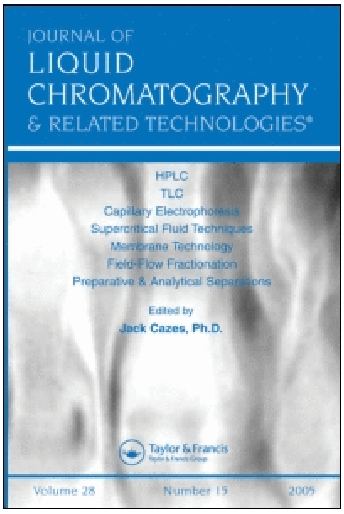

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Theoretical Foundations of Liquid Adsorption Chromatography with Mixed Eluent

M. Jaroniec[a]; J. A. Jaroniec[a]
[a] Institute of Chemistry, M. Curie-Skłodowska University, Lublin, Poland

To cite this Article Jaroniec, M. and Jaroniec, J. A.(1984) 'Theoretical Foundations of Liquid Adsorption Chromatography with Mixed Eluent', Journal of Liquid Chromatography & Related Technologies, 7: 10, 393 — 431
To link to this Article: DOI: 10.1080/01483918408073944
URL: http://dx.doi.org/10.1080/01483918408073944

JOURNAL OF LIQUID CHROMATOGRAPHY, 7(S-2), 393-431 (1984)

THEORETICAL FOUNDATIONS OF LIQUID ADSORPTION CHROMATOGRAPHY WITH MIXED ELUENT

M. Jaroniec and J.A. Jaroniec
Institute of Chemistry, M.Curie-Skłodowska University,
20031 Lublin, Poland

INTRODUCTION

One of the main advantages of liquid-solid (adsorption) chromatography (LSC) with mixed eluent is the possibility of modification of the capacity ratio over a wide range by changing the eluent composition [1]. It means that the resolution and the analysis time may be optimized by correct choice of the eluent composition (isocratic LSC) or by eluent programing during the chromatographic process (gradient LSC). Optimization of the chromatographic process requires of the knowledge of dependence of the chromatographic quantities on the eluent composition [2-5]. Increasing interest in gradient LSC [2-13] has created a pressing need for the elucidation of the theoretical basis of LSC with mixed eluent.

Many attempts have been made to describe the dependence of the capacity ratio on the eluent composition [14-21]. The fundamental ideas in this field have been formulated by Snyder [14,21,22], Ościk [23-25] and Soczewiński [15,26], and developed theoretically by Jaroniec et al. [27-34]. They pointed many factors determining the LSC process with mixed eluent : (a) competitive character of solute and solvent adsorption,

0148-3919/84/07S2-0393$3.50/0

(b) non-specific and specific solute-solvent and solvent-solvent interactions in the mobile and surface phases,

(c) association or dissociation of components in the mobile and surface phases,

(d) differences in molecular sizes of solutes and solvents,

(e) multilayer character of the surface phase and contribution of the partition phenomena in the LSC process,

(f) orientation of solute and solvent molecules in the surface phase, and

(g) energetic heterogeneity of the adsorbent and topography of adsorption sites onto surface.

These factors determined mainly the adsorption effects in the LSC process.The other group of factors, such as : diffusion, porous structure of the adsorbent, parameters characterizing the eluent flow, etc., determines kinetics of the LSC process. The problem of their optimization is described in the many monographs devoted to chromatography.

In this chapter we shall present the theoretical studies dealing with the effects specified in the points (a) - (g). One of the first formulations of the LSC process with mixed eluent has been made by Ościk [23-25].Basing on the thermodynamics of conformal solutions [35], he derived an equation for the $R_{M,s}$ value of the s-th solute chromatographed in n-component eluent. This equation has been derived for energetically homogeneous solid surfaces.Its theoretical analysis is presented in the papers [25,27,16].The clasical Ościk's equation has been recently extended to energetically heterogeneous solid surfaces [36-38]. Moreover,it has been widely examined by using the thin-layer chromatographic (TLC) data [39-45].It is difficult to discuss the influence of the factors (a)-(g) on the LSC process in terms of the Ościk's formulation,because it is too much general and gives a scanty information about mechanism of the LSC process. Therefore,our discussion will be concentrated on the theoretical treatments assuming a definite model of the LSC process.

The most popular treatment of LSC with mixed eluent has been formulated by Snyder [14,22],which assumes the competitive character of solute and solvent adsorption.This treatment involves also energetic heterogeneity of the solid surface [14] and solute-solvent localization effects [46].Recently,Snyder's treatment has been extended to LSC with multicomponent eluent [16,27,47-49].The LSC model of Snyder [14,21] has been considerably enriched by Soczewiński studies [15,26].On the other hand, Jaroniec et al.[16,27-34] described theoretically the LSC process by applying the general theory of adsorption from multicomponent liquid mixtures on solid surfaces and utilizing the fundamental studies of Snyder [14,22] and Soczewiński [15,26].The treatment of Jaroniec et al. involves energetic heterogeneity of the solid surface [27-29,50-55],non-ideality of both phases [27,28,33], differences in molecular sizes of solute and solvents [29,31,56], and solute-solvent and solvent-solvent interactions in the mobile phase [30,31,57-60].Recent studies of Jaroniec et al.[29,37,56,61] concern the correlation between adsorption and chromatographic parameters.An attempt of a global description of the LSC process with mixed eluent,involving different effects specified in the points (a)-(g),has been undertaken by M.Jaroniec and J.A.Jaroniec [31].This chapter has been written basing on the paper [31]. We shall show that the majority of equations derived for the capacity ratio in LSC with mixed eluent may be obtained from our general treatment; they are : equations of Snyder [14], Snyder-Soczewiński [21,26], Slaats et al.[62].

GENERAL CONSIDERATIONS

One of the most important quantities in LSC is the capacity ratio k'_s ,which is defined as the ratio of the number of moles of the s-th component in the surface phase to the number of moles of this component in the mobile phase.The other fundamental chromatographic quantities, such as retention volume, retention time, selectivity and resolution, may be expressed by means of the capacity ratio. The capacity ratio k'_s is proportional to the distribution coefficient k_s :

$$k_s = x^s_s/x^l_s = C\ k'_s \tag{1}$$

where C is a parameter which is assumed, to a first approximation, to be characteristic of a given adsorbent and independent of the nature of the eluent [14,33]. In the above x^s_s and x^l_s are the total mole fractions of the s-th solute in the surface (s) and mobile (liquid) (l) phases, respectively.

The fundamental quantities employed in TLC are R_F and R_M. These values are related to the capacity ratio by the following equation [63] :

$$R_{M,s} = \log\ [(1-R_{F,s})/R_{F,s}] = \log\ k'_s \tag{2}$$

Eq.(2) may be used for interconversion of equations applied in LSC and TLC.

Let us consider the LSC process for the s-th substance (solute) chromatographed in n-component eluent. The components of the mixed eluent are numbered successively beginning from the most efficient eluting solvent to the weakest solvent. Thus, 1-st solvent is the more efficient one, however, n-th component is the weakest solvent. One of the main assumptions of the proposed model is that concerning the competitive character of solute and solvent adsorption.

The adsorption process may be represented by the following reversible phase-exchange reactions [28] :

$$i^{(l)} + n^{(s)} \rightleftarrows i^{(s)} + n^{(l)} \quad \text{for } i = 1,2,\dots,n-1 \tag{3}$$

$$s^{(l)} + r\ i^{(s)} \rightleftarrows s^{(s)} + r\ i^{(l)} \quad \text{for } i = 1,2,\dots,n \tag{4}$$

where the subscripts (l) and (s) refer to the mobile and surface phases, respectively, "i" and "s" denote molecules of the i-th solvent and s-th solute, and r is the ratio of molecular sizes of the s-th solute and the i-th solvent. The reactions (3) and (4) have been written by assuming the equality of molecular sizes of all solvents, i.e.,

$$w_1 = w_2 = \cdots = w_n = w \qquad (5)$$

and inequality of molecular sizes of solute and solvents :

$$w_s \neq w \qquad (6)$$

Thus,the parameter r is defined as follows :

$$r = w_s/w \qquad (7)$$

The next assumptions are following :

(a) the surface phase is assumed to be monolayer,

(b) the total number of moles of all solvents in the surface phase is constant and independent upon the presence of solute molecules,because the solute concentration is infinitely low,and

(c) molecules of solute and solvents have a spherical shape.

Further assumptions concern interactions in the surface and mobile phases and energetic heterogeneity of the adsorbent surface.

A MODEL INVOLVING NON-SPECIFIC INTERACTIONS BETWEEN MOLECULES OF SOLUTE AND SOLVENTS

Homogeneous solid surfaces

The non-specific interactions between molecules of solute and solvents in the mobile and surface phases are described in terms of the activity coefficients.The activities of the s-th solute and i-th solvent in the mobile and surface phases are defined as follows:

$$a_s^l = x_s^l f_s^l \qquad (8a)$$

$$a_i^l = x_i^l f_i^l \quad \text{for } i=1,2,\ldots,n \qquad (8b)$$

$$a_s^s = x_s^s f_s^s \qquad (9a)$$

$$a_i^s = x_i^s f_i^s \quad \text{for } i=1,2,\ldots,n \qquad (9b)$$

where f_s^s , f_i^s , f_s^l and f_i^l are the activity coefficients of the s-th solute and i-th solvent in the surface and mobile phases,respectively. The activity coefficients f_s^s and f_i^s are functions of the composition of the surface solution,whereas, f_s^l and f_i^l are functions of the composition of the bulk solution.

