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Review

Partition and displacement models in reversed-phase liquid chromatography with mixed eluents

M. Jaroniec

Department of Chemistry, Kent State University, P.O. Box 5190, Kent, OH 44242-0001 (USA)

ABSTRACT

The partition and displacement mechanisms of the solute's retention are reviewed in terms of phenomenological thermodynamics with special emphasis on their use in modeling reversed-phase liquid chromatography with mixed eluents. This review contains some thermodynamic arguments for representing the solute's retention on chemically bonded phases by a combined partition–displacement model. A simplified version of this model, which represents the formation of the solvent–surface stationary phase via a displacement mechanism and the distribution of the solute between the mobile and stationary phases via a partition mechanism, is discussed in order to demonstrate its utility for characterizing RPLC systems. The composition of the solvent–surface stationary phase may be studied on the basis of independent excess sorption measurements for the eluent-bonded phase system. Also, the RPLC data can provide information about the composition of solvents in the stationary phase. Analysis of the solvent sorption effects on the basis of sorption measurements as well as on the basis of the methylene selectivity data show that the presence of solvents in the chemically bonded phases affects significantly the solute's retention in typical RPLC systems.

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1. INTRODUCTION

The so-called "normal" mode of liquid chromatography comprises systems with a polar stationary phase (*e.g.*, silica gel) and non-polar mobile phase (*e.g.*, benzene–hexane mixture). However, in reversed-phase liquid chromatography (RPLC) the polarity of the phases is reversed, *i.e.*, the mobile phase is polar and the stationary phase is non-polar. Although different

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non-polar materials can be used in RPLC as the column packings (*e.g.*, solid supports coated with non-polar compounds, carbon-based packings, etc.), several packings with chemically bounded phases (*e.g.*, silica-based alkyl bonded phases) reached the greatest popularity in RPLC applications because they are chemically stable and possess microparticulate structure which assures a rapid mass transfer and a high degree of reproducibility. At present RPLC is frequently identified with the high-performance liquid chromatography with chemically bonded phases and it will be subject of the current review.

Two extreme molecular processes, *i.e.*, displacement and partition, are most often used in liquid chromatography (LC) to represent the solute's distribution between the mobile and stationary phases (see reviews [1–13] and references therein). Displacement is a surface process which occurs at the solid–liquid interface. According to this process the solute's molecules migrate from the mobile phase to the interface and displace the physically adsorbed molecules of solvents. The displacement process, called also competitive adsorption, is controlled by the difference between the solute's and solvents' sorption free energies. This type of the solute's distribution between the mobile and stationary phases dominates in the normal-phase mode LC systems, in which the stationary phase is a monolayer or bilayer formed on a polar solid surface.

An alternative mechanism of the solute's distribution is partition, which is a volume process. The partition mechanism is favored when the stationary phase is "thick" enough in order to accommodate solute molecules in its volume. This condition is fully fulfilled in the liquid–liquid chromatographic systems, in which the stationary and mobile phases are immiscible liquids. Also, the stationary phase in RPLC systems with chemically bonded ligands is relatively "thick" [11,13–16] and suitable for accommodating the solute molecules via the partitioning mechanism. However, the solute's partitioning that occurs in the RPLC systems differs significantly from that taking place between two immiscible liquid phases because the chemically bonded phase with incorporated solvent molecules is by no means a bulk liquid [17]. A common feature of the partition phenomena occuring in the liquid–liquid and RPLC systems is their molecular mechanism, which involves: (i) the creation of a solute-sized cavity in the stationary phase, (ii) the transfer of a solute molecule from the mobile phase to the formed cavity in the stationary phase and (iii) the closing of a solute-size cavity in the mobile phase [11]. As should be evident from the above description, the solute's partitioning is controlled by the differences in the molecular interactions of solute molecules in the stationary and mobile phases.

A brief description of the solute's retention given above shows that a variety of interactions exists in LC systems, which must be identified in order to understand the LC process. These include the solute–solvent and solvent–solvent interactions in both the mobile and stationary phases and the interactions of the solute and solvents with the solid surface (*e.g.*, refs. 4,7,8 and 17–19). For LC systems with chemically bonded phases a significant contribution to the solute's retention arises from the interactions of the solute and solvent molecules with the bonded ligands (*e.g.*, refs. 2 and 11). In addition, the solute's retention can be influenced by the other factors such as: the composition of solvents in the stationary phase [17,20–27], dissociation, complexation and/or association equilibria (*e.g.*, refs. 28–37), surface heterogeneity [38–42], size and shape of the solute molecules [21,43–45], as well as the orientation, dynamics and conformation of chemically bonded phases [46–49]. Although the existing statistical thermodynamic descriptions of the solute's retention incorporate the majority of molecular interactions [45,50–56], they are inconvenient for interpreting the LC data because the resulting equations are frequently quite complicated. Because of such difficulties, simple retention models are very popular in LC.

In the current work the partition and displacement models are reviewed with a special emphasis on their utility for describing the solute's retention in LC systems under reversed-phase conditions. This review shows that a combination of these models seems to be necessary for representing the overall process of the solute's retention in RPLC. Also, the present work addresses an important role of the stationary phase effects in the RPLC process. These effects were often ignored in some earliest retention models [57–60] and even at present they are sometimes underestimated in modelling RPLC processes.

2. THERMODYNAMIC MODELLING OF LIQUID CHROMATOGRAPHY

2.1. Two-stage nature of chromatographic processes at the liquid–solid interface

In a typical RPLC system the stationary phase consists of chemically bonded ligands, which are essentially not removable from the silica surface, and incorporated molecules of a organic compound (*e.g.*, methanol, acetonitrile) and water, which are used as the components of the mobile phase. The injected amount of solute should be infinitely low in analytical applications of RPLC and does not alter the solvent composition of the stationary phase. The concentrations of solvents in the stationary phase are established according to the conditions of thermodynamic equilibrium and usually they differ from the composition of the mobile phase. The stationary phase composition of solvents depends on the mobile phase composition, chemical nature of the bonded ligands, and their surface concentration and conformation. In addition, the thickness of the stationary phase in RPLC can change with the mobile phase composition because the conformational structure of the bonded ligands is different in aqueous and organic environments [46–49].

Another important factor that controls the composition and structure of the stationary phase in RPLC is silica, *i.e.*, its porosity, surface properties and the amount of unreacted silanol groups. The "silanophilic" interactions, ignored initially in the interpreting the solute's retention under reversed-phase conditions [61–63], have been found to play an important role in RPLC process [64–71]. It is obvious that the amount of unreacted surface silanols controls the concentration of water molecules in the stationary bonded phase and consequently, it influences significantly the composition of solvent molecules in this phase. The above brief description of the stationary phase in RPLC shows that its structural and compositional properties differ significantly from the physicochemical properties of immiscible liquid phases used in classical partitioning. A comparative study of partition mechanisms in liquid–liquid and RPLC systems showed essential differences between them [72].

