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**On the Retention Mechanism in Liquid-solid Chromatography with Mixed Solvents:
Effects of Molecular Sizes, Intermolecular Interactions, Heterogeneity of the Solid,
and Multilayer Adsorption of the Solvents**

Mechanizm retencji w cieczowej chromatografii adsorpcyjnej z mieszaną fazą ruchomą: wpływ rozmiarów cząsteczek, oddziaływań międzycząsteczkowych, heterogeniczności ciała stałego i wielowarstwowej adsorpcji rozpuszczalników

Механизм удерживания в жидкостно-адсорбционной хроматографии с многокомпонентной подвижной фазой: эффект разных размеров молекул, межмолекулярных взаимодействий, неоднородности твердого тела и полимолекулярной адсорбции растворителей

INTRODUCTION

The theory of LSC is a special edition of the theories of adsorption from multicomponent liquid mixtures on solid surfaces, when one of the components of the mixture (solute) appears in a very small concentration. This adsorption process is governed by several physical factors, the most important of them being:

1. The interactions between solvent and solute molecules in the surface and the bulk phase;
2. The differences in the surface areas occupied by different molecules;
3. The effects of multilayer adsorption;
4. The energetic heterogeneity of solid surfaces.

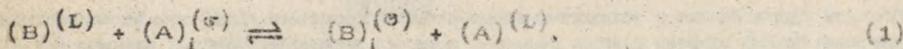
There is no general theoretical solution for this problem. However, several attempts have been made; most of them based on lattice theories of solutions. Surprisingly, their application to the specific case of LSC was very small [1-3]. There may be several reasons for that:

Firstly, the simple theories of LSC [4-18] were good enough to describe the retention data at the common degree of the experimental accuracy. Secondly, the more advanced theories of LSC must still be tractable for the majority of the scientists working in LSC.

This publication presents the theory of LSC, which takes into account all the basic physical factors enumerated above. This theory is applied successfully to describe quantitatively the retention data in the typical LSC systems, investigated by S i a a t s et al. [13].

THEORY

Let us consider firstly the competitive adsorption of the molecules A and B in the i -th lattice plane. Assuming that the molecules occupy the same surface (lattice) area, this competitive adsorption can be expressed as the following quasi-chemical reaction,



The related condition for the thermodynamic equilibrium reads,

$$\mu_B^{(L)} + \mu_{A,i}^{(G)} = \mu_{B,i}^{(G)} + \mu_A^{(L)} \quad (2)$$

where $\mu^{(L)}$ and $\mu^{(G)}$ are appropriate chemical potentials in the bulk phase, and in the i -th lattice plane. Denoting by the symbols x and γ appropriate mole fractions and activity coefficients and using the relation

$$\mu = {}^0\mu + kT \ln x \quad (3)$$

one can rewrite equ. (2) to the following equivalent form,

$$\frac{x_A^{(L)} \gamma_A^{(L)}}{x_{A,i}^{(G)} \gamma_{A,i}^{(G)}} \frac{x_{B,i}^{(G)} \gamma_{B,i}^{(G)}}{x_B^{(L)} \gamma_B^{(L)}} = K_{BA,i} \quad (4)$$

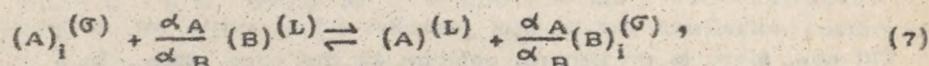
where

$$K_{BA,i} = \exp \left\{ \frac{\circ\mu_B^{(L)} - \circ\mu_{B,i}^{(\sigma)}}{kT} - \frac{\circ\mu_A^{(L)} - \circ\mu_{A,i}^{(\sigma)}}{kT} \right\}. \quad (5)$$

Equation (3) can be rewritten to the following Langmuir-like form

$$x_{A,i}^{(L)} = \frac{x_A^{(L)} (\gamma_A^{(L)} / \gamma_{A,i}^{(\sigma)})}{x_A^{(L)} (\gamma_A^{(L)} / \gamma_{A,i}^{(\sigma)}) + K_{BA,i} x_B^{(L)} (\gamma_B^{(L)} / \gamma_{B,i}^{(\sigma)})}. \quad (6)$$

Now, let us consider the case, when the molecules A and B occupy different surface areas α_A and α_B . Then, eqs. (1-5) take the following form,

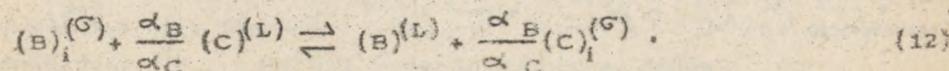
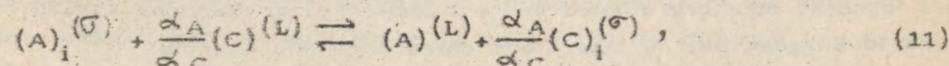


$$\mu_{A,i}^{(\sigma)} + \frac{\alpha_A}{\alpha_B} \mu_B^{(L)} = \mu_A^{(L)} + \frac{\alpha_A}{\alpha_B} \mu_{B,i}^{(\sigma)}, \quad (8)$$

$$\frac{x_A^{(L)} \gamma_A^{(L)}}{x_{A,i}^{(\sigma)} \gamma_{A,i}^{(\sigma)}} \left(\frac{x_{B,i}^{(\sigma)} \gamma_{B,i}^{(\sigma)}}{x_B^{(L)} \gamma_B^{(L)}} \right) \frac{\alpha_A}{\alpha_B} = K_{BA,i}^{\alpha}, \quad (9)$$

$$K_{BA,i} = \exp \left\{ \frac{\alpha_A}{\alpha_B} \frac{\circ\mu_B^{(L)} - \circ\mu_{B,i}^{(\sigma)}}{kT} - \frac{\circ\mu_A^{(L)} - \circ\mu_{A,i}^{(\sigma)}}{kT} \right\}. \quad (10)$$

Let us consider now the simultaneous competitive adsorption of a third component C, which we shall assume to be the solute appearing in very small concentrations, its competitive adsorption in the i -th lattice plane will be described by the following set of the quasi-chemical reactions:



When $\alpha_A = \alpha_B = \alpha_C$, the statistical thermodynamics yields the following equation for the adsorption isotherm of C in the presence of A and B

$$x_{C,i}^{(\sigma)} = \frac{x_C^{(L)} (\gamma_C^{(L)} / \gamma_{C,i}^{(\sigma)})}{x_C^{(L)} (\gamma_C^{(L)} / \gamma_{C,i}^{(\sigma)}) + K_{AC,i} x_A^{(L)} (\gamma_A^{(L)} / \gamma_{A,i}^{(\sigma)}) + K_{BC,i} x_B^{(L)} (\gamma_B^{(L)} / \gamma_{B,i}^{(\sigma)})} \quad (13)$$

Moreover, since $x_C^{(L)}$ is very small, the above equation reduces to the simpler form,

$$x_{C,i}^{(\sigma)} = \frac{x_C^{(L)} (\gamma_C^{(L)} / \gamma_{C,i}^{(\sigma)})}{K_{AC,i} x_A^{(L)} (\gamma_A^{(L)} / \gamma_{A,i}^{(\sigma)}) + K_{BC,i} x_B^{(L)} (\gamma_B^{(L)} / \gamma_{B,i}^{(\sigma)})} \quad (14)$$

Till now, there is no general solution for the case when $\alpha_A \neq \alpha_B \neq \alpha_C$, i.e., for adsorption isotherm from multicomponent (ternary) liquid mixtures of molecules occupying different surface (lattice) areas. Below, we are going to propose some approximate but general solution of this problem. Let us remark to this purpose that the denominator in equ. (14) has the following meaning,

$$\begin{aligned} & K_{AC,i} x_A^{(L)} (\gamma_A^{(L)} / \gamma_{A,i}^{(\sigma)}) + K_{BC,i} x_B^{(L)} (\gamma_B^{(L)} / \gamma_{B,i}^{(\sigma)}) = \\ & = K_{AC,i} \left[\frac{x_A^{(L)} \gamma_A^{(L)}}{\gamma_{A,i}^{(\sigma)}} + K_{BA,i} \frac{x_B^{(L)} \gamma_B^{(L)}}{\gamma_{B,i}^{(\sigma)}} \right] = K_{AC,i} \frac{x_A^{(L)} \gamma_A^{(L)}}{x_{A,i}^{(\sigma)} \gamma_{A,i}^{(\sigma)}} \quad (15) \end{aligned}$$

Because of its small concentration, the presence of solvent C will not affect much the ratio $(x_A^{(L)} \gamma_A^{(L)} / x_{A,i}^{(\sigma)} \gamma_{A,i}^{(\sigma)})$. We may, therefore, assume that the deviations of (α_A / α_C) or (α_B / α_C) from unity could be taken into account in a form of a correction in equ. (14), which will remain basically unchanged. Writing the equations for the thermodynamic equilibria related to the quasi-chemical reactions (11-12) seems to suggest, how to take these corrections into account:

$$\mu_C^{(L)} + \frac{\alpha_C}{\alpha_A} \mu_{A,i}^{(\sigma)} = \mu_{C,i}^{(\sigma)} + \frac{\alpha_C}{\alpha_A} \mu_A^{(L)} \quad (16)$$

$$\mu_C^{(L)} + \frac{\alpha_C}{\alpha_B} \mu_{B,i}^{(\sigma)} = \mu_{C,i}^{(\sigma)} + \frac{\alpha_C}{\alpha_B} \mu_B^{(L)}. \quad (17)$$

We can see that the deviations of (α_C/α_A) and (α_C/α_B) from unity cause the solvents A and B to exhibit some apparent effective value of their chemical potentials in the quasi-chemical reactions, in both bulk and the surface phase. These apparent values of $\mu^{(L)}$ and $\mu^{(\sigma)}$ are equal to their true values, multiplied by the factors (α_C/α_A) and (α_C/α_B) .

Now, we are coming to the essential point of our approximation. Namely, we shall keep the basic form of equ. (14), but the terms in the denominator will be replaced by $K_{AC,i}^\alpha (x_A^{(L)} \gamma_A^{(L)} / \gamma_{A,i}^{(\sigma)})^{\alpha_C/\alpha_A}$ and $K_{BC,i}^\alpha (x_B^{(L)} \gamma_B^{(L)} / \gamma_{B,i}^{(\sigma)})^{\alpha_C/\alpha_B}$ according to what we have said above. Doing so, we arrive at the following form of the distribution coefficient ${}^x K_{C,i}$ of solute,

$${}^x K_{C,i} = \frac{x_{C,i}^{(\sigma)}}{x_C^{(L)}} = \frac{(\gamma_C^{(L)} / \gamma_{C,i}^{(\sigma)})}{K_{AC,i}^\alpha (x_A^{(L)} \gamma_A^{(L)} / \gamma_{A,i}^{(\sigma)})^{\alpha_C/\alpha_A} + K_{BC,i}^\alpha (x_B^{(L)} \gamma_B^{(L)} / \gamma_{B,i}^{(\sigma)})^{\alpha_C/\alpha_B}}. \quad (18)$$

The experimentally measured distribution coefficient ${}^x K_C$ represents some average over all the adsorbed layers (lattice planes), where the concentration of C is different from $x_C^{(L)}$. However, because of the small concentration of C, and the usual condition that ${}^x K_{C,1} \gg \gg {}^x K_{C,2} \dots \dots \dots {}^x K_{C,i}$ the solute C will practically be adsorbed only in the first layer. At the same time, however, the solvents may well be adsorbed in a multilayer fashion. Such a model of surface phase will be accepted in our further consideration.