According to our previous studies [16,28,31] the reaction (4) for i=1 and the set of reactions (3) characterize synonymously the LSC process with mixed eluent. The thermodynamic equilibrium constants corresponding to these reactions may be written in the following form :

$$K_{s1}^{th} = \frac{a_s^s}{a_s^l}\left(\frac{a_1^l}{a_1^s}\right)^r = \frac{x_s^s}{x_s^l}\left(\frac{x_1^l}{x_1^s}\right)^r \cdot \beta_{s1} \qquad (10)$$

$$K_{in}^{th} = \frac{a_i^s}{a_i^l} \cdot \frac{a_n^l}{a_n^s} = \frac{x_i^s}{x_i^l} \cdot \frac{x_n^l}{x_n^s} \cdot \beta_{in} \quad \text{for } i= 1,2,\ldots,n-1 \qquad (11)$$

where

$$\beta_{s1} = \frac{f_s^s}{f_s^l}\left(\frac{f_1^l}{f_1^s}\right)^r \qquad (12)$$

$$\beta_{in} = \frac{f_i^s}{f_i^l} \cdot \frac{f_n^l}{f_n^s} \quad \text{for } i= 1,2,\ldots,n-1 \qquad (13)$$

Combining eqs.(1) and (10) we obtain the most general equation for the capacity ratio of the s-th solute chromatographed in n-component eluent on an energetically homogeneous solid surface :

$$k_s' = K_{s1}^{th}\,(C\,\beta_{s1})^{-1}\,(x_1^s/x_1^l)^r \qquad (14)$$

or

$$\ln k_s' = \ln(K_{s1}^{th}/C) + r\ln(x_1^s/x_1^l) - \ln \beta_{s1} \qquad (15)$$

The mole fraction of 1-st solvent in the surface phase may be calculated according to the following expression :

$$x_1^s = \frac{(K_{1n}^{th}/\beta_{1n})\,x_1^l}{x_n^l + \sum_{i=1}^{n-1}(K_{in}^{th}/\beta_{in})\,x_i^l} \qquad (16)$$

Eq.(16) is one of the fundamental equations in the theory of adsorption from multicomponent liquid mixtures [64-68]. This equation describes adsorption of 1-st solvent from n-component liquid mixture on a homogeneous solid surface by assuming equality of molecular sizes of all solvents (eq.5) and non-ideality of the bulk and surface solutions ($\beta_{in} \neq 1$ for $i=1,2,\dots,n-1$).Similarly,eq.(14) has been derived by applying these same assumptions as in the case of eq.(16) and including an additional assumption (6).

Now,we shall consider the special cases of eq.(14).Assuming in eq.(14) ideality of the surface phase ($f^s_s = f^s_1 = f^s_2 = \dots = f^s_n = 1$), non-ideality of the mobile phase ($f^l_s \neq f^l_1 \neq f^l_2 \neq \dots \neq f^s_n \neq 1$) and $r \neq 1$ (difference in the molecular sizes of solute and solvents) we have :

$$k'_s = K^{th}_{s1} \, (f^l_s/C) \, (x^s_1/a^l_1)^r \tag{17}$$

and

$$x^s_1 = K^{th}_{1n} \, a^l_1 \, / (a^l_n + \sum_{i=1}^{n-1} K^{th}_{in} \, a^l_i) \tag{18}$$

If the elution strength of the 1-st solvent is considerably greater than the strengths of the other solvents,then the mole fraction x^s_1 is practically equal to unity in the whole concentration region of x^l_1 except at low concentrations of the 1-st solvent.Taking this fact into account in eq.(17) we get the relationship :

$$\ln k'_s = \ln(K^{th}_{s1}/C) - r \ln a^l_1 + \ln f^l_s \tag{19}$$

The above relationship has been derived and examined experimentally by Slaats et al.[62].However,eq.(19) with $r=1$ and a regular mobile phase has been discussed by Jaroniec et al.[33].

Assuming both phases to be ideal and $r \neq 1$ in eq.(14) we have :

$$k'_s = (K^{th}_{s1}/C) \, (x^s_1/x^l_1)^r \tag{20}$$

where

$$x^s_1 = K^{th}_{1n} \, x^l_1/(x^l_n + \sum_{i=1}^{n-1} K^{th}_{in} \, x^l_i) \tag{21}$$

Eq.(20) has been derived by Jaroniec et al.[56] and it was widely examined by using TLC data for binary eluents.For $x^s_1=1$ (large difference in elution strength between the 1-st and other solvents), eq.(20) gives :

$$\ln k'_s = \ln(K^{th}_{s1}/C) - r \ln x^1_1 \qquad (22)$$

Theoretical studies [27,33] show that the capacity ratio of the s-th solute in the 1-st pure solvent is connected with K^{th}_{s1} in the following way :

$$k'_{s1} = K^{th}_{s1}/C \qquad (23)$$

Then,eq.(22) assumes a more simpler form :

$$\ln k'_s = \ln k'_{s1} - r \ln x^1_1 \qquad (24)$$

Eq.(24) ,known as the Snyder-Soczewiński relationship [21,26], is one of the most popular equations in the theory of LSC.Jandera and Churacek [69] derived this equation by using Snyder's relationship for elution strength of a binary solvent [14,21].The correct analysis of Snyder's treatment [14] leads to eq.(24) with r=1 .The derivation of eq.(24) in terms of Snyder's treatment [14] by Jandera and Churacek [69] is slightly inconsistent [27,70].However,the full form of this equation results from theoretical considerations of Soczewiński [26] and our studies [16,29,31,56].Eq.(24) is widely used for characterizing LSC systems [71-86]; in reference [71] the chromatographic systems comply with this equation are discussed.

The very important relationship (25) may be obtained from eqs.(20),(21) and (23) for r = 1 ; it is

$$1/k'_s = \sum_{i=1}^{n-1} x^1_i/k'_{si} \qquad (25)$$

This relationship has been derived by Jaroniec et al.[27] in terms of the theory of adsorption from ideal multicomponent liquid mixtures on homogeneous solid surfaces.It may be rewritten in the equivalent form:

$$k'_s = \sum_{i=1}^{n-1} x^s_i\, k'_{si} \qquad (26)$$

Eq.(66) assumes the additivity of the capacity ratios k'_{si} for $i=1,2,\ldots,n$,and in this form it has been written by Snyder [14]. Eq.(25) for n=2 gives the following important relationship [70]:

$$1/k'_s = 1/k'_{s2} + (1/k'_{s1} - 1/k'_{s2})\, x_1^l \tag{27}$$

The same type of dependence of the capacity ratio upon the mobile phase composition results from Scott and Kucera treatment [18].

Heterogeneous solid surfaces

Let us consider an energetically heterogeneous solid surface showing L types of adsorption sites.Let h_l be the ratio of the number of adsorption sites of the l-th type to the total number of adsorption sites.The ratios h_l for $l=1,2,\ldots,L$ fulfil the relationship :

$$\sum_{l=1}^{L} h_l = 1 \tag{28}$$

The capacity ratio of the s-th solute on the entire heterogeneous solid surface $k'_{s,t}$ is defined as follows [14,16,34]:

$$k'_{s,t} = \sum_{l=1}^{L} h_l\, k'_{s,l} \tag{29}$$

where $k'_{s,l}$ is the capacity ratio of the s-th solute for the l-th type of adsorption sites.The mathematical form of $k'_{s,l}$ is analogous to eq.(14).Since eq.(14) contains the activity coefficients of solute and solvents in the surface phase,which are functions of the surface phase composition,we consider their definitions by assuming two different distributions of adsorption sites on the surface.Theoretical considerations of adsorption models with non-ideal surface phase require always of an additional assumption about topography of adsorption sites on the surface [67,68].Usually two models of heterogeneous surfaces are considered.According to the first model the adsorption sites are distributed randomly onto surface,whereas, the second assumes the patchwise distribution of adsorption sites.

For the patchwise surfaces the activity coefficients are functions of composition of surface solution being on the l-th surface patch. However, for surfaces of random distribution of adsorption sites the activity coefficients are functions of the mole fractions of solute and solvents refering to the entire surface solution. The total mole fraction $x^s_{1,t}$, refering to the entire surface, is expressed as follows :

$$x^s_{1,t} = \sum_{l=1}^{L} h_l \, x^s_{1,l} \tag{30}$$

Taking into account the above discussion concerning the activity coefficients in the surface phase and eq.(14), we can write the following expressions for $k'_{s,l}$:

$$k'_{s,l} = K^{th}_{s1,l} \, (C \, \beta_{s1,l})^{-1} \, (x^s_{1,l}/x^l_1)^r \text{ for patchwise surfaces} \tag{31}$$

$$k'_{s,l} = K^{th}_{s1,l} \, (C \, \beta_{s1,t})^{-1} (x^s_{1,l}/x^l_1)^r \quad \text{for random surfaces} \tag{32}$$

Substituting eqs.(31) and (32) to eq.(29) we obtain the expressions for the capacity ratio on heterogeneous surfaces of patchwise and random distribution of adsorption sites. The most important equation is obtained for random surfaces; it is :

$$k'_{s,t} = C^{-1} \frac{f^l_s}{f^s_{s,t}} \left(\frac{f^s_{1,t}}{a^l_1} \right)^r \sum_{l=1}^{L} h_l \, K^{th}_{s1,l} \, (x^s_{1,l})^r \tag{33}$$

where $f^s_{s,t}$ and $f^s_{1,t}$ are functions $x^s_{1,t}$, $x^s_{2,t}$,...., $x^s_{n,t}$.
It has been shown in the paper [34] that for adsorbents characterized by quasi-Gaussian energy distribution eq.(33) may be approximated as follows :

$$k'_{s,t} = C^{-1} \frac{f^l_s}{f^s_{s,t}} \left(\frac{f^s_{1,t}}{a^l_1} \right)^r \bar{K}^{th}_{s1} \, (x^s_{1,t})^{r/m} \tag{34}$$

where

$$x^s_{1,t} = (\bar{K}^{th}_{1n} \, x^l_1/\beta_{1n,t})^m \Big/ \left[(x^l_n)^m + \sum_{i=1}^{n-1} (\bar{K}^{th}_{in} \, x^l_i/\beta_{in,t})^m \right] \tag{35}$$

and m is the heterogeneity parameter relating to the width of the quasi-Gaussian distribution and $\bar{K}^{th}_{s1}$ is an average from $K^{th}_{s1,i}$ values.

Now,we consider the special cases of eq.(34) in a manner analogous to that adopted in the previous section.

For ideal surface phase and non-ideal mobile phase eqs.(34) and (35) assume the following form:

$$k'_{s,t} = C^{-1} f^l_s (a^l_1)^{-r} \bar{K}^{th}_{s1} (x^s_{1,t})^{r/m} \tag{36}$$

and

$$x^s_{1,t} = (\bar{K}^{th}_{1n} a^l_1)^m / \left[(a^l_n)^m + \sum_{i=1}^{n-1} (\bar{K}^{th}_{in} a^l_i)^m \right] \tag{37}$$

For m=1 eq.(37) reduces to eq.(18); however, for $x^s_{1,t} = 1$ it becomes eq.(19).According to eq.(36) ,for a large difference in elution strengths between the 1-st and other solvents,the energetic heterogeneity of the adsorbent surface does not influence the capacity ratio,because we obtain for $x^s_{1,t} = 1$ the same relationship as for homogeneous solid surfaces (cf.eq.19).Since eq.(36) has been obtained for ideal surface phase,it may be applied for heterogeneous surfaces showing quasi-Gaussian energy distribution and arbitrary topography of adsorption sites[28].

