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Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597273>

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To cite this Article Ościk-Mendyk, B.(1991) 'Studies of Molecular Interactions in Adsorption Liquid Chromatography with Binary Mobile Phases', *Journal of Liquid Chromatography & Related Technologies*, 14: 15, 2891 – 2905

To link to this Article: DOI: 10.1080/01483919108049364

URL: <http://dx.doi.org/10.1080/01483919108049364>

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STUDIES OF MOLECULAR INTERACTIONS IN ADSORPTION LIQUID CHROMATOGRAPHY WITH BINARY MOBILE PHASES

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ABSTRACT

For all examined chromatographic systems with binary mobile phases the linear relationship taking into account the specific molecular interactions was stated. This relationship correlates all equilibrium constants (association and adsorption) characterizing LSC process. In the case of strong polar component of the mobile phase the association and solvation equilibrium constants can be evaluated separately.

INTRODUCTION

The process of liquid adsorption chromatography is a complex phenomenon and depends on many factors, such as:

- competitive adsorption of the system components;
- specific and nonspecific molecular interactions of these components in mobile and stationary phases;
- differences in the dimensions and shape of the molecules present in the system, etc.

Including all factors affecting the chromatographic retention complicates significantly the analysis of the process. It is well known, however, that only several factors play a more significant role.

Jaroniec et. al. (1-4) as well as Ościk-Mendyk et. al. (5-9) have proposed the model of the chromatographic process taking into account the specific molecular interactions in mixed mobile phase. Formation of intermolecular associates in this phase plays a significant role in the process of the chromatographic retention. In the proposed model the specific molecular interactions are described by the equilibrium constants of binary associates formation. The interactions with the adsorbent surface are illustrated by the equilibrium constant of the phase exchange reaction of the system components between bulk and surface phases.

The equation based on the proposed model of chromatographic retention can be presented in the linear form:

$$\frac{y_1}{k'_s x_1} = \alpha + \beta x_1 \quad (.1)$$

where $\alpha = q/K_{s1}$ and $\beta = q(C_1 - 2L_2)/K_{s1}$; x_1 and y_1 denote the molar fractions of the more polar component of the mobile phase in bulk and surface phases, respectively; k'_s is the capacity factor of the chromatographic substance s ; C_1 is the equilibrium constant of the associates formation of the $s-1$ type (one molecule of the chromatographed substance and one molecule of the more polar component "1" of the mobile phase); L_2 is the equilibrium constant of binary autoassociates formation of more polar component molecules of mobile phase (associates of 1-1 type); K_{s1} is the exchange reaction constant of the molecules of the chromatographed substance and more polar component of mobile phase between bulk and surface phases; q denotes the constant dependent on the nature of adsorbent.

The effect of surface phase composition on the course of the relationship $y_1/k'_s x_1$ vs. x_1 has been investigated (8). It was stated that for evaluation parameters of eq.(1) the boundary conditions of $1/k'_s x_1$ vs. x_1 relationship for $x_1 \geq 0.5$ can be applied.

The investigations described in the previous papers (4-8) were mainly related to applicability of eq.(1) for analysis of the chromatographic process

mechanism. It was stated that application of this equation broadened significantly the possibility of experimental chromatographic data interpretation. Testing of eq.(1) was limited, however, to determination both of its parameters and the effect of predominant molecular association on the chromatographic process (positive or negative values of β parameter).

For different chromatographic systems with binary and ternary mobile phases and SiO_2 or Al_2O_3 as adsorbents the numerical values of α , β and $\beta/\alpha = C_1 - 2L_2$ parameter determined for different substances varied largely (α from 0.18 to 6.50, β from -19.9 to 2.33, $C_1 - 2L_2$ from -0.88 to 3.82) (5,6,9). The mutual dependence of numerical values of these parameters in different systems with mixed mobile phases was not examined. One can suppose that the determination of these dependences for a great number of chromatographic systems with mixed mobile phases and a great number of the chromatographed substances will permit to formulate the rules describing the changes of eq.(1) parameters. This will allow for better knowledge of chromatographic mechanism and improvement of the process conditions. Such investigations are the main purpose of the paper.