Let us assume for the moment that the distribution of the solute C between the surface, and the bulk phase is caused only by the interactions between the solute and the solvents molecules. In other words, we are staying purely on the ground of the "interaction" model of HPLC. The difference between the concentrations of the solute in the surface, and the bulk phase is caused by the different concentrations of the (A+B) solutions in the surface and the bulk phase, in which the solute is "solute". In such a refined form, the "interaction" model has been formulated firstly by O ś c i k [4]. The distribution coefficient ${}^x K_{C,in}$ for this model is defined as follows

$$x_{K_{C,1}^{in}} = \frac{x_C^{(G)}}{x_C^{(L)}} = \frac{\gamma_C^{(L)}}{\gamma_{C,1}^{(G)}} \quad (19)$$

Thus, in our general treatment, the distribution coefficient $x_{K_{C,1}}$ can be written in the following form

$$x_{K_{C,1}} = x_{K_{C,1}^{in}} \cdot x_{K_{C,1}^{com}} \quad (20)$$

where $x_{K_{C,1}^{com}}$ is the "competitive" distribution coefficient,

$$x_{K_{C,1}^{com}} = \left[K_{AC,1}^{\alpha} x_A^{(L)} \frac{\gamma_A^{(L)}}{\gamma_{A,1}^{(G)}} \frac{\alpha_C}{\alpha_A} + K_{BC,1}^{\alpha} x_B^{(L)} \frac{\gamma_B^{(L)}}{\gamma_{B,1}^{(G)}} \frac{\alpha_C}{\alpha_B} \right]^{-1} \quad (21)$$

In the absence of intermolecular interactions, i.e., when $\gamma^{(L)} \rightarrow 1$ the total distribution coefficient $x_{K_{C,1}}$ reduces to the "competitive" factor $x_{K_{C,1}^{com}}$. Beginning from now, we shall drop the subscript "1", in $x_{K_{C,1}}$, since we assume the monolayer adsorption of solute C.

Let us consider now another important physical factor which affects the distribution of solute between the surface, and the bulk phase. This is the energetic heterogeneity of real solid surfaces, which causes the adsorption sites to be distributed among various adsorption energies. In our notation, it means some dispersion of the values of the parameters $K_{AC,1}^{\alpha}$ and $K_{BC,1}^{\alpha}$.

We shall assume further a random model of surface topography i.e., the lack of any spatial correlations between adsorption sites exhibiting the same value of $K_{AC,1}^{\alpha}$ and $K_{BC,1}^{\alpha}$. Let $\chi_A(K_{AC,1}^{\alpha})$ and $\chi_B(K_{BC,1}^{\alpha})$ represent the differential distributions of adsorption sites among various values of $K_{AC,1}^{\alpha}$ and $K_{BC,1}^{\alpha}$. Assuming that these functions are normalized to unity, we obtain

$$x_{K_{C,1}^{com}} = \int_{\Omega_A} dK_{AC,1}^{\alpha} \int_{\Omega_B} dK_{BC,1}^{\alpha} \left[K_{AC,1}^{\alpha} x_A^{(L)} \frac{\gamma_A^{(L)}}{\gamma_{A,1}^{(G)}} \frac{\alpha_C}{\alpha_A} + \right. \quad (22)$$

$$+ K_{BC,1}^{\alpha} \left(x_B^{(L)} \frac{\gamma_B^{(L)}}{\gamma_{B,1}^{(G)}} \right)^{\frac{\alpha C}{\alpha_B}} - 1 \cdot \chi_A(K_{AC,1}^{\alpha}) \chi_B(K_{BC,1}^{\alpha}) \quad (22)$$

where Ω_A and Ω_B denote the range of variations of $K_{AC,1}^{\alpha}$ and $K_{BC,1}^{\alpha}$.

The hitherto investigation of the competitive adsorption from binary liquid mixtures on solid surfaces, have shown, that the distribution function χ is in general a gaussian-like function. We shall approximate it further by the following analytical function,

$$\chi(y) = \frac{1}{r} \frac{\exp\left(\frac{y - y^0}{r}\right)}{\left[1 + \exp\left(\frac{y - y^0}{r}\right)\right]^2} \quad (23)$$

where the parameter r describes the width of the distribution $\chi(y)$ function, whereas y^0 is the most probable value of the variable y . In the limit $r \rightarrow 0$, $\chi(y)$ degenerates into Dirac delta distribution $\delta(y - y^0)$, related to an ideally homogeneous surface, characterized by $y = y^0$. The analytical form of the distribution function (23) makes the following expansion possible, for a function $F(y)$, continuous with all its derivatives,

$$\int_{-\infty}^{+\infty} F(y) \chi(y) dy = F(y^0) + 2 \sum_{n=1}^{\infty} \frac{(\Pi r)^{2n}}{(2n)!} (2^{2n-1} - 1) B_n \left[\frac{\partial^{2n} F}{\partial y^{2n}} \right]_{y=y^0} \quad (24)$$

where B_n is Bernoulli's number. The investigation of adsorption from binaries on solid surfaces have shown, that the distribution function is, in general, a narrow one. That means, that r can, in general, be treated as a small parameter, and expansion (24) can be cut after the second quadratic term. Doing so, we obtain,

$$\int_{-\infty}^{+\infty} F(y) \chi(y) dy = F(y^0) + \frac{\Pi^2 r^2}{6} \left[\frac{\partial^2 F}{\partial y^2} \right]_{y=y^0} \quad (25)$$

Let us remark yet, that when $\lambda(y)$ is narrow, one can safely replace the integration interval $(-\infty, +\infty)$ by a finite domain Ω such that $y^0 \in \Omega$. Further, according to the random model of surface topography, accepted here by us, we can apply the expansion (24) when evaluating the multiple integral (22). Then, neglecting in this expansion the terms higher than quadratic with respect to the parameters r 's, we arrive at the following equation for ${}^x K_{C,com}$

$${}^x K_{C,com} = {}^x K_{C,com}^0 \left\{ 1 + \frac{\mathbb{J}^2}{3} ({}^x K_{C,com}^0)^2 \cdot \left[r_{AC}^2 \left(x_A^{(L)} \frac{\gamma_A^{(L)}}{\gamma_{A,1}^{(\sigma)}} \right)^{2 \frac{\alpha_C}{\alpha_A}} + r_{BC}^2 \left(x_B^{(L)} \frac{\gamma_B^{(L)}}{\gamma_{B,1}^{(\sigma)}} \right)^{2 \frac{\alpha_C}{\alpha_B}} \right] \right\} \quad (26)$$

In equ. (26), ${}^x K_{C,com}^0$ means the competitive distribution coefficient for an ideally homogeneous surface,

$${}^x K_{C,com}^0 = \left[K_{AC,1}^{\alpha,0} x_A^{(L)} \frac{\gamma_A^{(L)}}{\gamma_{A,1}^{(\sigma)}} \frac{\alpha_C}{\alpha_A} + K_{BC,1}^{\alpha,0} x_B^{(L)} \frac{\gamma_B^{(L)}}{\gamma_{B,1}^{(\sigma)}} \frac{\alpha_C}{\alpha_B} \right] - 1 \quad (27)$$

whereas r_{AC} and r_{BC} are the parameters, describing the dispersion of the coefficients $K_{AC,1}^{\alpha}$, $K_{BC,1}^{\alpha}$, and $K_{AC,1}^{\alpha,0}$, $K_{BC,1}^{\alpha,0}$ are their most probable values.