If both phases are ideal,eqs.(34) and (35) reduce to the following expressions :

$$k'_{s,t} = C^{-1} \bar{K}^{th}_{s1} (x^l_1)^{-r} (x^s_{1,t})^{r/m} \tag{38}$$

where

$$x^s_{1,t} = (\bar{K}^{th}_{1n} x^l_1)^m / \left[(x^l_n)^m + \sum_{i=1}^{n-1} (\bar{K}^{th}_{in} x^l_i)^m \right] \tag{39}$$

For $x^s_{1,t} = 1$ eq.(38) becomes the Snyder-Soczewiński relationship (24).

For r=1 (equal molecular sizes of solutes and solvents) eqs.(38) and (39) give the following relationship :

$$(1/k'_{s,t})^m = \sum_{i=1}^{n} (x_i^l/k'_{si,t})^m \tag{40}$$

Eq.(40) defines the capacity ratio $k'_{s,t}$ by means of the capacity ratios $k'_{si,t}$ and the parameter m. This equation has been derived by Jaroniec et al.[34]. This equation may be rewritten in the other form :

$$k'_{s,t} = \sum_{i=1}^{n} k'_{si,t} \, (x_{i,t}^s)^{1/m} \tag{41}$$

which for m=1 reduces to the relationship (26).

Eq.(40) was examined by using HPLC data [34] and TLC data for binary [51] and ternary eluents [52,53]. The chromatographic data for binary eluents were presented in the following linear form :

$$(k'_{s,t} \, x_1^l)^{-m} = (k'_{s1,t})^{-m} + (k'_{s2,t})^{-m} \, (x_2^l/x_1^l)^m \tag{42}$$

In the case of TLC data eq.(42) may be rewritten as follows [51]:

$$(x_1^l \, 10^{R_{M,s}})^{-m} = A_2 \, (x_2^l/x_1^l)^m + B_2 \tag{43}$$

where

$$A_2 = 10^{-mR_{M,s2}} \quad ; \; B_2 = 10^{-m \, R_{M,s1}} \tag{44}$$

However, in the case of ternary eluents eq.(40) for TLC gives [52,53]:

$$F = (x_2^l \, 10^{R_{M,s}})^{-m} = A_3 (x_1^l/x_2^l)^m + B_3 \tag{45}$$

where

$$A_3 = 10^{-m \, R_{M,s1}} \tag{46}$$

and

$$B_3 = 10^{-m \, R_{M,s2}} + (x_3^l/x_2^l)^m \, 10^{-m \, R_{M,s3}} \tag{47}$$

If the experimental data $R_{M,s}$ are measured at x_3^l/x_2^l = const , the dependence F vs. $(x_1^l/x_2^l)^m$ is linear.

For the purpose of illustration we presented the results of numerical

analysis of TLC data made by means of eq.(45).These results concern the TLC data for eight polycyclic hydrocarbons chromatographed in chloroform(1)/toluene(2)/benzene(3) and chloroform(1)/toluene(2)/ carbon tetrachloride(3) eluents on silica gel at 25°C [52].
All measurements were carried out at $x_3/x_2=1.0$ .Fig.1 shows the linear dependence (45) for selected solutes.It follows from this figure that eq.(45) gives a good representation of the above TLC data.The parameters m , A_3 and B_3 ,found from the linear plots (45),are summarized in Table 1.In this table the R_M-values for polycyclic hydrocarbons chromatographed in single solvents, i.e., $R_{M,s1}$, $R_{M,s2}$, $R_{M,s3}$ are also given.These values have been used for prediction of the parameters A_3 and B_3 according to eqs.(46) and (47), and are denoted by A_3^o and B_3^o (c.f., Table 1).The parameters A_3^o and B_3^o,calculated directly from experimental values of $R_{M,s1}$, $R_{M,s2}$ and $R_{M,s3}$ according to eqs.(46) and (47),and those evaluated from TLC data for ternary eluents by means of eq.(45), are compared in Table 1 .It follows from this comparison that differences between A_3 and A_3^o , B_3 and B_3^o are rather small.Analysis of the parameter m shows that it is practically independent on the kind of polycyclic hydrocarbon ;it is characteristic for a given eluent and adsorbent. Similar results were also obtained for other TLC systems [34,51,87]. A good agreement between A_3 and A_3^o , B_3 and B_3^o ,and insignificant dependence of m on type of the solute create possibility for predicting the $R_{M,s}$-values for solutes chromatographed in ternary eluents by means of the experimental values of $R_{M,s1}$, $R_{M,s2}$, $R_{M,s3}$ and the parameter m .Such prediction is impossible for chromatographic systems,which show great differences in A_3 and A_3^o , B_3 and B_3^o ,and for which the parameter m depends strongly upon type of the solute.A great difference between A_3 and A_3^o , B_3 and B_3^o is observed for mobile phases of strong specific interactions between molecules of solute and solvents.In the next section we shall discuss the equations involving the specific solute-solvent and solvent-solvent interactions in the mobile phase.

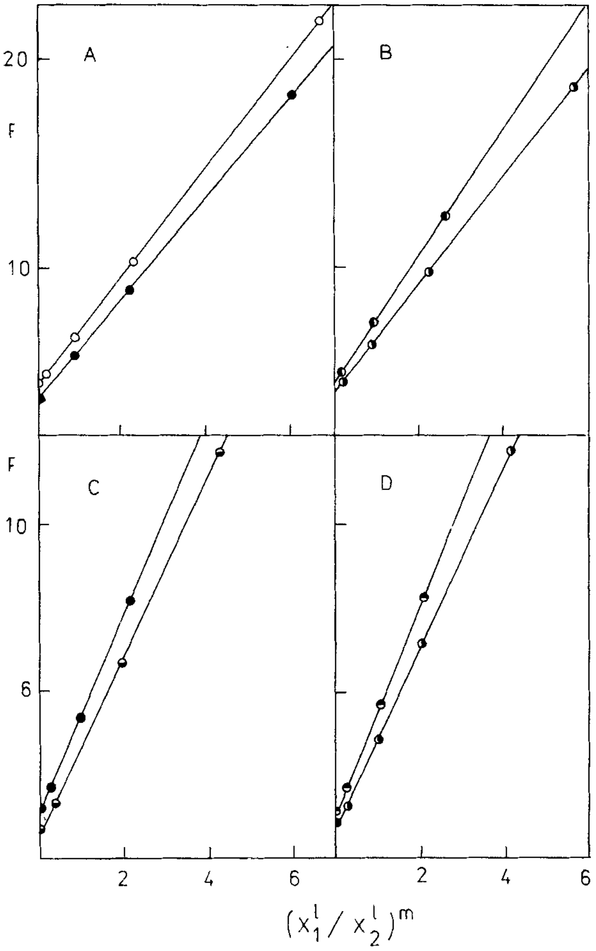

Figure 1. Linear dependences plotted according to Eq. 45 for selected polycyclic hydrocarbons in chloroform (1)/toluene (2)/ benzene (3) (parts A & B) and chloroform (1)/toluene (2)/carbon tetrachloride (3) (parts C & D).
● = pyrene; ◑ = benzopyrene; ○ = phenanthrene; ◓ = chrysene; ◒ = fluoranthene; ◐ = naphthalene. Figure taken from ref. [52], with permission of the copyright owner.

The mathematical properties of equations involving the adsorbent heterogeneity we shall illustrate by using the following expression :

$$R_M = -(1/m)\ \log[(x_1^l 10^{-R_{M,s1}})^m + (x_2^l 10^{-R_{M,s2}})^m] \qquad (48)$$

Eq.(48) has been obtained by combining eq.(40) for n=2 and eq.(2').

Table 1

Parameters Characterizing TLC Data of Polycyclic Hydrocarbons in Three-Component Mobile Phases on Silica Gel at 25°C [52]

Substance	$R_{M,s1}$	$R_{M,s2}$	$R_{M,s3}$	m	A_3	A_3^o	B_3	B_3^o
chloroform(1)/toluene(2)/benzene(3)								
Pyrene	−0.43	−0.27	−0.25	0.98	2.44	2.65	3.62	3.58
Benzopyrene	−0.41	−0.25	−0.37	1.02	2.55	2.62	3.96	4.17
Phenanthrene	−0.41	−0.27	−0.39	1.04	2.60	2.66	4.30	4.44
Chrysene	−0.41	−0.25	−0.35	1.04	2.47	2.66	4.37	4.12
Fluoranthene	−0.41	−0.24	−0.36	1.06	2.53	2.72	4.27	4.19
Anthracene	−0.41	−0.23	−0.37	1.06	2.68	2.72	3.89	4.21
Diphenyl	−0.41	−0.28	−0.39	1.04	2.82	2.99	5.07	4.93
Naphthalene	−0.43	−0.27	−0.40	1.04	2.75	2.81	4.49	4.50
chloroform(1)/toluene(2)/carbon tetrachloride (3)								
Pyrene	−0.43	−0.27	0.02	0.90	2.29	2.44	3.10	2.72
Benzopyrene	−0.41	−0.25	0.17	0.84	2.00	2.21	2.91	2.33
Phenanthrene	−0.41	−0.27	0.16	0.82	1.94	2.16	3.04	2.40
Chrysene	−0.41	−0.25	0.14	0.88	2.11	2.29	2.96	2.41
Fluoranthene	−0.41	−0.24	0.12	0.80	1.95	2.12	2.74	2.33
Anthracene	−0.41	−0.23	0.16	0.80	1.94	2.12	2.82	2.30
Diphenyl	−0.41	−0.28	0.11	0.80	1.89	2.13	3.03	2.49
Naphthalene	−0.43	−0.27	0.02	0.76	2.13	2.13	2.81	2.63

Fig.2 shows the dependence $R_{M,s}$ on x_1^1 calculated according to eq.(48) for $R_{M,s1}=0.5$, $R_{M,s2}=1.0$ (fig.2A) , $R_{M,s1}=-0.5$, $R_{M,s2}=1.0$ (fig.2B) and for different values of m .The dependence $R_{M,s}(x_1^1)$ calculated for m=1 (homogeneous solid surface) is a decreasing function. However,the curves $R_{M,s}(x_1^1)$ relate to m smaller than unity can show a minimum.This minimum is deeper when difference between $R_{M,s1}$ and $R_{M,s2}$ is small and the parameter m is close to zero.Thus,a strong heterogeneity of the adsorbent surface (m close to zero) may be the reason of minimum on the curve $R_{M,s}(x_1^1)$ [34].