In earlier models of the LC process the solute's retention was identified with the distribution of the solute between both the mobile and stationary phases (see refs. cited in ref. 8). For example, one of the most popular equations in the theory of LC with the mixed mobile phases, the Snyder–Soczewinski equation [4,43], ignores the composition of solvents in the stationary phase. In 1979 Jaroniec *et al.* [21] derived, in terms of the displacement model, a general expression for the solute's retention, which involves the surface phase composition effects. According to this expression the surface phase composition significantly affects the solute's retention at low concentrations of the more polar solvent. However, in the range of high concentrations it reduces to the Snyder–Soczewinski relationship. This example illustrates that each rigorous model of the solute's retention should take into account the stationary phase composition effects, which often are ignored. The importance of the surface phase composition effects have been strongly underlined by Jaroniec and Martire [17,73] in their thermodynamic treatment of LC with mixed mobile phases. According to this treatment each rigorous model of the solute's retention should distinguish two stages of LC process: (i) the formation of a combined solvent–surface stationary phase and (ii) the distribution of the solute between the mobile phase and the solvent–surface stationary phase. A brief discussion of these stages is given below.

2.2. Formation of the solvent–surface stationary phase

Formation of the solvent–surface stationary phase is an independent stage of the LC process and takes place during conditioning the chromatographic column. Before injection of the solute a mixed eluent is pumped through column and during this process the equilibrium composition of the stationary phase is established via competitive sorption of eluting solvents. This composition is not altered by injection of the solute because its amount supposed to be infinitely small. Generally, the equilibrium composition of the solvents in the stationary phase, which depends on the type of chemically bonded ligands, their surface concentration, and the surface and structural properties of the silica support, is a function of the mobile phase composition. In the case of simple chromatographic systems it may be estimated in terms of the theory of competitive adsorption at the liquid–solid interface (see reviews [8,74,75] and references therein). In the other cases the surface composition of the solvents can be determined by a direct dynamic or static measurement of the excess sorption isotherm for the solvents–chromatographic packing system (this problem will be discussed later). Information about the surface composition of solvents can be also obtained on the basis of LC measurements [26,27].

In terms of phenomenological thermodynamics the competitive sorption of solvents, which is a displacement process, is usually represented by a series of the phase-exchange quasi-chemical reactions for all possible solvents' pairs [21]. For the pair of solvents i and j this reaction can be written as follows:

$$r_j(i)^l + r_i(j)^\sigma \leftrightharpoons r_j(i)^\sigma + r_i(j)^l \qquad (1)$$

where $(i)^\rho$ denotes a molecule of the ith solvent in the ρth phase, and $\rho = l$ (mobile phase) and σ (stationary phase). The parameter r_i is a measure of the molecular size and denotes the total number of segments in one molecule of the ith solvent [21]. Although the phase-exchange reaction given by eqn. 1 suggests a monolayer character of the surface phase, the theoretical studies by Dabrowski *et al.* [76] showed that it can be used to represent the formation of a multilayer with a special molecular order. At thermodynamic equilibrium the phase-exchange reaction 1 is characterized by the equilibrium constant K_{ij}:

$$K_{ij} = \left(\frac{a_i^\sigma}{a_i^l}\right)^{r_j} \left(\frac{a_j^l}{a_j^\sigma}\right)^{r_i} \quad \text{for } i \neq j \qquad (2)$$

where a_j^ρ denotes the activity of the ith solvent in the ρth phase, which is defined in terms of the volume fraction, φ_i^ρ, and the activity coefficient, γ_i^ρ:

$$a_i^\rho = \varphi_i^\rho \gamma^\rho i \quad \text{for } \rho = l, \sigma \,. \qquad (3)$$

Eqn. 2 is a general expression, which describes the thermodynamic equilibrium of the phase-displacement for the solvents i and j. This equation contains the activity coefficients of solvents in the mobile and stationary phases. Special forms of eqn. 2 can be obtained by expressing these activity coefficients in terms of the volume fractions of all solvents. The mobile phase activity coefficients can be evaluated on the basis of the independent measurements, *e.g.*, gas–liquid chromatography [77–79], liquid–vapor equilibria [80]. However, analytical expressions for the activity coefficients can be only obtained by assuming a molecular model for the liquid phase [80]. For instance, Jaroniec and Martire [17] discussed eqn. 2 with the activity coefficients formulated in terms of the theory of regular solutions.

In many models of the solute's retention the surface phase composition of solvents is expressed by means of Everett's equation [81]:

$$x_1^\sigma = \frac{K_{12} x_1^l}{(x_2^l + K_{12} x_1^l)} \qquad (4)$$

Eqn. 4 expresses the mole fraction, x_1^σ, of the 1st solvent in the surface phase in terms of the mobile phase composition, x_1^l and $x_2^l = 1 - x_1^l$. This equation corresponds to the simplest adsorption model that assumes: (i) thermodynamic equilibrium of an ideal binary liquid mixture of non-electrolytes on an inert solid, (ii) identical sizes and spherical shapes of all molecules, (iii) ideality of the surface (stationary) phase and (iv) energetic homogeneity of the solid. In mathematical language, these assumptions can be formulated as follows: (i) all activity coefficients in eqn. 2 are equal to unity, (ii) the parameters r_i and r_j are identical and (iii) only one value of the constant K_{ij} is necessary for describing the overall phase-displacement process between molecules of the solvents i and j; the first two assumptions define ideality of both phases, whereas the third one defines the solid's homogeneity. Application of the above assumptions to eqn. 2 gives Everett's eqn. 4. Although eqn. 4 corresponds to a very simple adsorption model, for many LC systems it is already sufficient to represent the surface phase composition of solvents (see ref. 8 and references therein). It was shown elsewhere [27,82,83] that in many cases the representation of the surface phase composition effects by eqn. 4 significantly improves description of LC retention data.

2.3. *Solute distribution between the mobile and stationary phases*

Any rigorous description of the distribution of the sth solute (being at the infinitely low concentration) between the mobile and stationary phases should take into account its competitive sorption with respect to all solvents and the different solute–solvent interactions in both phases [73]. In general, this process can be characterized by the equilibrium constant K_{si} (analogous to the constant K_{ij} given by eqn. 2), which is defined in terms of the activities of the sth solute and ith solvent, i.e.,

$$K_{si} = \left(\frac{a_s^\sigma}{a_s^l}\right)^{r_i}\left(\frac{a_i^l}{a_i^\sigma}\right)^{r_s} \qquad (5)$$

where a_s^ρ denotes the activity of the sth solute in the ρth phase, where $\rho = l, \sigma$. It is noteworthy that one equilibrium constant K_{si} is sufficient for representing the solute's interactions with the other solvents because a simple combination of K_{si} with the solvents' equilibrium constant, *e.g.*, K_{ij}, gives K_{sj}:

$$K_{sj} = K_{si}K_{ij} \qquad (6)$$

Expressing all activities in eqn. 5 in terms of the activity coefficients and the volume fractions (cf., eqn. 3) and defining the solute's distribution coefficient k_s as the ratio of the solute's volume fractions in the stationary and mobile phases, *i.e.*,

$$k_s = \left[\frac{\varphi_s^\sigma}{\varphi_s^l}\right]_{\varphi_s^l \to 0} \qquad (7)$$

one can transform eqn. 5 and obtain the following general expression for k_s:

$$\ln k_s = \ln K_{si}^* + \ln\left(\frac{\gamma_s^l}{\gamma_s^\sigma}\right) + n\ln\left(\frac{\varphi_i^\sigma}{\varphi_i^l}\right) + n\ln\left(\frac{\gamma_i^\sigma}{\gamma_i^l}\right) \qquad (8)$$

where

$$K_{si}^* = (K_{si})^{1/r_i} \quad \text{and} \quad n = r_s/r_i \qquad (9)$$

It was shown elsewhere [17,73] that eqn. 8 generates the majority of the known relationships that describe the mobile-phase dependence of the solute's distribution coefficient. Two of them are the most popular relationships because they describe the solute's distribution according to the displacement and partition models. It was proved in ref. 17 that after neglecting all solute–solvent and solvent–solvent interactions in both phases, eqn. 8 gives the following simple relationship:

$$\ln k_s = \ln K_{si}^* + n\ln\left(\frac{\varphi_i^\sigma}{\varphi_i^l}\right) \qquad (10)$$