In a similar way, one can take into account the effects of surface heterogeneity in the competitive adsorption of the solvents A and B:

$$x_{A,1}^{(\sigma)} = x_{A,1}^{(\sigma),0} + \frac{\mathbb{J}^2 r_{AB}^2}{6} \left[\frac{\partial^2 x_{A,1}^{(\sigma)}}{\partial (K_{BA,1}^{\alpha})^2} \right] K_{BA,1}^{\alpha} = K_{BA,1}^{\alpha,0} \quad (28)$$

where $x_{A,1}^{(\sigma),0}$ is evaluated from equ. (9), taking $K_{BA,1}^{\alpha} = K_{BA,1}^{\alpha,0}$, and r_{AB} is appropriate heterogeneity parameter.

Now, let us consider at last the problem of activity coefficients in both the adsorbed and the bulk phase. In the case of bulk activity coefficients the problem is relatively simple: Here, the power expansions for the logarithm of the activity coefficients are applied

$$\ln \gamma_A^{(L)} = a_A (x_B^{(L)})^2 + b_A (x_B^{(L)})^3 + c_A (x_B^{(L)})^4 + \dots \quad (29)$$

$$\ln \gamma_B^{(L)} = a_B (x_A^{(L)})^2 + b_B (x_A^{(L)})^3 + c_B (x_A^{(L)})^4 + \dots \quad (30)$$

The coefficients a , b , c , are related to the molar excess free enthalpy of mixing $g_{AB}^{ex,(L)}$, by various theories of solutions. Let us consider, for instance, the very popular Redlich-Kister theory, which gives the following expression for $g_{AB}^{ex,(L)}$,

$$g_{AB}^{ex,(L)} = x_A^{(L)} x_B^{(L)} \left[A + B(x_A^{(L)} - x_B^{(L)}) + C(x_A^{(L)} - x_B^{(L)})^2 + D(x_A^{(L)} - x_B^{(L)})^3 + \dots \right] \quad (31)$$

Application of the Rowlinson's relationship to equ. (31), yields the following relations between the coefficients a , b , c and A , B , C :

$$\begin{aligned} a_A &= A + 3B + 5C + 7D & a_B &= A - 3B + 5C - 7D \\ b_A &= -4(B + 4C + 9D) & b_B &= 4(B - 4C + 9D) \\ c_A &= 12(C + 5D) & c_B &= 12(C - 5D) \\ d_A &= -32D & d_B &= 32D. \end{aligned} \quad (32)$$

Thus, knowing the activity coefficient of one component of the mixture (A+B), makes it possible to calculate easily the other one, by solving the linear system of equations (32).

In the case of the solute C, we approximated its bulk activity coefficient $\ln \gamma_C^{(L)}$ by the following equation,

$$\ln \gamma_C^{(L)} = A_{CA} x_A^{(L)} + A_{CB} x_B^{(L)} + B_{CA} (x_A^{(L)})^2 + B_{CB} (x_B^{(L)})^2 - \frac{g_{AB}^{ex,(L)}}{kT} \quad (33)$$

in which the quadratic terms have to account for the deviations from a regular solution behaviour, as described by Scatchard-Hildebrand theory. However, for $g_{AB}^{ex,(L)}$ we used the quite general expression,

$$g_{AB}^{ex(L)} = x_A^{(L)} \ln \gamma_A^{(L)} + x_B^{(L)} \ln \gamma_B^{(L)}. \quad (34)$$

We shall show it in the next section, that eqs. (33-34) offer a very effective approximation for $\ln \gamma_C^{(L)}$.

Now, we are coming to the very essential point of our consideration, concerning the activity coefficients of the solvents A and B, and the solute C in the adsorbed phase. Everett suggests [19], that the deviations from ideality in the adsorbed phase should be fairly comparable with those in the equilibrium bulk phase. Following this suggestion, we approximated $\ln \gamma_{A,i}^{(G)}$, $\ln \gamma_{B,i}^{(G)}$ and $\ln \gamma_{C,i}^{(G)}$ by the same equations (29), (30), (33) and (34), except that bulk mole fractions $x^{(L)}$ were replaced there by some locally averaged surface concentrations $\bar{x}_i^{(G)}$

$$\bar{x}_i^{(G)} = px_i^{(G)} + m \left[x_{i-1}^{(G)} + x_{i+1}^{(G)} \right]. \quad (35)$$

In equ. (35) p is the fraction of the nearest neighbours lattice (adsorption) sites in the same lattice plane, whereas m is that fraction in the lattice planes below or above the considered lattice plane. In the case of the first lattice plane, i.e., when $i=1$, it is assumed that the lattice plane lying below is empty.

NUMERICAL RESULTS AND DISCUSSION

For the purpose of illustration we will consider the experimental data by Slaats et al. [13]. We analyzed these data numerically neglecting the effects of the non-ideality of the adsorbed phase, as well as the effects of the surface heterogeneity. With these simplifications we were not able to describe well the capacity coefficients of the solutes: Nitrobenzene and benzyl acetate, chromatographed in the two mixed mobile phases: (n-heptane + 2-propanol) and (n-heptane + ethyl acetate), on Partisil 10. Below, we are going to prove, what kind of agreement between theory and experiment can be obtained on the ground of our present theory, taking the effects of the non-ideality in the adsorbed phase, and the effects of surface heterogeneity into account.