A MODEL INVOLVING SOLUTE-SOLVENT AND SOLVENT-SOLVENT SPECIFIC INTERACTIONS IN THE MOBILE PHASE

Homogeneous solid surfaces

The specific interactions between molecules of solute and solvents in the mobile phase may be represented by suitable quasi-chemical reactions,the products of which are multimolecular complexes (associates).We assume that such associates form in the

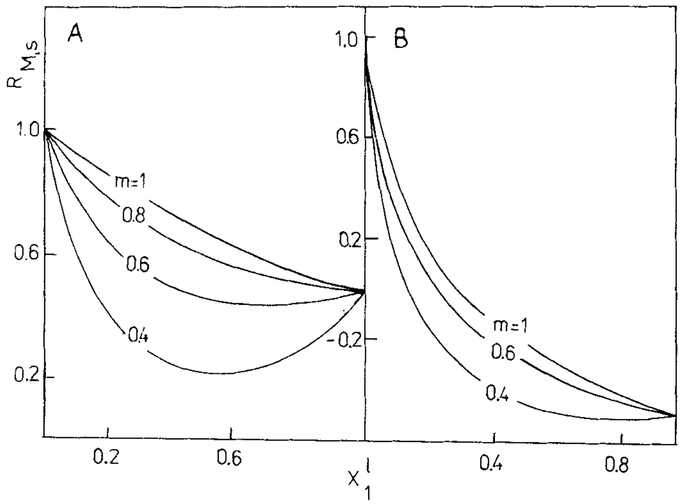

Figure 2. Theoretical functions $R_{M,s}(x_1^l)$ calculated according to Eq. 48 for $R_{M,s1}=0.5$; $R_{M,s2}=1.0$ (part A); $R_{M,s1}=-0.5$, $R_{M,s2}=1.0$ (part B) and different values of m. Figure taken from Ref. [51] with permission of the copyright owner.

mobile phase only [31].However,the silanol groups of the silica surface or other active groups in the case of other adsorbents can compete with complexes in the surface phase.Thus,stronger interactions of molecules of solute and solvents with the active groups and adsorption sites can preclude solute-solvent and solvent-solvent associates in the surface phase.Taking into account the possibility of destruction of solute-solvent and solvent-solvent associates in the surface phase by the active groups,we assume that these complexes form in the mobile phase only.

In n-component mobile phase the different types of multimolecular associates can be formed.Therefore,in theoretical considerations we assume formation of the most probable associates.Three types of associates play an important role in the chromatographic process. They are [30,31] :

(1) associates consisted from one molecule of solute and some molecules of the most polar solvent,

(2) associates consisted from molecules of the most polar solvent,and

(3) associates consisted from molecules of the most polar solvent and molecules of another solvent.

The chromatographic models assuming the formation of double associates of 1-st, 2-nd and 3-rd type in the mobile phase were discussed theoretically in the ref.[30].In [30] the three main equations for the capacity ratio have been derived by assuming that only one type of double associates can be formed.However,in [57] a model assuming the simultaneous formation of double associates of 1-st and 2-nd type in the mobile phase was discussed.A most general model has been considered in the ref.[31].According to this model molecules of solute and 1-st solvent form associates in the mobile phase.This process may be described by the following quasi-chemical reversible reactions :

$$s^{(l)} + q\,1^{(l)} \rightleftarrows (1_q s)^{(l)} \tag{49}$$

$$p\,1^{(1)} \rightleftarrows (1_p)^{(1)} \tag{50}$$

The first reaction represents the formation of (q+1)-molecular associates in the mobile phase,which consist from one molecule of solute and q molecules of 1-st solvent.However,the reaction (50) represents the formation of p-molecular associates by molecules of 1-st solvent only.The equilibrium constants of the reactions (49) and (50) are expressed as follows :

$$L_q = x_q/[\,x_s(x_1)^q] \tag{51}$$

$$M_p = x_p/(x_1)^p \tag{52}$$

In the above x_s and x_1 are the mole fractions of unassociated molecules of the s-th solute and 1-st solvent,respectively,however, x_q and x_p are mole fractions of (q+1)-molecular and p-molecular associates formed in the mobile phase according to the reactions (49) and (50).The mole fractions x_q and x_p are defined as the ratio of the number of associates to the total number of molecules in the mobile phase.The total mole fractions of the s-th solute and all solvents in the mobile phase are expressed as follows :

$$x_s^l = x_s + x_q = x_s + L_q\, x_s (x_1)^q \qquad (53)$$

$$x_1^l = x_1 + q\, x_q + p\, x_p \approx x_1 + p\, M_p\, (x_1)^p \qquad (54)$$

$$x_i^l = x_i \quad \text{for } i=2,3,\ldots,n \qquad (55)$$

Since, the value of the mole fraction x_q is limited by the mole fraction x_s, however, x_s^l is infinitely low, the term $q\, x_q$ in eq.(54) is very small in comparison to x_1 and may be neglected. However, in the surface phases the association effects are neglected, i.e.,

$$x_s^s = y_s \quad \text{and} \quad x_i^s = y_i \text{ for } i=1,2,\ldots,n \qquad (56)$$

where y_s and y_i are the mole fractions of unassociated molecules of the s-th solute and i-th solvent in the surface phase, respectively.

The solution of eq.(54) with respect to x_1 is a function of x_1^l, i.e.,

$$x_1 = X(x_1^l;\ p, M_p) \qquad (57)$$

For double associates (p=2) the solution of eq.(54) is the following :

$$x_1 = X(x_1^l;\ 2, M_2) = [(1+8M_2 x_1^l)^{1/2} - 1]/(4M_2) \qquad (58)$$

Analytical solutions of eq.(54) are also possible for three- and four-molecular complexes, i.e., p=3 and p=4. However, eq.(53) may be easily solved with respect to x_s :

$$x_s = x_s^l/(1 + L_q x_1{}^q) \qquad (59)$$

Next, we assume that in the phase-exchange reaction (4) the unassociated molecules take part only. Thus, the equlibrium constant K_{s1}^{th} is defined as follows (c.f. eq.10):

$$K_{s1}^{th} = (y_s/x_s)(x_1/y_1)^r \qquad (60)$$

Taking into account eq.(56), i.e., $y_s = x_s^s$ and $y_1 = x_1^s$, and substituting eqs.(57) and (59) to eq.(60), we have

$$K_{s1}^{th} = (x_s^s/x_s^l)[\,X(x_1^l;p,M_p)/x_1^s\,]^r\,[1 + L_q X^q(x_1^l;p,M_p)] \qquad (61)$$

Combining eqs.(61) and (1) we obtain a general equation for the capacity ratio involving the solute-solvent and solvent-solvent association :

$$k'_s = (K^{th}_{s1}/C)[\, x^s_1/X(x^1_1;p,M_p)]^r \, [1 + L_q X^q(x^1_1;p,M_p)]^{-1} \tag{62}$$

For $x^1_1 = 1$ eq.(62) gives the expression for the capacity ratio k'_{s1} of the s-th solute in 1-st solvent :

$$k'_{s1} = (K^{th}_{s1}/C)\, D_p^{-r} \, [1 + L_q \, D_p^{\,q}\,]^{-1} \tag{63}$$

where

$$D_p = X(1;p,M_p) \tag{64}$$

Eq.(62) may be rewritten in the form,which contains k'_{s1} instead of K^{th}_{s1}. For this purpose the equilibrium constant K^{th}_{s1} may be evaluated from eq.(63) and substituted to eq.(62) :

$$k'_s = k'_{s1} \, D_p^{\,r} \, [1+L_q D_p^{\,q}][x^s_1/X(x^1_1;p,M_p)]^r \, [1+L_q X^q(x^1_1;p,M_p)]^{-1} \tag{65}$$

Now,we consider the special cases of eq.(62) or its other form, eq.(65).For $M_p = 0$ (then p=1) eq.(54) gives

$$x_1 = X(x^1_1;1,0) = x^1_1 \tag{66}$$

Then,eq.(62) reduces to the following expression :

$$k'_s = (K^{th}_{s1}/C) \, (x^s_1/x^1_1)^r/[1+L_q(x^1_1)^q\,] \tag{67}$$

Eq.(67) involves solute-solvent association in the mobile phase and difference in molecular sizes of solute and solvents.For $L_q = 0$ (absence of solute-solvent association) eq.(67) gives the relationship (20),however, for $L_q = 0$ and $x^s_1 = 1$ it becomes the Snyder-Soczewiński relationship (22).These relationships were discussed in the section devoted to non-specific interactions in LSC process. Similarly,for $L_q = 0$ and $r = 1$ eq.(67) gives eq.(25),which was discussed in the previous section.

Eq.(67) may be transformed to the following linear form :

$$(k'_s)^{-1}(x_1^s/x_1^l)^r = (K_{s1}^{th}/C)^{-1} + (L_qC/K_{s1}^{th})(x_1^l)^q \qquad (68)$$

Two special cases of eq.(68) are interesting for analysis of the chromatographic data.They are obtained from eq.(68) for r=1 :

$$x_1^s/(k'_sx_1^l) = (K_{s1}^{th}/C)^{-1} + (L_qC/K_{s1}^{th})\,(x_1^l)^q \qquad (69)$$

and for q=1 :

$$(k'_s)^{-1}(x_1^s/x_1^l)^r = (K_{s1}^{th}/C)^{-1} + (L_1C/K_{s1}^{th})\,x_1^l \qquad (70)$$

The mole fraction x_1^s appearing in equations (69) and (70) may be evaluated by means of eq.(21).Assuming $x_1^s=1$ (this assumption is frequently used in LSC) eqs.(69) and (70) reduce to the very simple relationships :

$$1/(k'_sx_1^l) = (K_{s1}^{th}/C)^{-1} + (L_qC/K_{s1}^{th})(x_1^l)^q \qquad (71)$$

$$(k'_s)^{-1}(x_1^l)^{-r} = (K_{s1}^{th}/C)^{-1} + (L_1C/K_{s1}^{th})\,x_1^l \qquad (72)$$

Eqs.(71) and (72) are especially convenient for interpretation of the chromatographic data,because they define in a simple way the capacity ratio.Eq.(71) for q=1 becomes the relationship obtained by Soczewiński [15], Jaroniec and Piotrowska [30]; it is

$$1/(k'_s\,x_1^l) = (K_{s1}^{th}/C)^{-1} + (L_1C/K_{s1}^{th})\,x_1^l \qquad (73)$$

This relationship was widely examined by using HPLC data [58,59].

In [57] the following equation for the capacity ratio has been derived :

$$k'_s=(16\,K_{s1}^{th}\,M_2{}^2/C)\,[\,(1+8M_2x_1^l)^{1/2}-1]^{-1}[\,4M_2 + L_1(1+8M_2x_1^l)^{1/2}-L_1]^{-1} \qquad (74)$$

For small values of M_2 eq.(74) gives [57]:

$$k'_s = (K_{s1}^{th}/C)\,(x_1^l)^{-1}[\,1+(L_1-2M_2)x_1^l\,]^{-1} \qquad (75)$$

Eqs.(74) may be obtained from eq.(62) by assuming **r=1** , q=1 and p=2 .For $L_1=0$ eq.(75) gives

$$1/(k'_s x^l_1) = (K^{th}_{s1}/C)^{-1} - (2M_2C/K^{th}_{s1})\, x^l_1 \tag{76}$$

The dependence $1/(k'_s x^l_1)$ vs. x^l_1 is linear for two different models:

(1) model assuming formation of double associates (1s) in the mobile phase, and

(2) model assuming formation of double associates from molecules of 1-st solvent in the mobile phase.