Eqn. 10 defines a simple displacement of the solvent molecules physically adsorbed in the surface phase through the solute molecules contained in the mobile phase. The simple displacement process is characterized by the difference in the solute–surface and solvent–surface interactions only [73]. It should be emphasized that eqn. 10, derived in terms of the displacement model [21], contains the volume fraction φ_i^σ, which characterizes the stationary phase composition. Expressing in eqn. 10 the volume fraction φ_i^σ by Everett's eqn. 4 or an equation for competitive adsorption of solvents on an energetically heterogeneous solid [74], one can obtain, respectively, analytical expressions for the solute's distribution coefficient on homogeneous and heterogeneous surfaces, as discussed in refs. 20–23. At higher concentrations of the most polar solvent, which interacts strongly with the surface, one can assume that other solvents are not present in the stationary phases (*i.e.*,

$\varphi_i^\sigma \rightarrow 1$) and eqn. 10 becomes the well-known Synder–Soczewinski equation [4,43]:

$$\ln k_s = \ln K_{si}^* - n \ln \varphi_i^l \tag{11}$$

Eqn. 11 is the most often used in normal-phase LC to represent the experimental dependence of the solute's distribution coefficient on the mobile phases composition (see reviews [4,8] and references therein).

The other important case of the general eqn. 8 is obtained by assuming the partition mechanism of the solute's distribution. This case can be obtained from eqn. 8 by equalizing the solute–surface and solvent–surface interactions [17,73]:

$$k_s = \gamma_s^l/\gamma_s^\sigma \tag{12}$$

Eqn. 12 defines the solute's distribution via the partition mechanism, which is controlled by the difference in the solute–solvent interactions in both phases. It was shown in refs. [84 and 85] that expressing in eqn. 12 the solute's activity coefficients in terms of the theory of regular solutions one can obtain the Oscik equation [5].

A series of the other equations for the solute's distribution coefficient can be generated directly from eqn. 8 by assuming the specific expressions for the activity coefficients of the solute and solvents. As it was suggested in ref. 17, the activity coefficient of a component, solute or solvent, in the mobile phase can be expressed as a simple product of two quantities:

$$\gamma_i^l = \gamma_{i,\mathrm{dis}}^l \gamma_{i,\mathrm{spe}}^l \tag{13}$$

where $\gamma_{i,\mathrm{dis}}^l$ describes the mobile phase non-ideality arising from dispersive interactions, and $\gamma_{i,\mathrm{spe}}^l$ characterizes the phase non-ideality arising from the specific interactions between molecules of the solute and solvents. In the case of the stationary phase an additional non-ideality of this phase arise form the energetic heterogeneity of the solid surface and it can be included to the overall activity coefficient as follows [86–88]:

$$\gamma_i^\sigma = \gamma_{i,\mathrm{dis}}^\sigma \gamma_{i,\mathrm{spe}}^\sigma \gamma_{i,\mathrm{het}}^\sigma \tag{14}$$

Combination of eqn. 8 with the suitable expressions for the activity coefficients permitted derivation of several relationships for the solute's distribution coefficient (see refs. 7, 17–18, 41 and 89]. Some of them were also derived in terms of the statistical thermodynamics [50–52,90].

3. PARTITION-DISPLACEMENT MODEL FOR RPLC WITH MIXED ELUENTS

3.1. A brief description of the partition–displacement model

A general description of the solute's retention in terms of phenomenological thermodynamics is given by eqns. 2 and 8; the first of these equations describes the competitive adsorption of solvents, whereas the second one characterizes the solute's distribution. For many RPLC systems, especially for systems with chemically bonded phases that contain a significant number of unreacted silanol groups, the mechanism of the solute's retention may be complex, as has been suggested in several works [64–71]. In these systems the solute's distribution is not only controlled by the solvophobic interactions [61–63] but also by the "silanophilic" interactions [65,66]. In the author's opinion the accessible silanol groups may cause also a dramatic change in the composition of solvents in the stationary phase. This opinion found already some justification through the studies of the excess adsorption isotherms of solvents on chemically bonded phases [91–97], as well as through the assessment of surface phase composition effects on the basis of the RPLC data [26,27,82,83,98]. If one assumes that the unreacted silanols control the stationary phase composition, then a simple partition mechanism can be assumed to represent the distribution of the infinitely small amount of the solute between the mobile phase and the solvent–surface stationary phase. The fact that the stationary bonded phase with the incorporated solvent molecules is relatively thick gives an additional justification for the above concept. However, formation of the solvent–surface stationary phase is usually associated with phase volume effects, which need to be treated in terms of the competitive adsorption (displacement) model. Thus, a realistic model for the solute's retention in RPLC systems with a mixed mobile phase may be obtained by a combination of *the displacement model* that represents the formation of the stationary phase and *the partition model* that describes the solute's distribution between the solvent-surface stationary phase and the mobile phase. Simple equations resulting from the partition–displacement (PD) model of the solute's retention are discussed below.

3.2. Fundamental relationships for the distribution coefficient

In mathematical language, the PD model can be formulated as follows: (i) the competitive adsorption of solvents, occuring via the displacement process, is characterized by the equilibrium constants K_{ij}, and the solute's partition is described by eqn. 12. The formulation of this model in terms of the theory of regular solutions gives the following expression for the distribution coefficient [85,98]:

$$\ln k_s = \varphi_1^\sigma \ln k_{s(1)} + \varphi_2^\sigma \ln k_{s(2)} + (\varphi_1^\sigma - \varphi_1^l) \ln \kappa_{s(1/2)} - \varphi_2^l \ln K_{12} + Y \quad (15)$$

where

$$Y = r_s \chi_{12}^\sigma \varphi_1^\sigma \varphi_2^\sigma - r_s \chi_{12}^l \varphi_1^l \varphi_2^l \quad (16)$$