We begin with the activity coefficients of the solvents and solutes in the bulk phase, which were measured independently by Slaats et al. [13]. Our numerical investigation has shown, that in the case of the mixture (n-heptane + 2-propanol), the activity coefficient of 2-propanol may well be represented by the polynomial of the seventh order,

$$\ln \gamma_B^{(L)} = 3.22(x_A^{(L)})^2 - 1.36(x_A^{(L)})^3 - 2.92(x_A^{(L)})^4 + 0.196(x_A^{(L)})^5 + 0.628(x_A^{(L)})^6 + 4.0(x_A^{(L)})^7 \quad (36)$$

where $x_A^{(L)}$ is used to denote the mole fraction of n-heptane. In the case of the solvent mixture (n-heptane + ethyl acetate) a satisfactory approximation for $\ln \gamma_B^{(L)}$ can be obtained by the following fifth-order polynomial only,

$$\ln \gamma_B^{(L)} = 4.53(x_A^{(L)})^2 - 4.53(x_A^{(L)})^3 - 3.04(x_A^{(L)})^4 + 4.47(x_A^{(L)})^5 \quad (37)$$

Figures 1 and 2 show graphically the effectiveness of the approximations (36) and (37). In the next Figures 3 and 4, the effectiveness of the approximation is demonstrated, which can be obtained on the ground of our eqs. (33), (34), for the bulk activity coefficients of the solutes. Table 1 reports the related coefficients A_{CA} , A_{CB} , B_{CA} , B_{CB} found by fitting best eqs. (33-34) to the experimental data by Slaats et al. [13].

Table 1

Solute	A_{CA}	A_{CB}	B_{CA}	B_{CB}
(n-heptane + 2-propanol)				
Nitrobenzene	1.05	1.54	2.54	0.358
Benzyl acetate	2.81	2.14	-0.349	0.325
(n-heptane + ethyl acetate)				
Nitrobenzene	0.816	0.932	-2.39	1.5
Benzyl acetate	-1.51	1.22	0.635	0.706

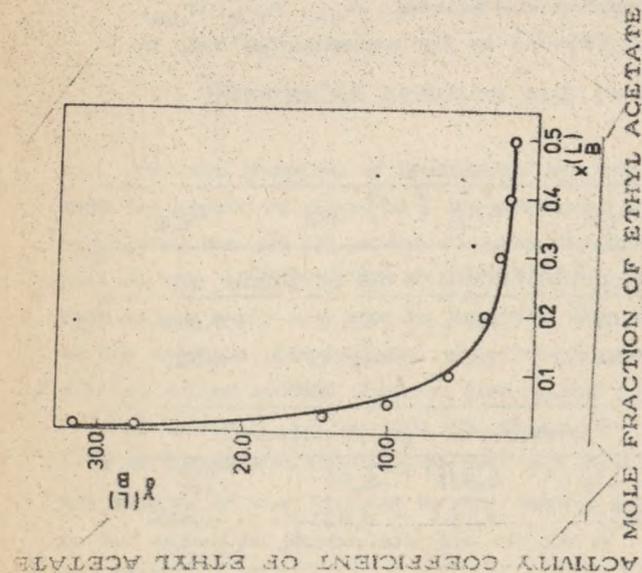


Fig. 1. Comparison of the experimental and the theoretical activity coefficients of 2-propanol in the mixture 2-propanol + n-heptane. The circles denote experimental data reported by Slaats et al. [13], whereas the solid line is given by eqn. (36)

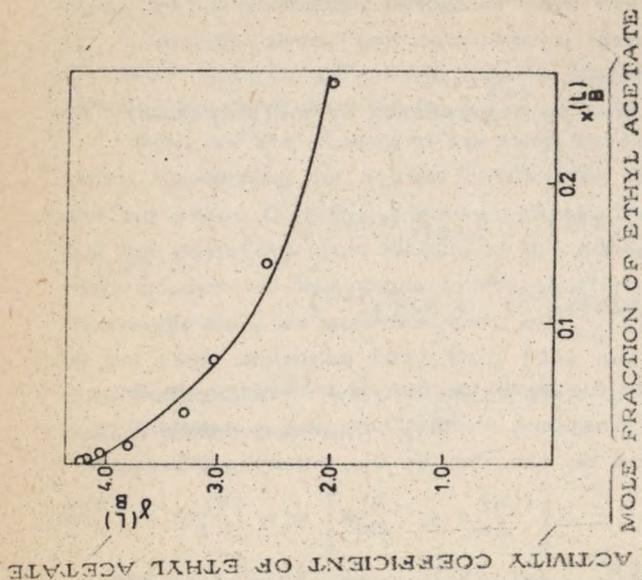
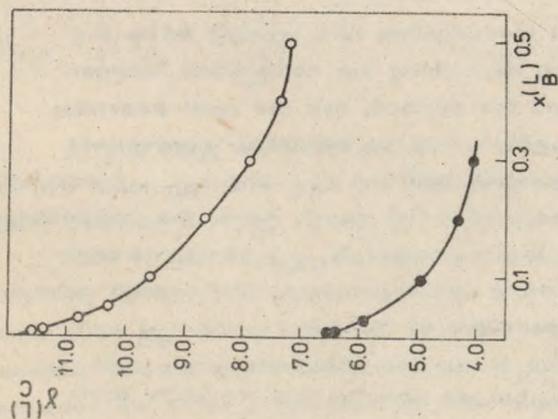


Fig. 2. Comparison of the experimental and the theoretical activity coefficients of ethyl acetate in the mixture ethyl acetate + n-heptane. The circles denote the experimental data reported by Slaats et al. [13], whereas the solid line is given by eqn. (37)

THE ACTIVITY COEFFICIENTS OF THE SOLUTES

MOLE FRACTION OF 2-PROPANOL



THE ACTIVITY COEFFICIENTS OF THE SOLUTES

MOLE FRACTION OF ETHYL ACETATE

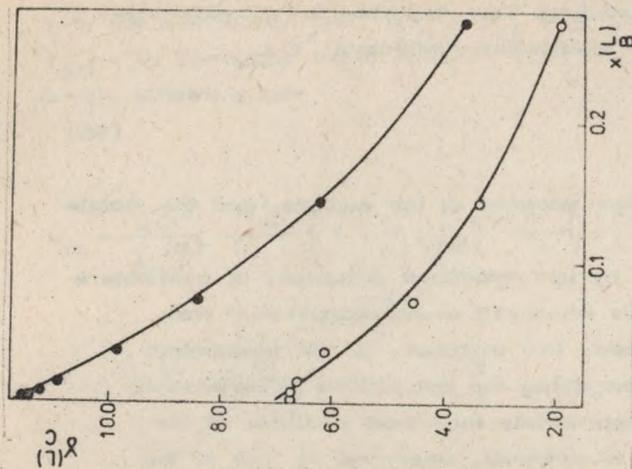


Fig. 3. Comparison of the experimental and the theoretical activity coefficients of benzyl acetate (2-propanol + n-heptane). The circles denote the experimental data reported by Slaats et al. [13], whereas the solid lines are given by eqs.(33-34) and the parameters collected in Table 1