The slope of eq.(73) is positive, whereas, the slope of eq.(76) is negative. This last difference can be very useful in interpretation of the experimental data. The positive slope of $(k'_s x^l_1)^{-1}$ vs. x^l_1 indicates that solute-solvent association dominate, however, the negative slope of this dependence means that solvent-solvent association play dominating role [30,88].

Now, we return to eq.(65). We shall discuss eq.(65) for r=1 and x^s_1 smaller than unity. This last assumption means that the surface phase contains molecules of all solvents. Such situation is observed for solvents having similar adsorption energies. In the case of association of 1-st solvent in the bulk phase, the mole fraction x^s_1 is given by the expression analogous to eq.(21):

$$x^s_1 = [\, K^{th}_{1n}\, X(x^l_1;p,M_p)]/[\, x^l_n + K^{th}_{1n}\, X(x^l_1;p,M_p) + \sum_{i=2}^{n-1} K^{th}_{in} x^l_i\,] \tag{77}$$

Combining eqs.(62) and (77) we have

$$k'_s = C^{-1} K^{th}_{s1}\, K^{th}_{1n} \left[x^l_n + K^{th}_{1n}\, X(x^l_1;p,M_p) + \sum_{i=2}^{n-1} K^{th}_{in} x^l_i \right]^{-1} \cdot$$

$$[1 + L_q X^q(x^l_1;p,M_p)]^{-1} \tag{78}$$

For boundary-concentrations, i.e., $x^l_1 = 1$ and $x^l_i = 0$ for $i=2,3,\ldots,n$, the capacity ratio k'_{s1} is defined by eq.(63) with r=1. The equilibrium constants K^{th}_{in}, K^{th}_{si} and K^{th}_{sn} fulfil the following condition :

$$K^{th}_{in} = K^{th}_{sn}/K^{th}_{si} \tag{79}$$

where

$$k'_{si} = K^{th}_{si}/C \quad \text{for } i=2,3,\dots,n \tag{80}$$

Since, 1-st solvent forms p-molecular complexes in the bulk phase, the relationship between k'_{s1} and K^{th}_{s1} is more complex than that defining k'_{si} $(i=2,3,\dots,n)$ by means of K^{th}_{si}. Taking into account eqs.(63) and (80) in eq.(78), we have :

$$k'_s = \left\{ X(x^l_1;p,M_p)/[k'_{s1}D_p(1+L_qD_p{}^q)] + \sum_{i=2}^{n}(x^l_i/k'_{si}) \right\}^{-1} \cdot \\ [\,1 + L_q\, X^q(x^l_1;p,M_p)]^{-1} \tag{81}$$

For $M_p=0$ eq.(81) gives :

$$k'_s = \left\{ x^l_1/[k'_{s1}(1+L_q)] + \sum_{i=2}^{n}(x^l_i/k'_{si}) \right\}^{-1} [1+L_q(x^l_1)^q]^{-1} \tag{82}$$

The influence of association constants on the dependence $k'_s(x^l_1)$ we shall discuss on the basis of eq.(81) for binary eluent, i.e.,

$$k'_s = \left\{ X(x^l_1;p,M_p)/[k'_{s1}D_p(1+L_qD_p{}^q)] + (x^l_2/k'_{s2}) \right\}^{-1} \cdot \\ [\,1+L_qX^q(x^l_1;p,M_p)]^{-1} \tag{83}$$

Figs. 3-5 present the theoretical dependences $k'_s(x^l_1)$ calculated according to eq.(83) for different values of q , L_q , p and M_p . In all figures the part A shows the functions $k'_s(x^l_1)$ calculated for $k'_{s1} = 1$ and $k'_{s2}=5$, however, the part B relates to $k'_{s1}=1$ and $k'_{s2}=100$. Moreover, in figs. 3-5, the dependences $\ln k'_s$ vs. x^l_1 are also presented.

Fig. 3 shows the k'_s-curves calculated for different values of L_q . The parameter q was equal to unity ; it means that one molecule of 1-st solvent bounds one molecule of the solute. The k'_s-curves for $k'_{s2} \gg k'_{s1}$ lie above the Snyder-Soczewiński curve . The distances between the successive k'_s-curves increase gradually with increasing of L_q . The more complex behaviour of the k'_s-curves is observed for similar values of k'_{s1} and k'_{s2} (c.f., fig.4A). This non-regular behaviour of k'_s-curves presented in fig.4A is caused by assuming

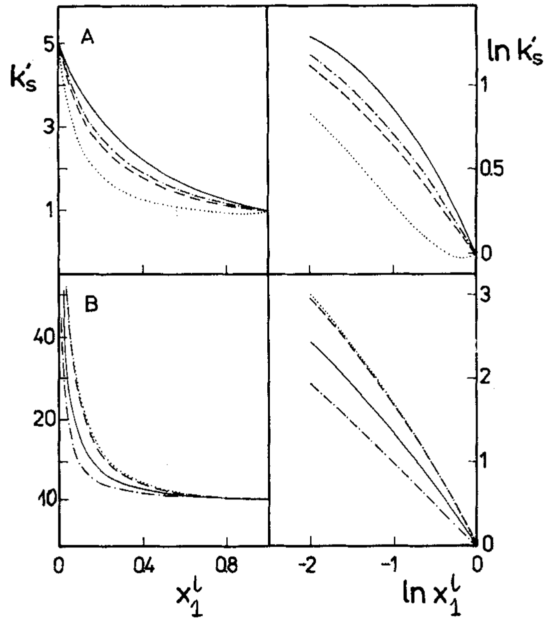

Figure 3. Theoretical functions $k'_s(x^l_1)$ and $\ln k'_s(\ln x^l_1)$ calculated according to Eq. 83 for $k_{s1}=1$, $k_{s2}=5$ (part A); $k'_{s1}=1$, $k'_{s2}=100$ (part B); $M_p=0$, $q=1$, and $L_q=1$ (the solid line), 5 (the dashed line, and 10 (the dotted line). The Snyder-Soczewinski curve is denoted by the dashed line.

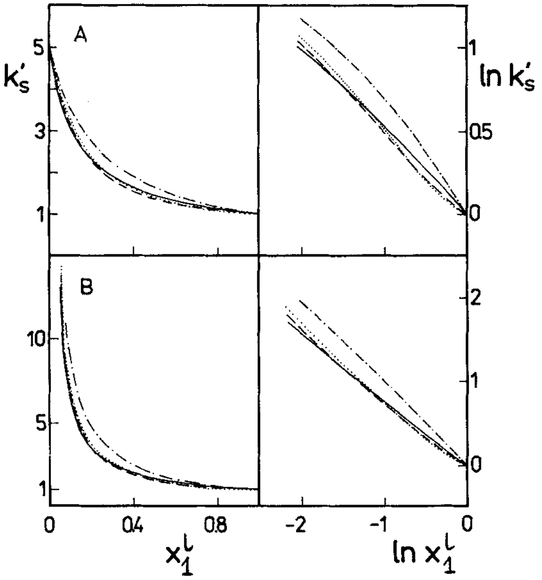

Figure 4. Functions as in Fig. 3 calculated for $L_q=0$, $M_p=1$ and p=2 (the solid line), 4 (the dashed line), and 6 (the dotted line). The other parameters as in Fig. 3.

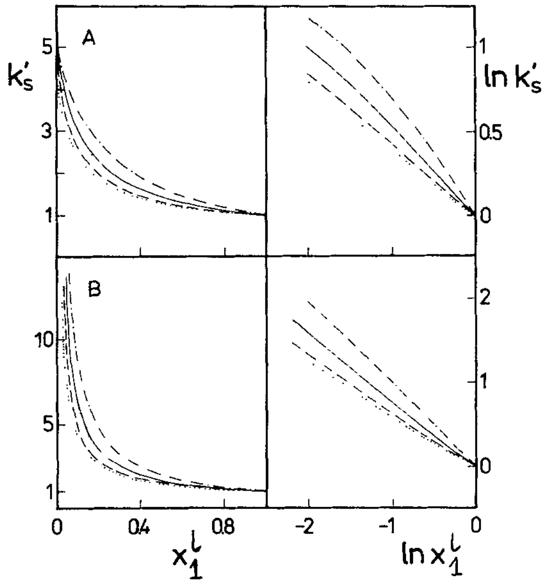

Figure 5. Functions as in Fig. 3 calculated for L_q=0, p=2, and M_p = 1 (the solid line), 5 (the dashed line), and 10 (the dotted line). The other parameters as in Fig. 3.

the constancy of k'_{s1} ; it means that the k'_s-curves are calculated at different values of K^{th}_{s1} (c.f., eq.63).A set of the k'_s-curves calculated for one value of K^{th}_{s1} shows a regular behaviour[60]

Fig. 4 shows the k'_s-curves calculated for L_q= 0 , M_p=1 and different values of p =2,4 and 6.However,fig.6 presents the k'_s-curves for L_q=0 , p=2 and M_p=1 , 5 and 10.These curves lie below the Synder-Soczewiński curve (the dashed-dotted line).Thus,association of molecules of 1-st solvent causes decrease of k'_s-values in comparison to those predicted by Snyder-Soczewiński model,however,association between molecules of solute and 1-st solvent gives opposite effect (c.f.,figs.4 and 6).