The symbols $k_{s(1)}$ and $k_{s(2)}$ denote, respectively, the distribution coefficients of the sth solute in the pure solvents 1 and 2, $\kappa_{s(1/2)}$ is the hypothetical partition coefficient of the solute between two pure solvents 1 and 2, r_s is the size parameter defined in eqn. 1, and χ_{12}^p is the interaction parameter for these solvents in the pth phase. Note that $-RT \ln k_s$ denotes the change in the Gibbs free energy, ΔG_s, for the solute's retention in LC with a mixed mobile phase. However, $-RT \ln k_{s(i)}$ denotes the change in the Gibbs free energy, $\Delta G_{s(i)}$, which characterizes the solute's retention in the ith pure solvent. Since for the stationary phase containing two solvents $\varphi_1^\sigma + \varphi_2^\sigma = 1$, the term $\varphi_i^\sigma \Delta G_{s(i)}$ $(i = 1, 2)$ denotes the contribution to the total ΔG_s arising from the solute's retention in the ith pure solvent. If ΔG_s for the overall retention process is an additive quantity, eqn. 15 should contain only the first two terms referring, respectively, to the solute's retentions in the pure solvents 1 and 2. Since this is not the case, the remaining three terms in eqn. 15, after multiplication by $-RT$, denote the excess in the Gibbs free energy. This excess quantity reflects the effects associated with the competitive adsorption of solvents (through the equilibrium constant K_{12}; see the fourth term in eqn. 15), the solute–solvent interactions in the mobile phases (through the hypothetical partition coefficient $\kappa_{s(1/2)}$; see the third term), and the solvent–solvent interactions in both phases (through the interaction parameters χ_{12}^l and χ_{12}^σ; see the fifth term). The competitive sorption effects are also reflected in the third term, which is directly proportional to the dimensionless adsorption excess of the 1st solvent $\varphi_1^\sigma - \varphi_1^l$. It was shown in ref. 5 that for many LC systems the surface and mobile phase solvent–solvent interaction terms are small and approximately cancel, rendering the quantity Y negligible in eqn. 15.

An interesting case of eqn. 15 is obtained by assuming that the sorption excesses of both solvents are equal to zero and $Y = 0$. For instance, the sorption excess of methanol from water on some alkyl bonded phases is small and sometimes it can be approximated by zero [27,82,83]. With the above-mentioned assumptions the last three terms in eqn. 15 become equal to zero, and then:

$$\ln k_s = \varphi_1^\sigma \ln k_{s(1)} + \varphi_2^\sigma \ln k_{s(2)} \quad (17)$$

Since the sorption excess of the solvents is equal to zero, *i.e.*, $\varphi_i^\sigma = \varphi_i^l$ for $i = 1, 2$, eqn. 17 can be also written in the following form:

$$\ln k_s = \varphi_1^l \ln k_{s(1)} + \varphi_2^l \ln k_{s(2)} \quad (18)$$

Eqn. 17 refers to a simple partition model of the solute's distribution between the mobile and stationary phases, the compositions of which are not affected by the competitive adsorption of solvents. In this case the logarithm of the solute's distribution coefficient is an additive quantity with respect to the solvent composition. However, for the simple displacement model of the solute's retention an additive quantity is the distribution coefficient [1,20]:

$$k_s = \varphi_1^\sigma k_{s(1)} + \varphi_2^\sigma k_{s(2)} \quad (19)$$

A comparison of eqns. 17 and 19 shows that the partition and displacement models of the solute's retention lead to essentially different results.

3.3. Selectivity

The selectivity, α_{sr}, is an important quantity, which is often used to study the nonspecific and specific interactions in chromatographic systems. It can be defined as the ratio of the distribution coefficients for two solutes: s and r, *i.e.*,

$$\alpha_{sr} = k_s / k_r \tag{20}$$

If α_{sr} is calculated for adjacent members in a homologous series, it is called the non-specific selectivity (or the methylene selectivity in the case of alkyl homologues) [99]. However, for two solutes differing in a functional group, α_{sr} can be called the specific (or polar) selectivity [100]. The methylene selectivity is highly popular in RPLC and is often used to investigate the hydrophobic interactions between solutes and chemically bonded phases [26,27,82,83,101–107]. For many types of homologous series this selectivity, calculated at a fixed composition of the mobile phase, is constant for a number of adjacent carbon atoms in the homologue's alkyl chain. The logarithm of the methylene selectivity multiplied by the factor $-RT$ is equal to the change in the Gibbs free energy that characterizes the transfer of the methylene group from the mobile to the stationary phase.

A very simple equation for the logarithm of the selectivity, $s_{sr} = \ln \alpha_{sr}$, can be obtained in terms of the PD model of the solute's retention. It is easy to obtain from eqn. 15 the following expression:

$$s_{sr} = \varphi_1^\sigma s_{sr(1)} + \varphi_2^\sigma s_{sr(2)} + (\varphi_1^\sigma - \varphi_1^l) s^*_{sr(1/2)} \tag{21}$$

where

$$s_{sr(i)} = \ln \alpha_{sr(i)} = \ln(k_{s(i)} / k_{s(i)}) \text{ for } i = 1, 2 \tag{22}$$

and

$$s^*_{sr(1/2)} = \ln(\kappa_{s(1/2)} / \kappa_{r(1/2)}) \tag{23}$$

Eqn. 21 defines the logarithm of the selectivity for two solutes charomatographed in a binary eluent in terms of the selectivities referring to one-component eluents and the sorption excess of the first solvent. Since the quantity Y in eqn. 15 is often negligible [5] and the forth term in eqn. 15 does not depend on the solute's nature, these terms do not provide a contribution to the logarithm of the selectivity. However, the composition of the solvent–surface phase is expressed by the volume fractions of both solvents (*cf.*, two first terms of eqn. 21). Additionally, the solvent sorption effects are reflected by the third term of eqn. 21, which through $s^*_{sr(1/2)}$ also includes the effects associated with the solvent-solvent interactions.

4. SORPTION EXCESSES OF SOLVENTS IN THE STATIONARY PHASE

As was mentioned in section 2.2, the composition of the solvents in the stationary bonded phase can be evaluated on the basis of the sorption excess measured for the mixed eluent–chromatographic packing system. There exist extensive literature dealing with the physicochemical interpretation and measurement of the sorption excesses at the liquid–solid interface (see reviews [74,75,108–116] and references therein). A special elaboration was prepared by the Commission on Colloid and Surface Chemistry of the IUPAC on reporting data for adsorption from solution at the solid–solution interface [117]. Although a rigorous thermodynamic description of liquid–solid adsorption was formulated by Everett in 1964 [81], its first application for elaborating the theory of LC with mixed mobile phases appeared in the literature fourteen years later [20]. The first use of the excess adsorption isotherms of solvents for characterizing the surface phase in normal-phase mode LC systems was demonstrated by Jaroniec *et al.* [21] in 1979. Although from this date several excess isotherms have been published for the normal-phase [21,23–25,118,119] and reversed-phase [93–97,120] systems, they are used rather seldom for interpreting LC data [21,23,118]. The sorption excesses of the solvents on chemically bonded phases can provide valuable information about the structure and composition of the stationary phase, which is essential for a proper description of the solute's retention in RPLC.