Fig. 4. Comparison of the experimental and the theoretical activity coefficients of benzyl acetate (2-propanol + n-heptane). The circles denote the experimental data reported by Slaats et al. [13], whereas the solid lines are given by eqs.(33-34) and the parameters collected in Table 1

Now, let us consider at last the essential problem of the effectiveness of the approximation for the experimental capacity coefficient k_C , which can be obtained on the ground of our theory developed in the previous section. This experimental quantity has the following relation to the distribution coefficient $^x K_{C,1}$

$$k_C = \frac{V^{(G)}}{V^{(m)}} \cdot {}^x K_{C,1} \quad (38)$$

where $V^{(G)}$ and $V^{(m)}$ are the volumes of the surface, and the mobile phase respectively.

The theory developed by us introduces a number of parameters which, theoretically, could be measured in an independent way, especially designed experiment. For instance, all the parameters $K_{BA,1}$, r_{AB} , (α_A/α_B) describing the competitive adsorption of solvents can be found by appropriate numerical analysis of the excess adsorption isotherm of solvents, measured by one of the static methods [20]. However, even in such a complete chromatographic experiment, as that carried out by Slaats et al. [13] this independent measurement of the excess isotherm of solvents was not performed.

The next necessary step in our theoretical treatment is to decide which parameters play the most crucial role, and which ones are of a smaller importance. This has the purpose to decrease the number of the parameters, to be found by fitting best our equations to experimental data.

Our extensive numerical investigation has brought us to the conclusion that the parameters describing the competition between the solute and the solvents on the surface, are the most essential ones. It should, however, be noted, that no essential improvement is achieved when one distinguishes between r_{AC} and r_{BC} , compared to situation when they are assumed to be equal. As to the competitive adsorption of solvents, only the parameter $K_{BA,1}$ affects strongly the agreement between the theory and experiment. The best-fit calculation has appeared to be insensitive to the parameters r_{AB} and (α_A/α_B) . Of course, also the interaction parameters may play a more or less important role, but we assume that we know them from an independent bulk experiment.

Looking for a possibility to decrease the number of the best-fit parameters, and to the results of our numerical investigation,

we propose to use (at least for the chromatographic systems under investigation), the following simplified version of our theory, obtained with the assumption that $\alpha_A = \alpha_B = \alpha$, $r_{AC} = r_{BC} = r$, and $r_{AB} = 0$. Then, the basic equation (20) of our theory can be written in the following form

$$k_C = \frac{\gamma_C^{(L)}}{\gamma_{C,1}^{(\sigma)}} \frac{K'_{BA}}{P_C} \left\{ 1 + (r' K'_{BA})^2 \frac{\pi^2}{3} \left[\left(x_A^{(L)} \frac{\gamma_A^{(L)}}{\gamma_{A,1}^{(\sigma)}} \right)^2 \frac{\alpha_C}{\alpha} + \left(x_B^{(L)} \frac{\gamma_B^{(L)}}{\gamma_{B,1}^{(\sigma)}} \right)^2 \frac{\alpha_C}{\alpha} \right] \right\} \quad (38)$$

where

$$P_C = \frac{K_{AC,1}^\alpha V^{(m)}}{V^{(\sigma)}} \quad (39)$$

$$r' = \frac{r}{K_{AC,1}^\alpha} \quad (40)$$

$$K'_{BA} = \left\{ \left(x_A^{(L)} \frac{\gamma_A^{(L)}}{\gamma_{A,1}^{(\sigma)}} \right)^2 \frac{\alpha_C}{\alpha} + K_{BA,1} \left(x_B^{(L)} \frac{\gamma_B^{(L)}}{\gamma_{B,1}^{(\sigma)}} \right)^2 \frac{\alpha_C}{\alpha} \right\} \quad (41)$$

In this way, we have arrived at a simplified version of our theory which includes now the following five parameters to be fitted best numerically: P_C , m , $K_{BA,1}$, (α_C/α) and r' .

Now let us explain the strategy of our best-fit calculation: Namely, for a given pair of solvents (A+B), we fitted simultaneously equ. (39) to the experimental data for both Nitrobenzene and Benzyl acetate, assuming that the parameter $K_{BA,1}$ must be the same, whereas the other parameters may be different. The results of this best-fit calculation are shown in Table 2.

Further, since we assumed that the competitive adsorption of solvents may have a multilayer character, we had to evaluate the

concentration profile of the solvents near the surface. To do it, we assumed that the surface forces of the adsorbent do not extend over the first adsorbed layer, i.e., that for the second and higher layers $K_{BA} = 1$. Having the mole fraction of the solvents in an adsorbed layer, say i , evaluated, we could find the adsorption excess $n_{B,i}^{(e)}$ of the more active solvent B,

$$n_{B,i}^{(e)} = x_{B,i}^{(G)} - x_B^{(L)} \quad (42)$$

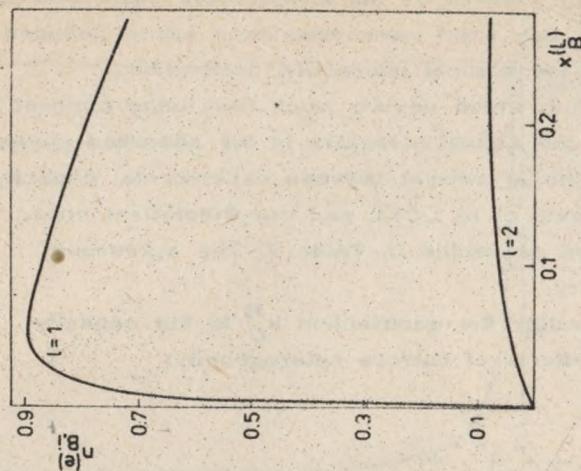
The total adsorption excess $n_B^{(e)}$ which could be measured by using static methods, is just the sum of the excesses $n_{B,i}^{(e)}$'s over all the adsorbed layers divided by the number of layers. The evaluation of the concentration profile had to be done in every step of our best-fit calculation. Figures 5 and 6 show the concentration profiles (adsorption excesses) corresponding to the best-fit parameters collected in Table 2.