The k'_s-curves presented in figs.3-5 were also plotted in the logarithmic scale.In this scale the Snyder-Soczewiński curve (the dashed-dotted line) is linear.It follows from figs. 3-5 that many curves $\ln k'_s$ vs. ln x_1^l may be approximated by the straight line

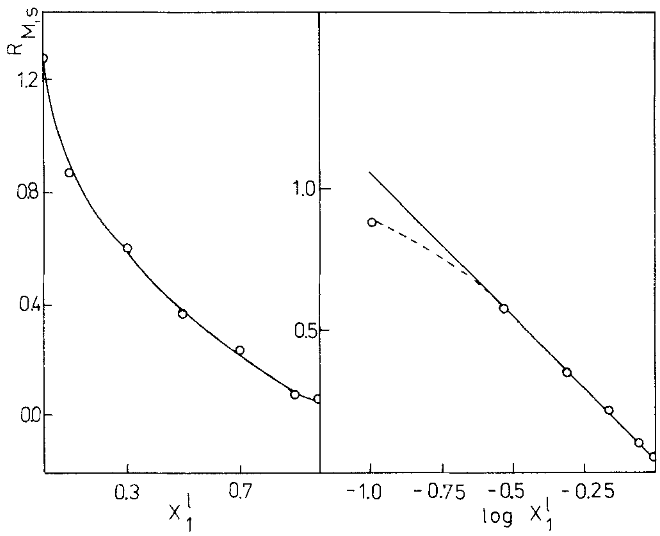

Figure 6. Experimental dependence $R_{M,s}$ vs. x_1^l and the linear dependence (22) for o-nitrophenol in benzene/cyclohexane eluent on silica gel at 20°C. Benzene is denoted as 1st solvent.

in a wide concentration region. Although, these curves have been plotted for r=1, their slopes are not equal to those predicted by Snyder-Soczewiński relationship (22). Thus, the analysis of the chromatographic data by means of Snyder-Soczewiński relationship (22) creates a difficulty in physico-chemical interpretation of its slope, because a good linearity of the dependence of ln k_s' vs. ln x_1^l is observed for different models of the LSC process. According to Snyder-Soczewiński model the ordinate of the linear plot (22) is equal to k_{s1}'. However, the ordinates of the linear segments of the ln k_s' -plots (c.f., figs. 3-5) are not equal to k_{s1}'. This fact may be very helpful during the interpretation of Snyder-Soczewiński plots.

Heterogeneous solid surfaces

The equations for the capacity ratio, discussed in the preceding section, have been derived by assuming association of solute and solvent molecules in the mobile phase and ideality of the surface phase. Moreover, these equations have been discussed for energetically homogeneous adsorbents. Extension of these equations to heterogeneous solid surfaces do not require of an additional information about topography of adsorption sites onto surface, because we assume ideality of the surface phase. This problem was discussed in the section devoted to non-specific interactions in LSC process and is exactly explained in the references [28,67,68]. Thus, the theoretical considerations presented in this section are valid for heterogeneous surfaces of different distributions of adsorption sites onto surface.

The total capacity ratio $k'_{s,t}$ for the LSC process with association effects in the mobile phase is defined by eq.(29) in which $k'_{s,l}$ is expressed by equation analogous to eq.(62) :

$$k'_{s,l} = (K^{th}_{s1,l}/C)\ [\ x^s_{1,l}/X(x^l_1;p,M_p)]^r\ [1+L_qX^q(x^l_1;p,M_p)]^{-1} \qquad (84)$$

Eqs.(29) and (62) give :

$$k'_{s,t} = C^{-1}[\ X(x^l_1;p,M_p)]^{-r}\ [1+L_qX^q(x^l_1;p,M_p)]^{-1}\cdot\sum_{l=1}^{L} h_lK^{th}_{s1,l}(x^s_{1,l})^{\ r} \qquad (85)$$

Eq.(85) is an extension of eq.(62) to energetically heterogeneous solid surfaces. For $M_p=0$ (neglect of association of 1-st solvent molecules) eq.(85) reduces to the following expression :

$$k'_{s,t} = C^{-1}\ (x^l_1)^{-r}\ [1+L_q(x^l_1)^q]^{-1}\sum_{l=1}^{L} h_l\ K^{th}_{s1,l}\ (x^s_{1,l})^r \qquad (86)$$

Similarly as in the case of eq.(34), for quasi-gaussian energy distribution eqs.(85) and (86) may be approximated by the following expressions :

$$k'_{s,t} = C^{-1}\ \bar{K}^{th}_{s1}\ (x^s_{1,t})^{r/m}\ [X(x^l_1;p,M_p)]^{-r}\ [1+L_qX^q(x^l_1;p,M_p)]^{-1} \qquad (87)$$

$$k'_{s,t} = C^{-1}\ \bar{K}^{th}_{s1}\ (x^s_{1,t})^{r/m}\ (x^l_1)^{-r}\ [1+L_q(x^l_1)^q]^{-1} \qquad (88)$$

Eqs.(87) and (88) for m=1 reduce to eqs.(62) and (67), respectively, which have been derived for homogeneous solid surfaces. However, for $M_p=0$ and $L_q=0$ (neglect of association effects in the mobile phase) eqs.(87) and (88) give the relationship (38), which relates to the LSC model with ideal both phases on a heterogeneous solid of quasi-gaussian energy distribution. However, assuming $x_1^s = 1$ in eqs.(87) and (88) we obtain :

$$k'_s = C^{-1}\, K_{s1}^{th}\, [X(x_1^l;p,M_p)]^{-r}\, [1+L_q X^q(x_1^l;p,M_p)]^{-1} \tag{89}$$

$$k'_s = C^{-1}\, K_{s1}^{th}\, (x_1^l)^{-r}\, [1+L_q (x_1^l)^q]^{-1} \tag{90}$$

where

$$\bar{K}_{s1}^{th} = K_{s1}^{th} \quad \text{for } m=1 \tag{91}$$

Eqs.(89) and (90) may be also obtained from eqs.(62) and (67) in which x_1^s is assumed to be unity. Substituting in equations derived for heterogeneous surfaces $x_1^s = 1$ we neglected the heterogeneity effects automatically.

An important equation is obtained from eq.(87) for r=1 :

$$k'_{s,t} = C^{-1}\, \bar{K}_{s1}^{th}\, (x_{1,t}^s)^{1/m}\, [\, X(x_1^l;p,M_p)]^{-1} [1+L_q X^q(x_1^l;p,M_p)]^{-1} \tag{92}$$

The mole fraction $x_{1,t}^s$ is given by the equation analogous to eq.(39):

$$x_{1,t}^s = [\, \bar{K}_{1n}^{th}\, X(x_1^l;p,M_p)]^m \Big/ \left\{ (x_n^l)^m + [\, \bar{K}_{1n}^{th}\, X(x_1^l;p,M_p)]^m + \sum_{i=2}^{n-1} (\bar{K}_{in}^{th} x_i^l)^m \right\} \tag{93}$$

Eq.(93) may be also applied to calculate $x_{1,t}^s$ in eqs.(87) and (88). Combining eqs.(92) and (93), we obtain

$$k'_{s,t} = C^{-1}\, \bar{K}_{s1}^{th}\, \bar{K}_{1n}^{th} \left\{ (x_n^l)^m + [\, \bar{K}_{1n}^{th} X(x_1^l;p,M_p)]^m + \sum_{i=2}^{n-1} (\bar{K}_{in}^{th} x_i^l)^m \right\}^{-1/m} \cdot [1+L_q X^q(x_1^l;p,M_p)]^{-1} \tag{94}$$

For $x_1^l = 1$ and $x_i^l=0$ ($i=2,3,\dots,n$) eq.(94) gives :

$$k'_{s1} = (\bar{K}_{s1}^{th}/C)\, [D_p(1+L_q D_p{}^q)]^{-1} \tag{95}$$

Taking into account the relationship (79) and eq.(95) in eq.(94), we have :

$$k'_{s,t} = \left\{ [\, X(x_1^l;p,M_p)(k'_{s1}D_p)^{-1}(1+L_qD_p{}^q)^{-1}]^m + \sum_{i=2}^{n}(x_i^l/k'_{si})^m \right\}^{-1/m} \cdot$$

$$[1 + L_qX^q(x_1^l;p,M_p)]^{-1} \tag{96}$$

For $M_p=0$ eq.(96) gives :

$$k'_{s,t} = \left\{ [x_1^l(k'_{s1})^{-1}(1+L_q)^{-1}]^m + \sum_{i=2}^{n}(x_i^l/k'_{si})^m \right\}^{-1/m} \cdot [1+ L_q(x_1^l)^q]^{-1} \tag{97}$$

However, for m=1 eqs.(96) and (97) give the relationship derived for homogeneous surfaces (c.f., eqs.81 and 82).

In this section we discussed many equations for the capacity ratio, which can be obtained from the general relationship (87). This relationship involves main factors determining the LSC process:

- competitive character of solute and solvent adsorption,
- differences in molecular sizes of solute and solvents,
- solute-solvent association in the mobile phase,
- association of molecules of the most polar solvent in the mobile phase, and
- energetic heterogeneity of the adsorbent.

Applying a similar procedure to that described above we can derive the further equations for the capacity ratio by assuming that the mobile phase contains some types of associates of 1-st solvent and they can bound one molecule of the solute. These equations contain many unknown parameters, therefore, they are less useful for analysing the HPLC and TLC data.

CORRELATION BETWEEN ADSORPTION FROM MULTICOMPONENT LIQUID MIXTURES AND LIQUID ADSORPTION CHROMATOGRAPHY WITH MIXED ELUENT

Ościk [23,24], Jaroniec et al. [27,28,60], Riedo and Kováts [89] pointed on a great similarity of the LSC process with mixed eluent and adsorption from multicomponent liquid mixtures. Theoretical studies of Riedo and Kováts [89] concentrate on derivation of relationships determining correlation between adsorption and chromatographic fundamental quantities.The studies of Ościk [23,24] and Jaroniec et al.[27,28,60] base on the fundamental definition (1),which determines the dependence between the mole fraction of the s-th solute in the surface phase (the typical adsorption quantity) and the capacity ratio (the typical chromatographic quantity),and tend for deriving the relationships describing adsorption and chromatographic multicomponent systems.

The LSC process with one solute and n-component eluent is very similar to the liquid adsorption process from (n+1)-component mixtures.In the LSC process concentration of a given solute is assumed to be infinitely low ; this process relates to adsorption of a solute from dilute n-component liquid mixtures [90].According to the theory of single-solute adsorption from dilute solutions on homogeneous solid surfaces,the mole fraction of the s-th solute in the surface phase is given by the following equation [90]:

$$x_s^s = K_{sn}^{th}\, x_s^l \,/(x_n^l + \sum_{i=1}^{n-1} K_{in}^{th}\, x_i^l) \qquad (98)$$

Eq.(98) has been derived for ideal both phases.Combining this equation with the definition (1) ,we obtain

$$k_s' = C^{-1}\, K_{sn}^{th}/(x_n^l + \sum_{i=1}^{n-1} K_{in}^{th}\, x_i^l) \qquad (99)$$

Combining eqs.(99),(79) and (80) we obtain the relationship (25). Applying for x_s^s different equations known in the theory of single-solute adsorption from dilute solutions on solid surfaces,we can derive by means of eq.(1) different equations for the capacity ratio. The procedure basing on eq.(1) and that basing on eq.(14) lead to the same equations for k_s' ,although the procedure basing on eq.(14) is more universal because involves differences in molecular sizes of solute and solvents.The procedure basing on eq.(1),introduced in the paper [27],was developed by Borówko et al.[55,60].
In [55] non-ideality and surface heterogeneity effects in LSC process

were investigated,however,the paper [60] is devoted to the association effects in LSC.