THEORETICAL

The parameters of eq.(1) are connected mutually by the relationship:

$$\beta = \alpha(C_1 - 2L_2) \quad (2)$$

The above relationship connects the values of all equilibrium constants. One can begin the interpretation of this relationship assuming that the molecular interactions of 1-1 and s-1 types are identical. In such a case the numerical values of equilibrium constants of molecular associates formation are also identical, i.e. $C_1 = L_2$. Then eq.(2) can be written in the form:

$$\beta = -\alpha L_2 \quad (3)$$

From the fact that $1/\alpha$ is always positive it results that $\beta < 0$. In the case of differentiated adsorption of test substances in a given system with binary mobile phase (different values of K_{s1}) the relationship of β vs. α will be linear.

The numerical value of equilibrium constant L_2 being the slope of this straight line depends on the energies of molecular interactions in the mobile phase.

The above assumptions idealise significantly the properties of the chromatographic systems. In real chromatographic systems the correlation between the molecular association process of mobile phase components and the adsorption of the test substances becomes more complicated. The analysis of a molecular mechanism of the chromatographic process leads, among others, to the following conclusions:

- autoassociation of the molecules of a more polar mobile phase component and association (solvation) of the molecules of the chromatographed substance and more polar solvent are the competitive processes;
- the proposed model of the chromatographic process assumes that only single molecules of the system components are adsorbed, thus autoassociation of the molecules of a more polar solvent promotes the adsorption of the substance s (it makes the molecules solvation difficult);
- strong molecular interactions of 1-1 and s -1 types are connected most often with the strong interactions of "1" and s molecules with the adsorbent surface (with surface groups). The associates getting into the region of adsorption forces undergo destruction.

The presented conclusions confirm a great complexity of the association process effect on the chromatographic retention mechanism. Theoretical predictions of the correlation between these processes are very difficult. For this reason, analysis of the results obtained for a great number of experimental chromatographic data, made on the basis of eq.(1), can facilitate significantly the solution this question.

METHODS

The measurements were carried out by thin-layer chromatography at 293K. Silica gel 60H (Merck, Darmstadt, FRG) was used as the adsorbent. Binary mobile phases, listed in Table 1 according to Pimentel and McClellan classi-

TABLE 1.

Mobile Phases Used for Chromatographic Measurements.

Solvents	Class
hexane+carbon tetrachloride	N-N
cyclohexane+benzene	N-N/B
carbon tetrachloride+benzene	N-N/B
carbon tetrachloride+trichloroethylene	N-A
heptane+acetone	N-B
carbon tetrachloride+ethyl acetate	N-B
carbon tetrachloride+acetone	N-B
carbon tetrachloride+n-propanol	N-AB
toluene+chloroform	N/B-A
benzene+acetone	N/B-B
toluene+acetone	N/B-B
toluene+ethyl acetate	N/B-B
benzene+methanol	N/B-AB
benzene+n-propanol	N/B-AB
toluene+isopropanol	N/B-AB
trichloroethylene+benzene	A-N/B
ethylene chloride+acetone	A-B

fication (10), are used at the concentrations (molar fractions) of 0.1, 0.3, 0.5, 0.7, 0.9 of a more polar solvent and two pure solvents. The chromatographed substances are listed in Table 2. Some substances cannot be used in the investigated systems because their R_M values exceed the optimum range i.e. from -1.5 to 1.5. Other details concerning TLC measurements are described elsewhere (11).

RESULTS AND DISCUSSION

The results of chromatographic measurements are presented in the form $1/k'_s x_1$ vs. x_1 relationships for $x_1 \geq 0.5$. For boundary conditions of these re-

TABLE 2.

Test Substances Used for the Chromatographic Measurements.

1.	1-naphthalene	22.	o-nitrophenol
2.	1-methylnaphthalene	23.	o-chlorophenol
3.	3-methylnaphthalene	24.	p-chlorophenol
4.	1.3-dimethylnaphthalene	25.	2.3-dichlorophenol
5.	1.4-dimethylnaphthalene	26.	2.4-dichlorophenol
6.	1.5-dimethylnaphthalene	27.	2.5-dichlorophenol
7.	2.3-dimethylnaphthalene	28.	2.6-dichlorophenol
8.	2.6-dimethylnaphthalene	29.	2.4.6-trichlorophenol
9.	1.6-dihydroxynaphthalene	30.	o-nitroaniline
10.	2.3-dihydroxynaphthalene	31.	m-nitroaniline
11.	2.7-dihydroxynaphthalene	32.	p-nitroaniline
12.	diphenyl	33.	2-nitro-p-toluidine
13.	anthracene	34.	4-nitro-o-toluidine
14.	9-methylanthracene	35.	5-nitro-o-toluidine
15.	phenanthrene	36.	o-nitrotoluene
16.	chrysene	37.	m-nitrotoluene
17.	pyrene	38.	o-bromonitrobenzene
18.	fluoranthene	39.	p-bromonitrobenzene
19.	N-phenyl-1-naphthylamine	40.	o-dinitrobenzene
20.	fluorenone	41.	p-dinitrobenzene
21.	carbazole	42.	6-methylquinoline
		43.	8-methylquinoline
		44.	quinoline
		45.	isoquinoline