Table 2

Solute	P_C	m	$K_{BA,1}^A$	d_C/d	r'
(n-heptane + 2-propanol)					
Nitrobenzene	1.97	0.416	300.0	0.536	0.649
Benzyl acetate	2.68	0.416	300.0	0.402	0.248
(n-heptane + ethyl acetate)					
Nitrobenzene	0.926	0.500	317.0	0.236	0.106
Benzyl acetate	0.422	0.500	317.0	0.418	0.229

It can be concluded from these figures that the competitive adsorption of the solvent mixture (n-heptane + 2-propanol) has a strong multilayer character, whereas in the case of the mixture (n-heptane + ethyl acetate) a double-layer model should be quite satisfactory. High values of the parameter m mean that the vertical interactions in the adsorbed phase are predominant. At least in the first adsorbed layer which makes the largest contribution to the total surface excess. Two things may be responsible for that: Firstly, the adsorption centers

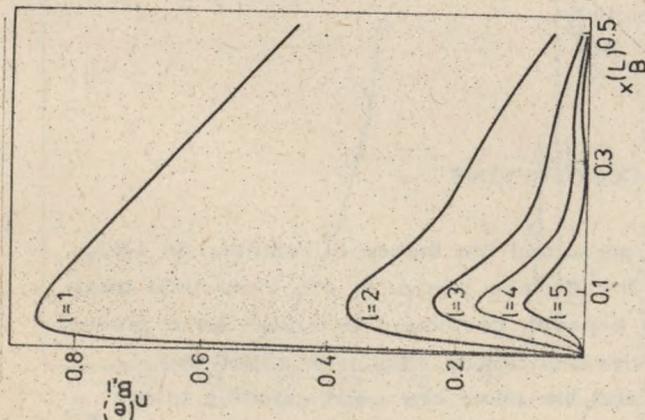
THE ADSORPTION EXCESS OF ETHYL ACETATE $n_{B,1}^{(e)}$



MOLE FRACTION OF ETHYL ACETATE

Fig. 6. The theoretically evaluated excess adsorption isotherms of 2-propanol, in the competitive adsorption from the binary mixture (ethyl acetate + n-heptane) on Partisil 10. The solid lines denote the excess of benzyl acetate in the first ($l=1$), second ($l=2$), and higher adsorbed layers

THE ADSORPTION EXCESS OF 2-PROPANOL $n_{B,1}^{(e)}$



MOLE FRACTION OF 2-PROPANOL

Fig. 5. The theoretically evaluated excess adsorption isotherms of 2-propanol, in the competitive adsorption from the binary mixture (2-propanol + n-heptane) on Partisil 10. The solid lines denote the excess of 2-propanol in the first ($l=1$), second ($l=2$), and higher adsorbed layers

on Aerosil surface may lie at distances, at which two solvent molecules adsorbed on two neighbouring centers do not exhibit more some stronger interactions. Secondly, there may exist some orientation effects induced by the surface, which make the vertical interaction preferential.

The values of (α_C / α) , which deviate much from unity suggest strong orientation effects of the solute molecules in the adsorbed phase.

Figures 7, 8, 9 show the agreement between experimental capacity coefficients measured by Slaats et al. [13], and our theoretical ones, evaluated with the parameters presented in Table 2. The agreement seems to be quite satisfactory.

Figure 10 shows separately the contribution k_C^H to the capacity coefficient k_C , due to the effects of surface heterogeneity

$$k_C^H = \frac{\gamma_C^{(L)}}{\gamma_{C,1}^{(G)}} \frac{K'_{BA}}{P_C} \frac{\pi^2}{3} (r' K'_{BA})^2 \quad (43)$$

$$\cdot \left[\left(x_A^{(L)} \frac{\gamma_A^{(L)}}{\gamma_{A,1}^{(G)}} \right)^2 \frac{\alpha_C}{\alpha} + \left(x_B^{(L)} \frac{\gamma_B^{(L)}}{\gamma_{B,1}^{(G)}} \right)^2 \frac{\alpha_C}{\alpha} \right]$$

for the case of Nitrobenzene. Similar pictures are obtained for other systems. It can be concluded from these figures, that the effects of surface heterogeneity are especially important at very small concentrations of the more active solvent.

CONCLUSIONS

In this paper we have presented the theory of retention in LSC, based on a lattice model of the surface phase. In our theoretical treatment, the expression for the capacity coefficient is written as a product of two terms: one of them corresponding to what was called the "interaction" theory in LSC, and the other one corresponding to the "competition" theory in LSC. It should, however, be noted that the "competitive" factor is also influenced by the interaction effects in both the surface and the bulk phase. On the other hand, the

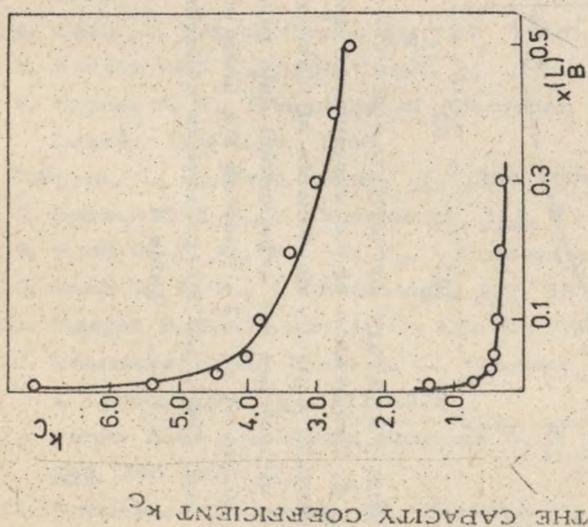


Fig. 7. Comparison of the experimental and theoretical capacity coefficients of benzyl acetate (O), and nitrobenzene (O). The circles are the experimental data reported by Slaats et al. [13], whereas the lines are given by equ. (38) and the parameters collected in Table 2