The capacity ratio for different LSC models is a function of the mole fractions of solvents in the mobile and surface phases, Of course, the mole fraction of a solvent in the surface phase is the function of the mobile phase composition.In all equations for the capacity ratio,discussed in the preceding sections,we calculated the mole fraction of 1-st solvent in the surface phase by using the equations known from the theory of adsorption from multicomponent liquid mixtures.Now,we sygnalize the other possibility of calculation of x_1^s ; it may be evaluated directly from the experimental excess adsorption isotherm n_1^e by using the following relationship [68] :

$$x_1^s = n_1^e/n^s + x_1^l \tag{100}$$

where n_1^e is the adsorption excess of 1-st component from n-component liquid mixture,which is measured for eluent/adsorbent system independently on the chromatographic measurements,and n^s is the total number of moles of all solvents in the surface phase. The parameter n^s may be determined directly from the excess adsorption isotherm n_1^e [91,92].Thus,in all equations for the capacity ratio,discussed in the previous sections,the quantities x_1^s and $x_{1,t}^s$ may be replaced by the expression (100).Substituting eq.(100) for x_1^s ,we eliminate the parameters appearing in equations for x_1^s and introduce the parameter n^s ,which may be evaluated from the excess adsorption isotherm.The studies of LSC process ,in which eq.(100) is utilized,were presented in series of the papers [29,36, 38,56,61].Now,we shall present some results illustrating a great utility of the excess adsorption data in interpretation of HPLC and TLC data .

In [56,61] the TLC data for o-nitrophenol and some dichlorophenols chromatographed in benzene/cyclohexane, acetone/benzene and ethyl acetate/carbon tetrachloride eluents on silica gel at 20°C were investigated. Application of Snyder-Soczewiński relationship (22) for describing these data gives deviations at low concentrations of x_1^l; it results from the fact that eq.(22) gives non-physical value of k'_s at $x_1^l = 0$.

Fig. 6 shows the experimental dependence $R_{M,s}$ vs. x_1^l for o-nitrophenol and the dependence $R_{M,s}$ vs. log x_1^l (c.f., eq.22), which is linear for the concentrations x_1^l greater than 0.3. In Fig. 7 the excess adsorption isotherms of benzene from cyclohexane, acetone from benzene and ethyl acetate from carbon tetrachloride on silica gel at 20°C are presented. These excess adsorption data have been applied to calculate the mole fraction x_1^s according to eq.(100). Substituting eq.(100) to eq.(20) and transforming eq.(20) to TLC, we obtain [56]:

$$R_{M,s} = R_{M,s1} + r \log [n_1^e/(n^s x_1^l) + 1] \qquad (101)$$

It follows from eq.(101) that $R_{M,s}$ is a linear function of $\log[n_1^e/(n^s x_1^l) + 1]$. In [56,61] we showed that the linear relationship (101), associating the excess adsorption data and TLC data, is fulfiled for many chromatographic systems. For the purpose of illustration Fig. 8 shows the linear dependence (101) for o-nitrophenol chromatographed in three different mobile phases, for which the excess adsorption isotherms are presented in Fig. 7. The experimental points (circles) lie on the straight lines even at low concentrations x_1^l, whereas, for eq.(22) we observe deviations from linearity at low values of x_1^l.

Similarly, a good results have been obtained for TLC data interpreted by eq.(38) associated with eq.(100); for TLC with binary eluent eqs.(38) and (100) give [29]:

$$R_{M,s} = R_{M,s1} + (r/m) \log [(n_1^e/n^s)(x_1^l)^{-m} + (x_1^l)^{1-m}] \qquad (102)$$

The parameters n^s and m were evaluated by means of the following equation [29]:

$$\log[x_{1,t}^s/(1-x_{1,t}^s)] = m \log \bar{K}_{12}^{th} + m \log (x_1^l/x_2^l) \qquad (103)$$

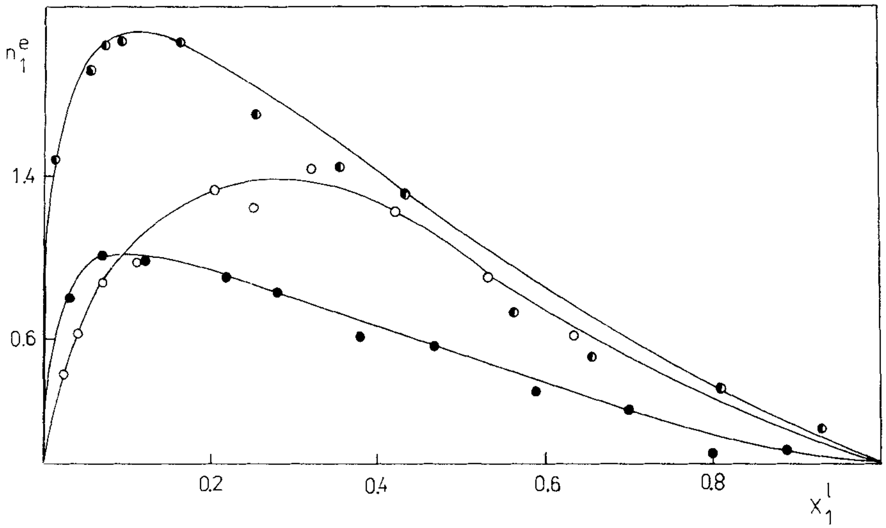

Figure 7. Excess adsorption isotherms for benzene (2)/acetone(1) (◐), cyclohexane(2)/benzene(1) (○) and carbon tetrachloride(2)/ ethylacetate(1) (●) on silica gel at 20°C. Figure taken from Ref [61] with permission of the copyright owner.

where $x_{1,t}^s$ is given by eq.(100).Eq.(103) is linear form of eq.(39) for n=2.

Recent studies in this problem concern the application of the excess adsorption data for characterization of the chromatographic systems showing association effects in the mobile phase.Such studies have been made by means of eq.(69) and equation analogous to eqs. (75) and (76) [88]:

$$G(x_1^l) = x_1^s/(x_1^l k_s') = (C/K_{s1}^{th}) + [(L_1-2M_2)C/K_{s1}^{th}]\ x_1^l \qquad (104)$$

Combining eqs.(104) and (100),we have

$$G(x_1^l) = n_1^e/(n^s x_1^l k_s') + 1/k_s' = (C/K_{s1}^{th}) + [(L_1-2M_2)C/K_{s1}^{th}]\,x_1^l \quad (105)$$

Eq.(105) describes the LSC process with mobile phase,which contains the mixed double solute-solvent associates and the pure associates consisting from two molecules of 1-st solvent.The other assumptions are following :

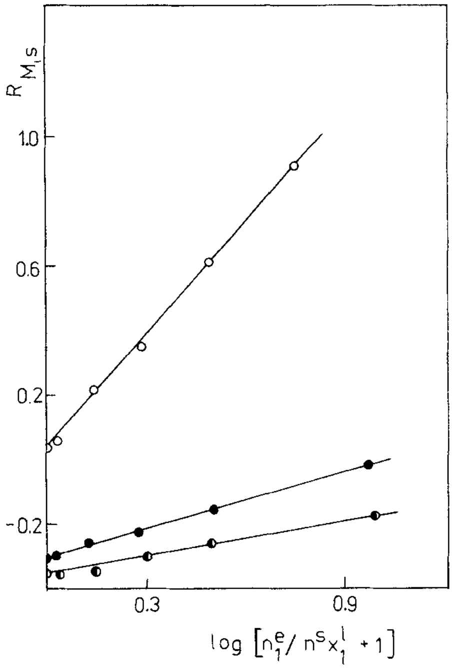

Figure 8. Dependence log($n_1^e/n^s x_1^1$ + 1) vs. $R_{M,s}$ for o-nitrophenol chromatographed in cyclohexane/benzene (○), carbon tetrachloride/ethylacetate (●) and benzene/acetone (◐) on silica gel at 20°C. Figure taken from Ref. [61] with permission of the copyright owner.

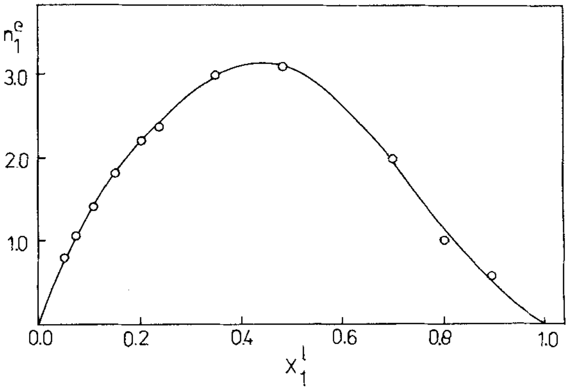

Figure 9. Excess adsorption isotherm for methanol from acetone on silica gel at 20°C. Figure taken from Ref. [88] with permission of the copyright owner.

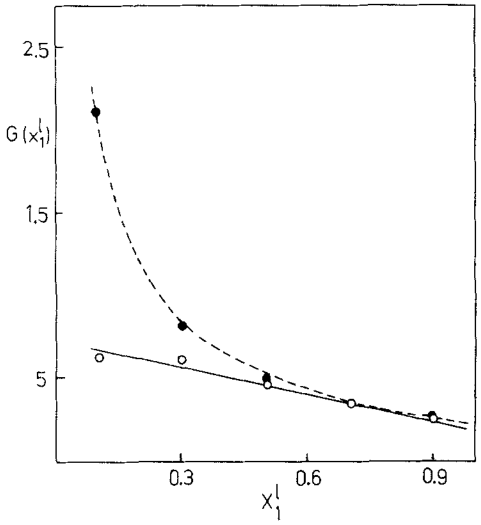

Figure 10. Dependence $G(x_1^1)$ vs. x_1^1 for 2,3-dihydroxynaphthalene in methanol/acetone on silica gel at 20°C. The solid line denotes $x_1^s/(k_s'x_1^1)$ vs. x_1^1, whereas the dashed line denotes $1/(k_s'x_1^1)$ vs. x_1^1.

- ideal surface phase,
- association in the mobile phase,
- surface phase contains molecules of all solvents ($x_1^s<1$),
- molecular sizes of solute and solvents are identical, and
- adsorbent is assumed to homogeneous.

In [88] the TLC data were measured for naphthalene derivatives in methanol/acetone eluent on silica gel at 20°C. Eqs. (22) and (102) do not fulfil of the above data. Fig. 9 presents the excess adsorption isotherm of methanol from acetone on silica gel at 20°C. However, Fig. 10 shows the dependence $(k_s'x_1^1)^{-1}$ vs. x_1^1 (the dashed line) and the dependence $x_1^s/(k_s'x_1^1)$ vs. x_1^1 (the solid line) for one selected solute. It follows from fig. 10 that a reasonable interpretation of TLC data for naphthalene derivatives chromatographed in methanol/acetone on silica gel requires of equations involving association effects in the mobile phase and changeability of the surface phase composition during the chromatographic process.