The available sorption data for the most popular eluents in RPLC, *i.e.*, for methanol–water and acetonitrile–water on alkyl bonded phases, show that the preferential sorption of acetonitrile is much stronger than that for methanol [92,96,120]. This means that in the case of acetonitrile its concentration in the stationary bonded phase is much greater than that in the mobile phase. A quantitative evaluation of the sorption effects for acetonitrile on alkyl bonded phases was performed in a few laboratories [92,93,95–97,120]. Fig. 1 presents an interesting comparison of the acetonitrile sorption excesses on octadecyl bonded phases. These excesses were measured at room temperature on different bonded phases in three different laboratories [93,96,120]. One excess isotherm was measured on the octadecyl bonded phase prepared by Tani and Suzuki (TS phase) [120], the others were obtained for Bondapak C_{18} (Waters Assoc.) [96] and LiChrosorb RP-18 (Merck, Darmstadt, Germany) [93]. Although all bonded phases were prepared on different samples of silica, their specific surface areas (about 300 m^2/g) and mean pore diameters (about 10 nm) were similar (see details in refs. 93, 96 and 120). Also, all packings studied were the endcapped polymeric phases. They differ in the carbon load, which for the Merck and TS phases were similar and, respectively, equal to 19.8% [121] and 18.5% [120]. However, the carbon load for the Waters phase was equal to 10% [122], *i.e.*, about half that of the Merck and TS phases. Fig. 1 demonstrates that the concentration of alkyl ligands on the silica surface, which is proportional to the % carbon load, significantly affects the excess sorption of acetonitrile. The excess isotherm for the Waters phase differs considerably from those measured on the Merck and TS phases with the high carbon load. At low concentration of acetonitrile in the mobile phase the acetonitrile sorption excess on the alkyl-rich phases is smaller than that for the phase of low density. However, at high concentrations of acetonitrile the opposite sequence of the excess isotherms is observed, *i.e.*, for the alkyl-rich bonded phases the acetonitrile excess assumes small positive values, whereas for the low-density phase the excess values are negative. The negative excess of acetonitrile denotes the positive excess of water, which is an indication that at high concentrations of acetonitrile the water molecules are preferentially incorporated to the low-density phase. The excess isotherm of acetonitrile on the Waters bonded phase is a nice illustration of the importance of the phase density in controlling the composition of solvents in the stationary phase. The other interesting feature shown in Fig. 1 is a surprising coincidence of the two excess isotherms measured on the Merck and TS bonded phases (note that these isotherms were measured at slightly different temperatures). Although both phases had similar carbon loads, they were prepared on the basis of different silica samples in two laboratories. Also, the excess isotherms were measured in two laboratories by employing the minor disturbance method and the method with the isotopically labelled compounds [93,120]. A good reproducibility of the excess data for acetonitrile on the alkyl-rich bonded phases facilitates their use for characterizing solvent-surface stationary phases in RPLC.

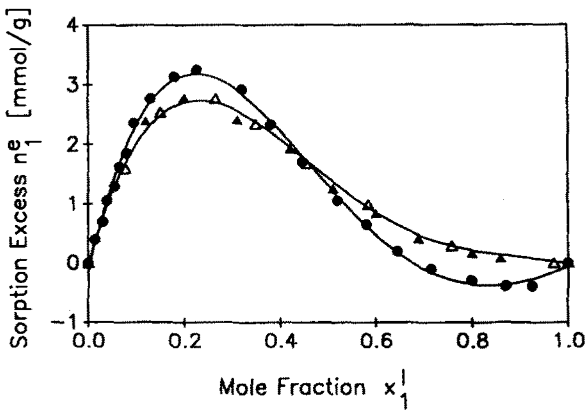

Fig. 1. A comparison of the excess sorption isotherms of acetonitrile from aqueous solutions on octadecyl bonded phases. The filled circles denote the excess data measured on μBondapak C_{18} at 298 K [96], the open triangles refer to the data on the Merck RP-18 phase at 295 K [93] and the filled triangles refer to the data on the TS phase at 303 K [120].

Fig. 2 illustrates the dependence of the solvent sorption on the length of the alkyl bonded chains. The excess isotherms shown in Fig. 2 were plotted on the basis of the sorption data measured by Slaats *et al.* [93] for acetonitrile from aqueous solutions on the phases with two,

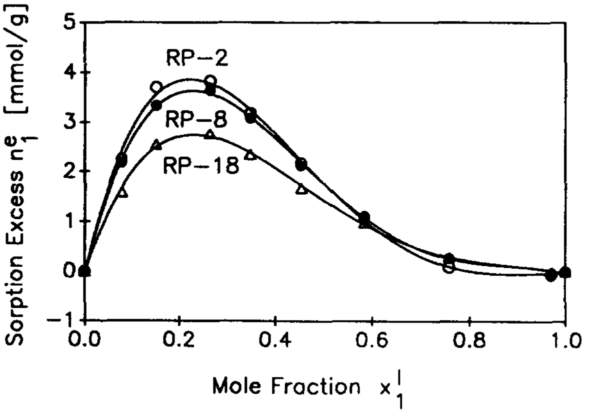

Fig. 2. A comparison of the excess sorption isotherms of acetonitrile from aqueous solutions on the Merck RP-2 (open circles), RP-8 (closed circles) and RP-18 (open triangles) phases at 295 K. The excess data taken from ref. 93.

eight and eighteen carbon atoms in the bonded alkyl ligands [93]. These bonded phases were from Merck (Darmstadt, Germany), known as the LiChrosorb RP-2, RP-8 and RP-18 chromatographic packings. The surface coverages of the Merck RP-2, RP-8 and RP-18 phases, evaluated by Buszewski and Nasuto [123], are respectively equal to 3.91, 3.23 and 3.17 μmol/m^2. These values indicate that RP-2, RP-8 and RP-18 can be treated as alkyl-rich bonded phases. The surface coverage of the RP-2 phase is about 20% higher than that for the RP-8 and RP-18 phases and the sorption excess isotherm of acetonitrile on this phase lies above the other isotherm curves. It lies close to the isotherm on RP-8 but differs significantly from that on RP-18. The sequence of the acetonitrile excess isotherms measured on the alkyl-rich RP phases (shown in Fig. 2) differs from that deduced on the basis of the RPLC data for the low-density bonded phases [27].

The excess data illustrates in Figs. 1 and 2 show that at present their physico-chemical interpretation is difficult because sorption of the RPLC solvents on chemically bonded phases is controlled by the various types of polar and non-polar interactions. Extensive and systematic studies of the solvent sorption effects in RPLC systems are desirable in order to improve our knowledge about the structure and composition of the solvent–surface stationary phases.

5. APPLICATIONS OF THE PARTITION-DISPLACEMENT MODEL IN RPLC

As was mentioned in section 3.3, the methylene selectivity is often used to study hydrophobic interactions in the RPLC systems. There is a great number of publications reporting the methylene selectivity data measured at the different compositions of the mobile phase [99–104,124–127]. For the methanol–water eluent the logarithm of the methylene selectivity, s_{sr}, changes almost linearly with the mobile phase composition [101,103]. However, non-linearity is observed for the other reversed-phase eluents such as: acetonitrile–water, tetrahydrofuran–water and isopropanol–water [99,101–103]. It was demonstrated [26,27,82,83,98] that the concentration-dependent methylene selectivity data can be interpreted in terms of the PD model of the solute's retention. Since interpretation of the non-linear behavior of s_{sr} in terms of the PD model is reasonable and interesting, its brief discussion is given here in order to illustrate the utility of this model for representing the solute's retention in the RPLC systems.

It is possible to show on the basis of eqn. 21 that the excess function, s^e_{sr}, associated with the logarithm of the methylene selectivity is proportional to the sorption excess of 1st solvent [98], *i.e.*,

$$s^e_{sr} \equiv s_{sr} - \varphi^l_1 s_{sr(1)} - \varphi^l_2 s_{sr(2)} = \text{constant}\ (\varphi^\sigma_1 - \varphi^l_1) \tag{24}$$

The symbol $s_{sr(i)}$ denotes the logarithm of the selectivity for the *s*th and *r*th solutes in the *i*th pure solvent; when the solutes *s* and *r* denote two adjacent homologues, this symbol refers to the methylene selectivity.