relationships α and β parameters of eq.(1) for all examined chromatographic systems were determined. Fig.1 presents the exemplary relationships $1/k'_1 x_1$ vs. x_1 for two mobile phases and several chromatographed substances. α and β parameters evaluated for the test substances in a given mobile phase are presented as β vs. α relationships. Figs 2-4 present these relationships for seven selected systems only. Analogous plots are determined also for other mobile phases.

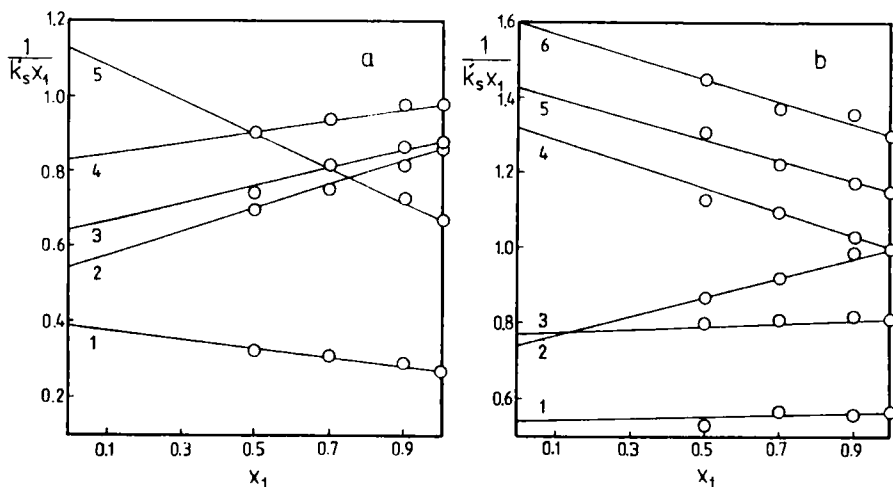


Figure 1. Relationships $1/k'_s x_1$ vs. x_1 for: a) 1-3,4-dichlorophenol, 2-2,4-dichlorophenol, 3-2,3-dichlorophenol, 4-2,6-dichlorophenol, 5-2,5-dichlorophenol in heptane + chloroform system and b) 1-2,5-dichlorophenol, 2-o-nitrophenol, 3-2,6-dichlorophenol, 4-m-nitrotoluene, 5-o-nitrotoluene, 6-p-bromonitrobenzene in cyclohexane+benzene system on silica gel at 293K.

The relationships are linear for all investigated systems. The circles marked by numbers correspond to the numerical values of α and β of eq.(1) determined for the substances listed in Table 2.

The obtained linear relationships can be described by the following equation:

$$\beta = b(\alpha - a) \quad (4)$$

where a denotes the distance of an intersection point of the straight line with α axis (abscissa) from the origin of co-ordinate axes; b - the slope of a straight line - b is always negative (Fig.5A). In Table 3 the numerical values of a and b parameters of eq.(4) for all binary mobile phases are listed.

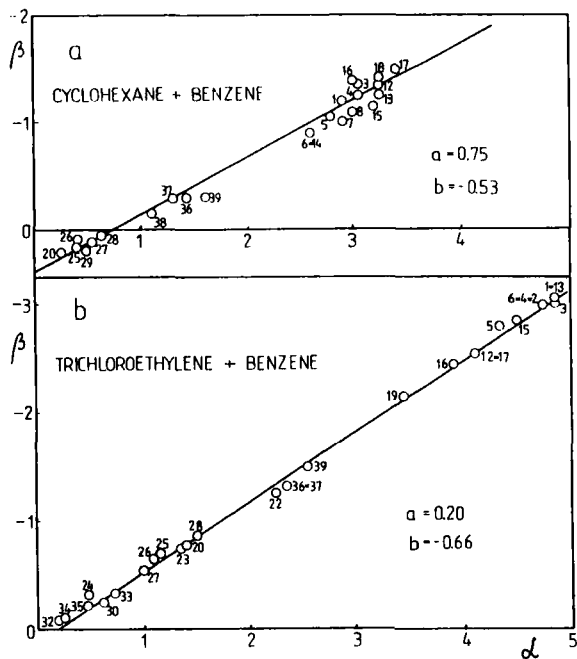


Figure 2. Relationships β vs. α for cyclohexane + benzene and trichloroethylene + benzene systems. Individual numbers refer to solutes from Table 2.