REFERENCES

1. L.R.Snyder and D.L.Saunders, J.Chromatogr.Sci., 7 (1969) 195.
2. M.Borówko, M.Jaroniec, J.Narkiewicz, A.Patrykiejew and W.Rudziński, J.Chromatogr., 153 (1978) 309.
3. M.Jaroniec, M.Borówko, J.Narkiewicz, A.Patrykiejew and W.Gołkiewicz, Chromatographia, 12 (1979) 29.
4. L.R.Snyder, in "HPLC :Advances and Perspectives",(ed.,C.Horvath), Academic Press, New York, vol.1 ,1980.
5. P.Jandera and J.Churacek, in "Advances in Chromatography", Marcel Dekker, New York, vol.19 , 1980 p.125 , (eds.J.C.Giddings, E.Grushka, J.Cazes and P.R.Brown).
6. M.Borówko, M.Jaroniec, J.Narkiewicz and A.Patrykiejew, J.Chromatogr., 153 (1978) 321.
7. P.J.Schoenmakers, H.A.H.Billiet, R.Tijssenaud and L.Galan, J.Chromatogr., 149 (1978) 519.
8. W.Gołkiewicz and M.Jaroniec, Journal HRC & CC, 1 (1978) 245.
9. W.Gołkiewicz and E.Soczewiński, Chromatographia, 11 (1978) 454.
10. W.Gołkiewicz, Chromatographia, 14 (1981) 411.
11. W.Gołkiewicz, Chromatographia, 14 (1981) 629.
12. G.Guiochon, in "HPLC :Advances and Perspectives",(ed.,C.Horvath), Academic Press, New York, vol.2 ,1980.
13. H.J.Issaq, J.R.Klose, K.L.McNitt, J.E.Haky and G.M.Muschik, J.Liquid Chromatogr., 4 (1981) 2091.
14. L.R.Snyder, "Principles of Adsorption Chromatography", Marcel Dekker, New York, 1968.
15. E.Soczewiński, Anal.Chem., 41 (1969) 179.
16. M.Jaroniec and J.Ościk, Journal HRC & CC, 5 (1982) 3.
17. R.P.W.Scott and P.Kucera, J.Chromatogr., 149 (1978) 93.
18. R.P.W.Scott and P.Kucera, J.Chromatogr., 112 (1975) 425.
19. R.E.Boehm and D.E.Martire, J.Phys.Chem., 84 (1980) 3620.
20. D.E.Martire and R.E.Boehm, J.Liquid Chromatogr.,3 (1980) 753.
21. L.R.Snyder and H.Poppe, J.Chromatogr., 184 (1980) 363.
22. L.R.Snyder, Anal.Chem., 46 (1974) 1384.

23. J.Ościk, Przem.Chem., 44 (1965) 129.

24. J.Ościk, in"Physical Adsorption from Multicomponent Phases" (in Russian), M.M.Dubinin and V.V.Serpinsky eds.,Nauka, Moscow,1972,pp.138-147.

25. J.Ościk and J.K.Różyło, Chromatographia, 4 (1971) 518.

26. E.Soczewiński, J.Chromatogr., 130 (1977) 23.

27. M.Jaroniec, J.Narkiewicz and M.Borówko, Chromatographia, 11 (1978) 581.

28. M.Jaroniec and A.Patrykiejew, J.Chem.Soc.Faraday I, 76 (1980)2486

29. M.Jaroniec and B.Ościk-Mendyk, J.Chem.Soc.Faraday I, 77 (1981) 1277.

30. M.Jaroniec and J.Piotrowska, Journal HRC & CC, 3 (1980) 257.

31. M.Jaroniec and J.A.Jaroniec, J.Liquid Chromatogr.,4 (1981) 2121.

32. M.Jaroniec, Annales M.Curie-Skłodowska Univ.,Sec.AA, 36 (1981) 73.

33. M.Jaroniec, J.Narkiewicz and B.Klepacka, J.Chromatogr., 177 (1979) 299.

34. M.Jaroniec, J.K.Różyło and W.Gołkiewicz, J.Chromatogr., 178 (1979) 27.

35. H.Buchowski, Thesis, University of Warsaw, 1963.

36. J.Ościk, J.K.Różyło, B.Ościk-Mendyk and M.Jaroniec, Chromatographia, 14 (1981) 95.

37. J.K.Różyło, J.Ościk, B.Ościk-Mendyk and M.Jaroniec, Journal HRC & CC, 4 (1981) 17.

38. J.K.Różyło, M.Jaroniec and B.Ościk-Mendyk, Chem.Anal., 26 (1981) 215.

39. J.Ościk and G.Chojnacka, Chromatographia, 11 (1978) 731.

40. J.Ościk and G.Chojnacka, J.Chromatogr., 93 (1974) 167.

41. J.K.Różyło, M.Jaroniec, J.A.Jaroniec and H.Kołodziejczyk, Journal HRC & CC , 2 (1979) 524.

42. J.K.Różyło, Chromatographia, 9 (1976) 74.

43. J.K.Różyło, J.Chromatogr., 116 (1976) 125.

44. J.K.Różyło, G.Chojnacka and I.Malinowska, Chromatographia, 13 (1980) 215.

45. J.K.Różyło, I.Malinowska and J.Gross, Journal HRC & CC, 3 (1980) 79.

46. L.R.Snyder and J.L.Glajch, J.Chromatogr., 214 (1981) 1 .

47. E.Paanakker, J.C.Kraak and H.Poppe, J.Chromatogr.,149 (1978)111.

48. J.L.Glajch and L.R.Snyder, J.Chromatogr., 214 (1981) 21.

49. L.R.Snyder, J.L.Glajch and J.J.Kirkland, J.Chromatogr.218(1981)299.

50. M.Jaroniec, J.K.Różyło, J.A.Jaroniec and B.Ościk-Mendyk, J.Chromatogr., 188 (1980) 27.

51. J.K.Różyło, J.A.Jaroniec, H.Kołodziejczyk and M.Jaroniec, Journal HRC & CC, 2 (1979) 236.

52. J.K.Różyło, M.Jaroniec, H.Kołodziejczyk, J.A.Jaroniec and J.Gross, Journal HRC & CC, 3 (1980) 180.

53. J.K.Różyło, H.Kołodziejczyk, J.A.Jaroniec and M.Jaroniec, J.Liquid Chromatogr., 2 (1979) 799.

54. M.Jaroniec, B.Ościk-Mendyk, A.Dąbrowski and H.Kołodziejczyk, J.Liquid Chromatogr., 4 (1981) 227.

55. M.Borówko and M.Jaroniec, Chromatographia, 12 (1979) 672.

56. M.Jaroniec, J.K.Różyło and B.Ościk-Mendyk, J.Chromatogr., 179 (1979) 237.

57. M.Jaroniec and J.A.Jaroniec, J.Chromatogr., 210 (1981) 130.

58. M.Jaroniec, J.A.Jaroniec and W.Gołkiewicz, Journal HRC & CC, 4 (1981) 89.

59. M.Jaroniec, J.K.Różyło and J.A.Jaroniec, Chem.Anal., 26 (1981).

60. M.Borówko and M.Jaroniec, J.Chem.Soc.Faraday I, in press.

61. B.Ościk-Mendyk, J.K.Różyło and M.Jaroniec, Journal HRC & CC, 4 (1981) 74.

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

63. E.C.Bate-Smith and R.G.Westall, Biochem.Biophys.Acta,4 (1950)427.

64. C.Minka and A.L.Myers, AIChE,19 (1973) 453.

65. M.Jaroniec, J.Res.Inst.Catalysis,Hokkaido Univ., 26 (1978) 155.

66. M.Borówko, M.Jaroniec and W.Rudziński, Monatsh.Chem., 112 (1981) 59.

67. M.Jaroniec, Thin Solid Films, 71 (1980) 273.

68. M.Jaroniec, A.Patrykiejew and M.Borówko, Progress in Surface and Membrane Sci., 14 (1981) pp.1-68.

69. P.Jandera and J.Churacek, J.Chromatogr.,91 (1974) 207.

70. J.Narkiewicz, M.Jaroniec, M.Borówko and A.Patrykiejew, J.Chromatogr., 157 (1978) 1.

71. E.Soczewiński and J.Jusiak, Chromatographia, 14 (1981) 23.

72. E.Soczewiński and W.Gołkiewicz, Chromatographia,5 (1972) 431.

73. E.Soczewiński and W.Gołkiewicz, Chromatographia,4 (1971) 501.

74. W.Gołkiewicz and E.Soczewiński,Chromatographia, 5 (1972) 594.

75. E.Soczewiński and W.Gołkiewicz, Chromatographia, 6 (1973) 269.

76. E.Soczewiński, W.Gołkiewicz and W.Markowski, Chromatographia, 8 (1975) 13.

77. W.Gołkiewicz, Chromatographia, 9 (1976) 113.

78. E.Soczewiński, W.Gołkiewicz and T.Dzido, Chromatographia, 10 (1977) 221.

79. E.Soczewiński, T.Dzido and W.Gołkiewicz, Chromatographia, 10 (1977) 98.

80. E.Soczewiński and J.Kuczmierczyk, J.Chromatogr., 150 (1978) 53.

81. T.Wawrzynowicz and T.Dzido, Chromatographia, 11 (1978) 335.

82. S.Hara, J.Chromatogr., 137 (1977) 41.

83. S.Hara, Y.Fujii, M.Hirasawa and S.Miyamoto, J.Chromatogr., 149 (1978) 143.

84. M.D.Palamareva and B.J.Kurtev, J.Chromatogr., 178 (1979) 139.

85. S.Hara, K.Kunihiro, H.Yamaquchi and E.Soczewiński, J.Chromatogr., 239 (1982) 687.

86. J.A.Perry, J.Chromatogr., 163 (1979) 117.

87. J.K.Różyło, I.Malinowska and M.Jaroniec, Journal HRC & CC, 3 (1980) 29.

88. M.Jaroniec, J.K.Różyło, B.Ościk-Mendyk and J.AJaroniec, J.Liquid Chromatogr., in press.

89. F.Riedo and E.Kováts, J.Chromatogr., 239 (1982) 1.

90. M.Jaroniec, Advances in Colloid Interface Sci., in press.

91. J.Ościk, Adsorption, E.Horwood Publ.,1982.

92. G.Schay and L.Nagy, J.Chim.Phys., 58 (1961) 149.