = 1, 2, \dots, n, s \quad (60)$$

In the above, $\tilde{\gamma}_{j,d}^{\rho}$ and $\tilde{\gamma}_{j,s}^{\rho}$ denote the activity coefficients of the j -th component in the ρ -th phase reflecting nonideality of the solution due to dispersive (d) and specific (s) interactions, whereas, $\tilde{\gamma}_{j,h}^{\sigma}$ denotes the activity coefficient of the j -th component in the surface phase reflecting nonideality of the surface solution due to adsorbent heterogeneity (h). Expressing activity coefficients of the solute and solvent in eqn. 20 by expressions of the type eqn. 59 it should be possible to derive equations for LSC involving adsorbent heterogeneity and association effects.

There is also the possibility of describing LC systems containing different numbers of components in both phases, *e.g.*, systems containing liquid components in the stationary phase, which are immiscible with the mobile phase and vice versa. Such a situation may appear in liquid-liquid chromatography with mixed phases and LC with chemically bonded phases. The activity coefficients for such systems may be expressed by eqn. 15, in which terms containing the volume fractions of components not appearing in the ρ -th phase are neglected.

As an example we present equations for LC containing one component in the stationary phase immiscible with the binary mobile phase, *e.g.*, LC with a homogeneous chemically bonded phase. Then the activity coefficient $\tilde{\gamma}_s^{\sigma}$ may be expressed as follows:

$$\ln \tilde{\gamma}_s^\sigma = \varphi_1^\sigma \ln \gamma_{s(1)}^\sigma + \varphi_2^\sigma \ln \tilde{\gamma}_{s(2)}^\sigma + \varphi_c^\sigma \ln \tilde{\gamma}_{s(c)}^\sigma - r_s \chi_{12}^\sigma \varphi_1^\sigma \varphi_2^\sigma - r_s \chi_{1c}^\sigma \varphi_1^\sigma \varphi_c^\sigma - r_s \chi_{2c}^\sigma \varphi_2^\sigma \varphi_c^\sigma \quad (61)$$

where φ_c^σ and $\tilde{\gamma}_{s(c)}^\sigma$ denote the volume fraction of the c -th immiscible component in the stationary phase and the activity coefficient of the s -th solute in the c -th pure component, respectively. The activity coefficient $\tilde{\gamma}_{s(c)}^\sigma$ in the c -th component bonded to the solid surface may be defined analogously to eqn. 14:

$$\ln \tilde{\gamma}_{s(c)}^\sigma = (1 - r_s/r_c) + r_s \chi_{sc}^\sigma + \Delta_{sc} \quad (62)$$

where Δ_{sc} is a correction term. A simple correction of the form shown is strictly valid when the chemically bonded phase is "collapsed" or nearly so, implying little uptake of solvent components 1 and 2 by the stationary phase, *i.e.*, φ_1^σ and φ_2^σ are small²⁴. In this collapsed-chain limit Δ_{sc} depends only on the surface coverage and intrinsic flexibility of the chemically bonded chains, and on the nature of the solute. However, the activity coefficient $\tilde{\gamma}_s^\sigma$ is given by eqn. 15 for $n = 2$. Combination of eqn. 33 defining the distribution coefficient of the s -th solute for the partition model with eqn. 61 and eqn. 15 for $n = 2$ gives:

$$\ln k_s = \varphi_1^l \ln k_{s(1/12c)} + \varphi_2^l \ln k_{s(2/12c)} - r_s \chi_{12}^l \varphi_1^l \varphi_2^l \quad (63)$$

where

$$\ln k_{s(i/12c)} = \ln (\tilde{\gamma}_{s(i)}^l / \tilde{\gamma}_s^\sigma) \quad \text{for } i = 1, 2 \quad (64)$$

The symbol $k_{s(i/12c)}$ denotes a hypothetical distribution coefficient for the s -th solute between the i -th bulk solvent and surface-influenced stationary phase (1 + 2 + c) having an equilibrium composition. Let us consider a case when the solvents are excluded from the stationary phase; then the distribution coefficient $k_{s(i/12c)}$ becomes a physically attainable quantity and represents partition of the s -th solute between the i -th pure solvent and a stationary phase containing only a component immiscible with this solvent. Under this condition we have

$$k_{s(i/12c)} = k_{s(i/c)} \quad \text{for } \varphi_1^\sigma = \varphi_2^\sigma = 0 \text{ and } i = 1, 2 \quad (65)$$

and eqn. 63 becomes

$$\ln k_s = \varphi_1^l \ln k_{s(1/c)} + \varphi_2^l \ln k_{s(2/c)} - r_s \chi_{12}^l \varphi_1^l \varphi_2^l \quad (66)$$

Eqn. 66 has been derived by Martire and Boehm²⁴ for LSC with chemically bonded phases in terms of statistical thermodynamics. This short derivation shows the great utility of the above description to derive equations involving adsorption and partition effects in liquid chromatographic systems with an arbitrary number of components in both phases.

Therefore, it has been demonstrated that various well-known retention-solvent composition relationships can be readily derived from the basic general equation under certain simplifying assumptions. These familiar relationships have been applied

extensively to the interpretation of liquid chromatographic data. Their limitations and range of applicability are a matter of record. It is clear that none of these simple relationships is completely adequate.

Indeed, as has also been recognized and studied by others³⁶⁻³⁹, retention behavior in liquid chromatographic systems is generally complex, especially with mixed mobile phases, and usually cannot be fully described through a single, simple mechanism. However, the problem of practical application of our general equation to a wide range of normal and reversed phase systems, although it is an important (and difficult) one, is beyond the scope of the present paper. It will be the subject of our future studies.

The aim of the present paper was to develop a comprehensive theoretical framework for liquid-solid chromatography. The resulting general equation has been phrased in terms of interaction parameters and activity coefficients, which would need to be evaluated or estimated in actual applications. It should be noted that, as a starting point, approximate methods^{35,40} exist for treating these thermodynamic quantities.

ADDED NOTE

As should be evident from the equations and text in the section titled "Adsorption and Partition Phenomena in LSC", by the term "partition" we refer to that contribution arising from the distribution of solute between a surface-influenced (stationary) liquid layer and a bulk-liquid mobile phase. Even though this effect is similar to liquid-liquid equilibria, we regarded such alternative terms as "solvation", "solution" or "liquid-liquid partition" to be misleading because the stationary layer is by no means a bulk liquid.

However, the Editor has pointed out that, strictly, the term "partition" has a broader connotation and should not be solely reserved to describe liquid-liquid equilibria (or, by extension, a process akin to it), despite its common usage in that regard. This point is well taken. We do not wish it to be inferred that we support or encourage propagation of this historical distortion. Simply, given the nature of the stationary layer and the role of the underlying solid surface in determining its existence and composition, the term "partition" was favored in the present instance by its very broadness.

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