On the basis of numerical values of these parameters one can divide the mobile phase systems used in our experiments into two groups. The first group includes these systems for which the parameters of eq.(4) are in the ranges:

$$0.05 \leq a \leq 0.75$$

$$-0.66 \leq b \leq -0.53$$

The second group includes the systems for which the parameters of eq.(4) are in ranges:

$$1.40 \leq a \leq 2.65$$

$$-1.00 \leq b \leq -0.77$$

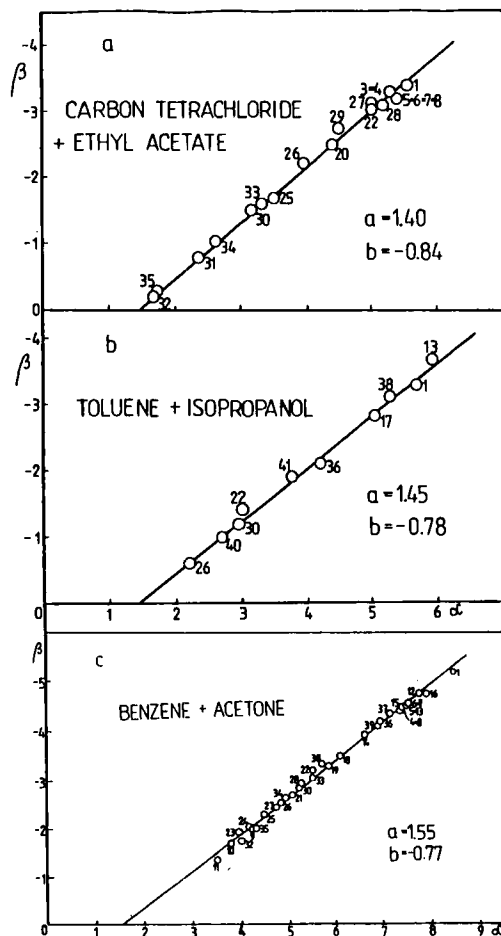


Figure 3. Relationships β vs. α for carbon tetrachloride + ethyl acetate , toluene + isopropanol and benzene + acetone systems. Individual numbers refer to solutes from Table 2.

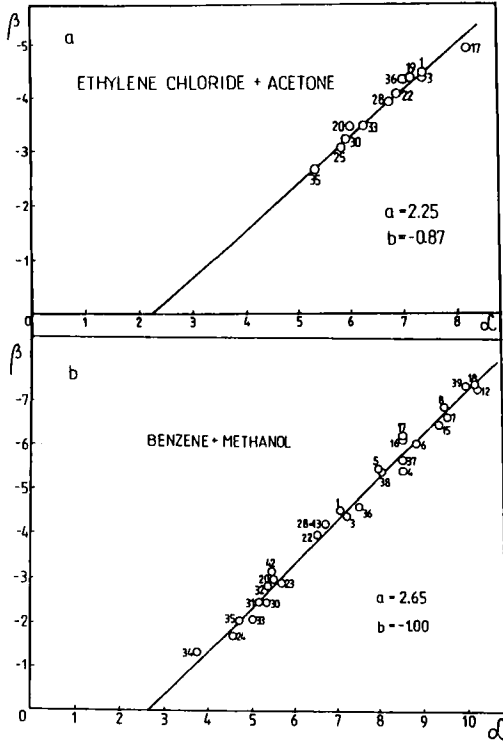


Figure 4. Relationships β vs. α for ethylene chloride + acetone and benzene + methanol systems. Individual numbers refer to solutes from Table 2.

In the second group the molecules of polar components of the mobile phase have high values of dipole moment and contain the active functional groups (methanol -OH and $\mu = 1.69\text{D}$, acetone $=\text{CO}$ and $\mu = 2.76\text{D}$). Four systems belonging to this group are characterized by very high values of a parameter (from 2.25 to 2.65) and by the highest negative values of b parameter (from -0.87 to -1.00).