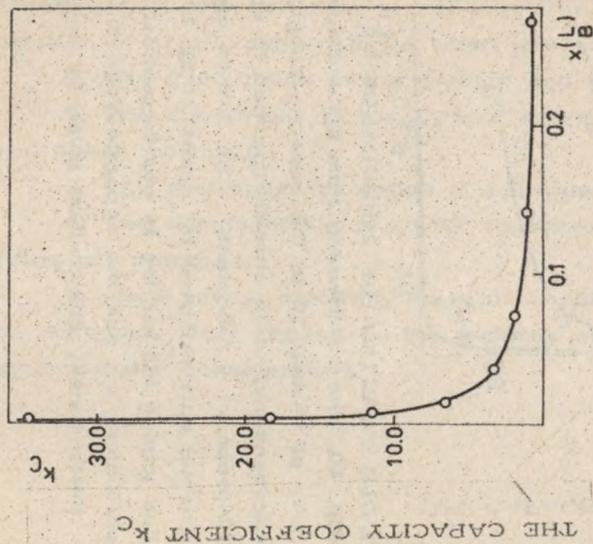
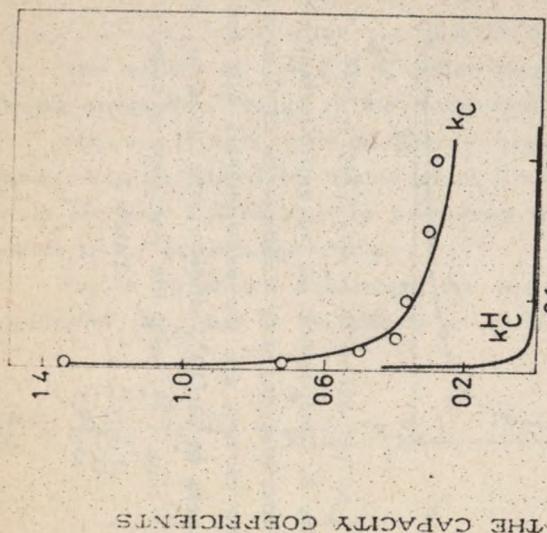


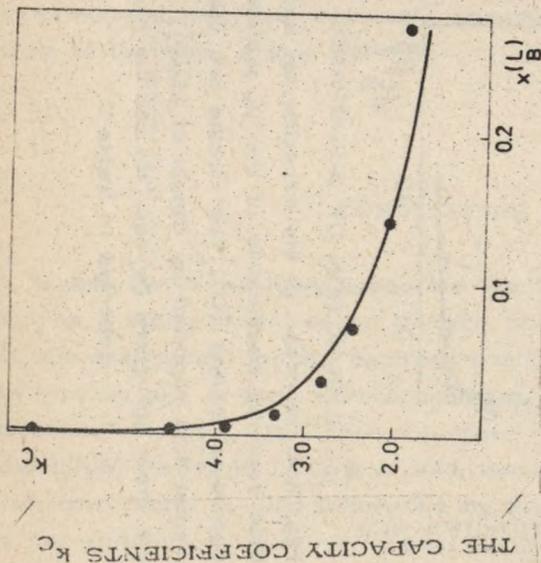
Fig. 8. Comparison of the experimental and the theoretical capacity coefficients of benzyl acetate. The circles are the experimental data reported by Slaats et al. [13], whereas the lines are given by our equ. (38) and the parameters collected in Table 2



THE CAPACITY COEFFICIENTS

MOLE FRACTION OF 2-PROPANOL x_B^L

Fig. 10. The contribution from the surface heterogeneity of Partisil 10 to the capacity coefficient of nitrobenzene, when chromatographed in the mixture (2-propanol + n-heptane). The circles are the experimental data reported by Slaats et al. 13, the solid line joining the circles is our theoretical capacity coefficient k_C , and the separate solid line is the heterogeneity contribution given by eqn. (43)



MOLE FRACTION OF ETHYL ACETATE

Fig. 9. Comparison of the experimental and the theoretical capacity coefficients of nitrobenzene. The circles are the experimental data reported by Slaats et al. 13, whereas the lines are given by eqn. (38), and the parameters collected in

Table 2

"interaction" term depends, (through surface activity coefficients), on the mechanism of the competitive adsorption on the surface.

Our numerical investigation has shown, that a satisfactory description of retention data in LSC requires some few basic characteristics of a LSC system to be taken into account:

1. The interactions in the surface and the bulk phase,
2. The differences in the surface areas occupied by solvent and solute molecules;
3. The multilayer adsorption of solvents;
4. The effects of the energetic heterogeneity of the solid (support) surfaces.

In some cases, however, several simplifying assumptions can be accepted. They depend on the features of the particular LSC system under consideration.

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STRESZCZENIE

Wyprowadzono równanie opisujące zależność współczynnika podziału w adsorpcyjnej chromatografii ciekowej od składu binarnej fazy ruchomej. Uwzględniono nieidealność fazy ruchomej, różnice w rozmiarach cząsteczek substancji chromatografowanej i rozpuszczalników, energetyczną niejednorodność powierzchni adsorbentu oraz wielowarstwowy charakter adsorpcji rozpuszczalników. Wyprowadzone równania zastosowano do opisu doświadczalnych współczynników pojemnościowych. W oparciu o uzyskane wyniki przedyskutowano wpływ wymienionych wyżej czynników na mechanizm retencji w adsorpcyjnej chromatografii ciekowej.

РЕЗЮМЕ

Ведено уравнение, описывающее зависимость коэффициента деления в адсорбционной жидкостной хроматографии от состава бинарной подвижной фазы. Учтено неидеальность подвижной фазы, различия в размерах частиц хроматографированного вещества и растворителей, энергетическую неоднородность поверхности адсорбента, а также многослойный характер адсорбции растворителей. Введенные уравнения использовано для описания экспериментальных емкостных коэффициентов. Опираясь на полученные результаты, продискутировали влияние вышеупомянутых факторов на механизм ретенции в адсорбционной жидкостной хроматографии.