If $s^e_{sr}(\varphi^l_1) = 0$ in the whole concentration range, then according to eqn. 24 the sorption excess of the first solvent is equal zero. The zero value of the sorption excess denotes that the compositions of solvents in both phases are identical. Thus, a deviation of the $s^e_{sr}(\varphi^l_1)$ dependence from

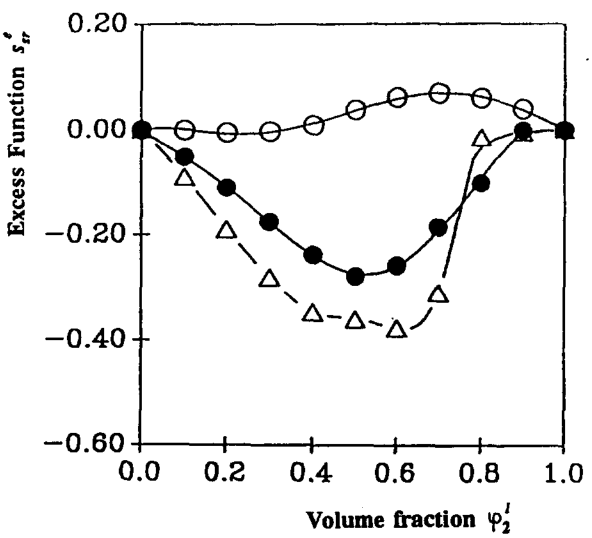

Fig. 3. Excess function of the methylene selectivity (*cf.*, eqn 24) plotted against the volume fraction of water in the binary hydro–organic mobile phases with methanol (○), acetonitrile (●) and tetrahydrofuran (△). These functions were plotted on the basis of the selectivity data measured at 298 K by Colin *et al.* [101]. From ref. 98.

zero indicates that the solvent concentrations in the stationary phase differ from those in the mobile phase. Thus, the $s^e_{sr}(\varphi_1^l)$ plot is a simple chromatographic test for assessment of the solvent sorption effects in RPLC. It is illustrated in Fig. 3, which was prepared on the basis of the methylene selectivity data published in ref. 101. This figure presents the excess selectivity function for three different binary hydro–organic mobile phases, *i.e.*, methanol–water, acetonitrile–water and tetrahydrofuran–water. For the methanol–water mobile phase the excess selectivity function is almost zero at low water concentrations and assumes small positive values in the range of high water concentrations. This result justifies neglection of the solvent sorption effects in interpreting the dependence of the methylene selectivity on the methanol–water composition. In this case eqn. 21 reduces to the following expression:

$$s_{sr} = \varphi_1^l s_{sr(1)} + \varphi_2^l s_{sr(2)} \qquad (25)$$

Eqn. 25, describing additivity of the s_{sr} quantity with respect to the solvent mobile phase composition, represents the linear behavior of the $s_{sr}(\varphi_1^l)$ function, as was observed experimentally [101,103]. However, for the acetonitrile–water and tetrahydrofuran–water phases the excess selectivity function deviates strongly from zero. This fact is a clear indication that the solvent sorption effects influence strongly the solute's retention in the above-mentioned systems.

In refs. [27, 82 and 83] a simplified version of the PD model was used for analyzing the non-specific selectivity data. It was shown in these references that a combination of eqn. 17 (which refers to a simple partition model of the solute's retention) with eqn. 4 (which describes the composition of the solvents in the stationary phase in terms of a simple displacement model) gives the following expression:

$$\frac{1}{(s_{sr(2)} - s_{sr})} = a + b\frac{\varphi_2^l}{\varphi_1^l} \qquad (26)$$

where

$$a = \frac{1}{(s_{sr(2)} - s_{sr(1)})} \quad \text{and} \quad b = \frac{K_{21}}{(s_{sr(2)} - s_{sr(1)})} \qquad (27)$$

The methylene selectivity data reported by Colin *et al.* [101] were plotted according to eqn. 26 (*cf.*, Fig. 4). As was mentioned in ref. 82, eqn. 24 gives a good representation of these data over the range of the water volume fractions from

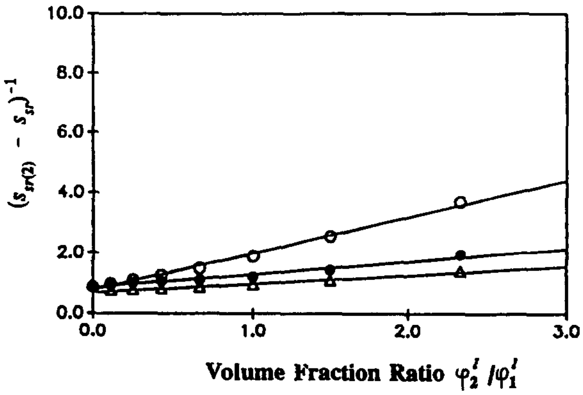

Fig. 4. The linear dependencies plotted according to eqn. 26 for the data shown in Fig. 3.

zero to 0.7. The observed deviation for the water-rich mobile phases is not unexpected since solution non-ideality effects are significant in this range; however, eqn. 4, used to obtain eqn. 26, was derived assuming ideality of both phases. The results presented in Fig. 4 show that interpretation of the methylene selectivity data can be improved significantly by taking into account the composition of solvents in the stationary phase. Even the use of a simple displacement model to represent the composition of solvents in the stationary phase, like that described by eqn. 4, gives a satisfactory description of RPLC systems. For instance, the equilibrium constant for the water–acetonitrile eluent evaluated according to eqn. 26 on the basis of the methylene selectivity data plotted in Fig. 4 is equal to 0.36. A value of K_{21} smaller than unity indicates a relatively strong sorption of acetonitrile from aqueous solutions, which is in a good agreement with the independent sorption measurements discussed in the previous section.

6. CONCLUDING REMARKS

The phenomenological thermodynamic description of the multicomponent sorption equilibria at the liquid–solid interface gives foundations for considering the solute's retention in LC with mixed mobile phases in terms of the partition and displacement models. In contrast to the LC processes occuring in some normal-phase systems or liquid–liquid systems, where the solute's retention can be represented, respectively, by the simple displacement or partition models, the RPLC process is more complex and its description by the above-mentioned models is not satisfactory. It is shown that a combined PD model needs to be used for representing this process. The current review demonstrates the theoretical and experimental arguments that justify the use of a simplified version of the PD model for studying RPLC systems. This simple model assumes that the solvent–surface phase is formed via a displacement mechanism and the solute's distribution occurs via a partition mechanism. The solvent–surface phase may be characterized on the basis of excess sorption measurements, as well as on the basis of RPLC data. A short discussion of this problem shows that further systematic studies are desirable in order to explain the role of the stationary phase in RPLC processes.

REFERENCES

1 L.R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.
2 W.R. Melander and Cs. Horváth, in Cs. Horváth (Editor), *High-Performance Liquid Chromatography — Advances and Perspectives*, Vol. 2, Academic Press, New York, 1980, p. 113.
3 R.P.W. Scott and C.F. Simpson, *Faraday Symp. Chem. Soc.*, 15 (1980) 69.
4 L.R. Snyder and H. Poppe, *J. Chromatogr.*, 184 (1980) 363.
5 M. Jaroniec and J. Oscik, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 3.
6 L.R. Snyder, in Cs. Horváth (Editor), *High-Performance Liquid Chromatography —Advances and Perspectives*, Vol. 3, Academic Press, New York, 1983, p. 157.
7 M. Jaroniec and J.A. Jaroniec, *J. Liq. Chromatogr.*, 7 (1984) 393.
8 M. Jaroniec, D.E. Martire and M. Borowko, *Adv. Colloid Interface Sci.*, 22 (1985) 177.
9 W. Rudzinski, in J.A. Jonsson (Editor), *Chromatographic Theory and Basis Principles*, Marcel Dekker, New York, 1987, p. 246.
10 L.C. Sander and A.A. Wise, *CRC Crit. Rev. Anal. Chem.*, 18 (1987) 417.
11 J.G. Dorsey and K.A. Dill, *Chem. Rev.*, 89 (1989) 331.
12 S. Gocan, in N. Grinberg (Editor), *Modern Thin-Layer Chromatography*, Marcel Dekker, New York, 1990, p. 175.
13 K.K. Unger, in K.K. Unger (Editor), *Packings and Stationary Phases in Chromatographic Techniques*, Marcel Dekker, New York, 1990, p. 331.
14 L.C. Sander, Ch.J. Clinka and S.A. Wise, *Anal. Chem.*, 62 (1990) 1099.
15 B. Buszewski and Z. Suprynowicz, *Chromatographia*, 24 (1987) 573.
16 P. Staszczuk and B. Buszewski, *Chromatographia*, 25 (1988) 881.
17 M. Jaroniec and D.E. Martire, *J. Chromatogr.*, 351 (1986) 1.
18 M. Jaroniec and D.E. Martire, *J. Liq. Chromatogr.*, 10 (1987) 541.
19 M. Jaroniec, *J. Liq. Chromatogr.*, 10 (1987) 1949.
20 M. Jaroniec, J. Narkiewicz and M. Borowko, *Chromatographia*, 112 (1978) 581.
21 M. Jaroniec, J.K. Rozylo and B. Oscik-Mendyk, *J. Chromatogr.*, 179 (1979) 237.
22 M. Jaroniec and A. Patrykiejew, *J. Chem. Soc., Faraday Trans. I*, 76 (1980) 2486.
23 M. Jaroniec and B. Oscik-Mendyk, *J. Chem. Soc., Farday Trans. I*, 77 (1981) 1277.

24 F. Koster and G.H. Findenegg, *Chromatographia*, 15 (1982) 743.

25 G.H. Findenegg and F. Koster, *J. Chem. Soc., Faraday Trans. I*, 82 (1986) 2691.

26 R.K. Gilpin, M. Jaroniec and S. Lin, *Anal. Chem.*, 62 (1990) 2092.

27 R.K. Gilpin, M. Jaroniec and S. Lin, *Anal. Chem.*, 63 (1991) 2849.

28 Cs. Horváth and W.R. Melander, *Chromatographia*, 18 (1984) 353.

29 B.L. Karger, J.N. LePage and N. Tanaka, *High Performance Liquid Chromatography*, Vol. 1, Academic Press, New York, 1980.

30 M. Borowko, M. Jaroniec and J. Piotrowska, *J. Liq. Chromatogr.*, 10 (1987) 2033.

31 M.T.W. Hearn, *Adv. Chromatogr.*, 18 (1980) 59.

32 Cs. Horváth, W. Melander and I. Molnár, *Anal. Chem.*, 49 (1977) 142.

33 M. Jaroniec and J. Piotrowska, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 257.

34 M. Jaroniec and J.A. Jaroniec, *J. Chromator.*, 210 (1981) 130.

35 M. Jaroniec and J.A. Jaroniec, *J. Liq. Chromatogr.*, 4 (1981) 2121.

36 M. Borowko and M. Jaroniec, *J. Chem. Soc., Faraday Trans. I*, 79 (1983) 363.

37 M. Jaroniec and J.A. Jaroniec, *J. Chromatogr.*, 295 (1984) 377.

38 M. Jaroniec, J.R. Rozylo and W. Golkiewicz, *J. Chromatogr.*, 178 (1979) 27.

39 M. Borowko and M. Jaroniec, *Chromatographia*, 12 (1979) 672.

40 M. Jaroniec and D.E. Martire, *J. Liq. Chromatogr.*, 8 (1985) 1953.

41 M. Jaroniec, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9 (1986) 452.

42 M. Jaroniec and R.K. Gilpin, *Langmuir*, 7 (1991) 1784.

43 E. Soczewinski, *J. Chromatogr.*, 130 (1977) 23.

44 M. Borowko, *J. Chem. Soc., Faraday Trans. I*, 84 (1988) 1961.

45 Ch. Yan and D.E. Martire, *J. Phys. Chem.*, 96 (1992) 3489, 3505.

46 R.K. Gilpin and J.A. Squires, *J. Chromatogr., Sci.*, 19 (1981) 195.

47 S.S. Yang and R.K. Gilpin, *J. Chromatogr.*, 394 (1987) 295.

48 S.S. Yang and R.K. Gilpin, *J. Chromatogr.*, 449 (1988) 115.

49 R.K. Gilpin, M.E. Gangoda and A.E. Krishen, *J. Chromatogr. Sci.*, 20 (1982) 345.

50 R.E. Boehm and D.E. Martire, *J. Phys. Chem.*, 84 (1980) 3620.

51 D.E. Martire and R.E. Boehm, *J. Phys. Chem.*, 87 (1983) 1045.

52 D.E. Martire and R.E. Boehm, *J. Liq. Chromatogr.*, 3 (1980) 753.

53 D.E. Martire and R.E. Boehm, *J. Phys. Chem.*, 91 (1987) 2433.

54 D.E. Martire, *J. Liq. Chromatogr.*, 10 (1987) 1569; 11 (1988) 1779.

55 K.A. Dill, *J. Phys. Chem.*, 91 (1987) 1980.

56 M.R. Bohmer, L.K. Koopal and R. Tijssen, *J. Phys. Chem.*, 95 (1991) 6285.

57 P. Jandera, *J. Chromatogr.*, 314 (1984) 13.

58 P. Jandera, H. Colin and G. Guiochon, *Anal. Chem.*, 54 (1982) 435.

59 H. Colin, G. Guiochon and P. Jandera, *Anal. Chem.*, 55 (1983) 442.

60 H. Colin, G. Guiochon and P. Jandera, *Chromatographia*, 17 (1983) 83.

61 Cs. Horváth, W. Melander and I. Molnar, *J. Chromatogr.*, 125 (1976) 129.

62 Cs. Horváth, W. Melander and A. Nahum, *J. Chromatogr.*, 186 (1979) 371.

63 W.R. Melander, J. Stoveken and Cs. Horváth, *J. Chromatogr.*, 185 (1979) 111.

64 K.G. Wahlund and A. Sokolowski, *J. Chromatogr.*, 151 (1978) 299.

65 A. Nahum and Cs. Horvath, *J. Chromatogr.*, 203 (1981) 53.

66 R.N. Nikolov, *J. Chromatogr.*, 288 (1984) 147.

67 L. Nondek, B. Buszewski and D. Berek, *J. Chromatogr.*, 360 (1986) 241.

68 J. Nawrocki and B. Buszewski, *J. Chromatogr.*, 449 (1988) 1.

69 B. Buszewski, Z. Suprynowicz, P. Staszczuk, K. Albet, B. Pfleiderer and E. Bayer, *J. Chromatogr.*, 499 (1990) 305.

70 H. Engelhardt, H. Low and W. Gotzinger, *J. Chromatogr.*, 544 (1991) 371.

71 P.C. Sadek and P.W. Carr, *J. Chromatogr. Sci.*, 21 (1983) 314.

72 M. Schantz, B.N. Barman and D.E. Martire, *J. Res. Natl. Bur. Stand.*, 93 (1988) 161.

73 M. Jaroniec and D.E. Martire, *J. Chromatogr.*, 387 (1987) 55.

74 M. Jaroniec and R. Madey, *Physical Adsorption on Heterogeneous Solids*, Elsevier, Amsterdam, 1988.

75 A. Dabrowski, M. Jaroniec and J. Oscik, *Colloid Surface Sci.*, 14 (1987) 83.

76 A. Dabrowski, M. Jaroniec and J.K. Garbacz, *Thin Solid Films*, 103 (1983) 399.

77 J.R. Conder and C.L. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley, Chichester, 1979.

78 A. Hussam and P.W. Carr, *Anal. Chem.*, 57 (1985) 793.

79 W.J. Cheong and P.W. Carr, *J. Chromatogr.*, 500 (1990) 215; 499 (1990) 373.

80 J.M. Prausnitz, *Molecular Thermodynaics of Fluid-Phase Equilibria*, Prentice-Hall, Englewood Cliffs, 2nd Ed., 1986.

81 D.H. Everett, *J. Chem. Soc., Faraday Trans.*, 60 (1964) 1803.

82 R.K. Gilpin, M. Jaroniec and S. Lin, *Chromatographia*, 30 (1990) 393.

83 M. Jaroniec, S. Lin and R.K. Gilpin, *Chromatographia*, 32 (1991) 13.

84 D.E. Martire and M. Jaroniec, *J. Liq. Chromatogr.*, 8 (1985) 1363.

85 M. Jaroniec, D.E. Martire and J. Oscik, *J. Liq. Chromatogr.*, 9 (1986) 2555.

86 M.M. Dubinin, T.S. Jakubov, M. Jaroniec and V.V. Serpinsky, *Polish J. Chem.*, 54 (1980) 1721.

87 A. Dabrowski, M. Jaroniec and J. Oscik, *Adsorption Sci. Technol.*, 3 (1986) 221.

88 A. Dabrowski, M. Jaroniec and J.K. Garbacz, *Chem. Scripta*, 29 (1989) 21.

89 E.H. Slaats, J.C. Kraak, W.J.T. Brugman and H. Poppe, *J. Chromatogr.*, 149 (1978) 255.

90 M. Borowko, *J. Colloid Interface Sci.*, 102 (1984) 519.

91 C.R. Yonker, T.A. Zwier and M.F. Burke, *J. Chromatogr.*, 241 (1982) 257, 269.

92 R.M. McCormick and B.L. Karger, *Anal. Chem.*, 52 (1980) 2249.

93 E.H. Slaats, W. Markowski, J. Fekete and H. Poppe, *J. Chromatogr.*, 207 (1981) 299.

94 F. Riedo and E. sz. Kováts, *J. Chromatogr.*, 239 (1982) 1.

95 N.L. Ha, J. Ungvaral and E. sz Kováts, *Anal. Chem.*, 54 (1982) 2410.

96 C.S. Koch, F. Koster and G.H. Findenegg, *J. Chromatogr.*, 406 (1987) 257.

97 A. Alvarez-Zepeda and D.E. Martire, *J. Chromatogr.*, 550 (1991) 285.

98 M. Jaroniec and R.K. Gilpin, *J. Liq. Chromatogr.*, 15 (1992) 1431.

99 B.P. Johnson, M.G. Khaledi and J.G. Dorsey, *J. Chromatogr.*, 384 (1987) 221.

100 P.C. Sadek, P.W. Carr and M. Ruggio, *Anal. Chem.*, 59 (1987) 1032.

101 H. Colin, G. Guiochon, Z. Yun, J.C. Diez-Masa and P. Jandera, *J. Chromatogr. Sci.*, 21 (1983) 179.

102 J.G. Dorsey and B.P. Johnson, *J. Liq. Chromatogr.*, 10 (1987) 2695.

103 B.L. Karger, J.R. Gant, A. Hartkopf and P.H. Weiner, *J. Chromatogr.*, 128 (1976) 65.

104 P. Dufek, *J. Chromatogr.*, 281 (1983) 49.

105 I.Z. Atamna, G.M. Muschik and H.J. Issaq, *J. Liq. Chromatogr.*, 12 (1989) 2227.

106 H. Colin and G. Guiochon, *J. Chromatogr. Sci.*, 18 (1980) 54.

107 K.B. Sentell and J.G. Dorsey, *J. Chromatogr.*, 461 (1989) 193.

108 D.H. Everett, *Colloid Science: Specialist Periodical Reports*, Vol. 1, Chemical Society, London, 1973, Ch. 2.

109 C.E. Brown and D.H. Everett, *Colloid Science: Specialist Periodical Reports*, Vol. 2, Chemical Society, London, 1975, Ch. 2.

110 D.H. Everett and R.T. Podoll, *Colloid Science: Specialist Periodical Reports*, Vol. 3, Chemical Society, London, 1979, Ch. 2.

111 J. Davis and D.H. Everett, *Colloid Science: Specialist Periodical Reports*, Vol. 4, Chemical Society, London, 1983, Ch. 3.

112 J. Oscik, *Adsorption*, Ellis Horwood, Chichester, 1982.

113 M. Jaroniec, *Adv. Colloid Interface Sci.*, 18 (1983) 149.

114 M. Borowko and M. Jaroniec, *Adv. Colloid Interface Sci.*, 22 (1985) 177.

115 A. Dabrowski and M. Jaroniec, *Adv. Colloid Interface Sci.*, 27 (1987) 211.

116 A. Dabrowski and M. Jaroniec, *Adv. Colloid Interface Sci.*, 31 (1990) 155.

117 D.H. Everett, *Pure Appl. Chem.*, 58 (1986) 967.

118 B. Oscik-Mendyk, J.K. Rozylo and M. Jaroniec, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 74.

119 B. Oscik-Mendyk, *J. Planar Chromatogr.*, 3 (1990) 322.

120 K. Tani and Y. Suzuki, *J. Chromatogr. Sci.*, 27 (1989) 698.

121 L.C. Sander and S.A. Wise, *J. Chromatogr.*, 316 (1984) 163.

122 *Waters Sourcebook of Chromatography*, Millipore-waters, Milford, MA, 1993.

123 B. Buszewski and R. Nasuto, *J. Anal. Chem. USSR (Engl. Transl.)*, 45 (1990) 1547.

124 H. Colin and G. Guiochon, *J. Chromatogr. Sci.*, 18 (1980) 54.

125 P.J. Schoenmakers, H.A.H. Billiet and L. de Galan, *J. Chromatogr.*, 218 (1981) 261.

126 M. Hirukawa, Y. Arai and T. Hanai, *J. Chromatogr.*, 395 (1987) 481.

127 P. Jandera, *J. Chromatogr.*, 314 (1984) 13.