Dividing eq.(4) by the α parameter we will obtain:

$$\frac{\beta}{\alpha} = b\left(1 - \frac{a}{\alpha}\right) \quad (5)$$

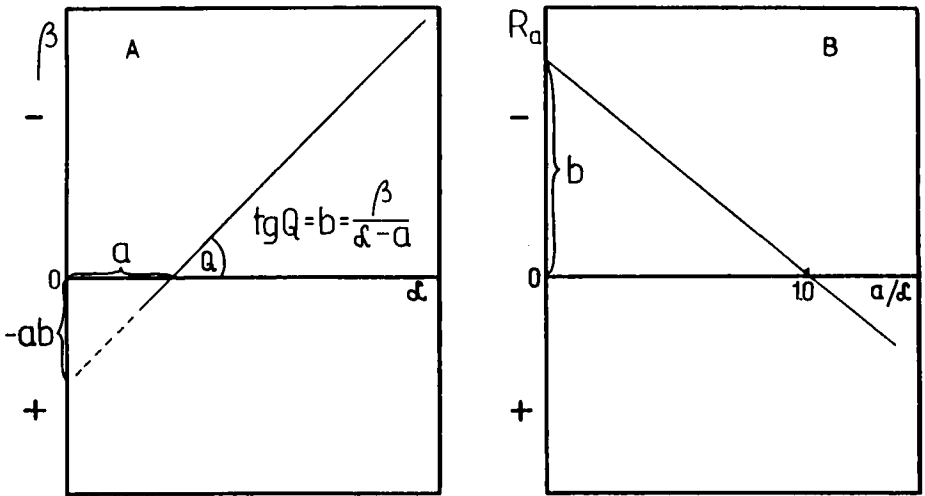


Figure 5. Theoretical relationships: (A) β vs. α and (B) R_a vs. a/α plotted according to eqs (4) and (6).

It is known that according to eq.(1) the quotient β/α is equal to $C_1 - 2L_2$. In order to analyze the correlation between α and β the term $R_a = C_1 - 2L_2$ was introduced. Then eq.(5) can be written in the form:

$$R_a = b\left(1 - \frac{a}{\alpha}\right) \tag{6}$$

The analysis of this equation leads to the following conclusions:

if $\alpha > a$ then $R_a < 0$ and $C_1 < 2L_2$

if $\alpha = a$ then $R_a = 0$ and $C_1 = 2L_2$

if $\alpha < a$ then $R_a > 0$ and $C_1 > 2L_2$

From the boundary conditions of eq.(6) it results that if $\alpha \rightarrow 0$ then $(1 - a/\alpha) \rightarrow -\infty$. Because $b < 0$ therefore $R_a \rightarrow \infty$. On the other hand, when $\alpha \rightarrow \infty$ then $(1 - a/\alpha) \rightarrow 1$ and $R_a = b$. This is illustrated in Fig.5B.

TABLE 3.

Parameters a and b Obtained According to Eq.(4).

Mobile phase	a	b
carbon tetrachloride+trichloroethylene	0.05	-0.57
hexane+carbon tetrachloride	0.10	-0.58
toluene+chloroform	0.10	-0.61
trichloroethylene+benzene	0.20	-0.66
carbon tetrachloride+benzene	0.50	-0.58
cyclohexane+benzene	0.75	-0.58
carbon tetrachloride+ethyl acetate	1.40	-0.84
carbon tetrachloride+n-propanol	1.40	-0.94
benzene+n-propanol	1.40	-0.94
toluene+isopropanol	1.45	-0.80
carbon tetrachloride+acetone	1.55	-0.77
benzene+acetone	1.55	-0.77
toluene+ethyl acetate	1.55	-0.83
ethylene chloride+acetone	2.25	-0.87
toluene+acetone	2.55	-1.00
heptane+acetone	2.60	-1.00
benzene+methanol	2.65	-1.00

Fig.6 presents the dependence of R_a vs. a/α for three examined chromatographic systems. It can be assumed with good approximation, that in the case of binary mobile phases containing one strongly polar solvent the equilibrium constant of autoassociation of its molecules is practically constant i.e. $L_2 = const.$ Then the change of R_a values with the changes in α values is connected only with the changes in the equilibrium constant C_1 (association of s-1 type i.e. solvation of the molecules of the test substance). With the assumption $\alpha \rightarrow \infty$ it can be said that $C_1 \rightarrow 0$, and then $R_a = b = -2L_2$ i.e. $L_2 = -b/2$. The above assumption related to a given chromatographic

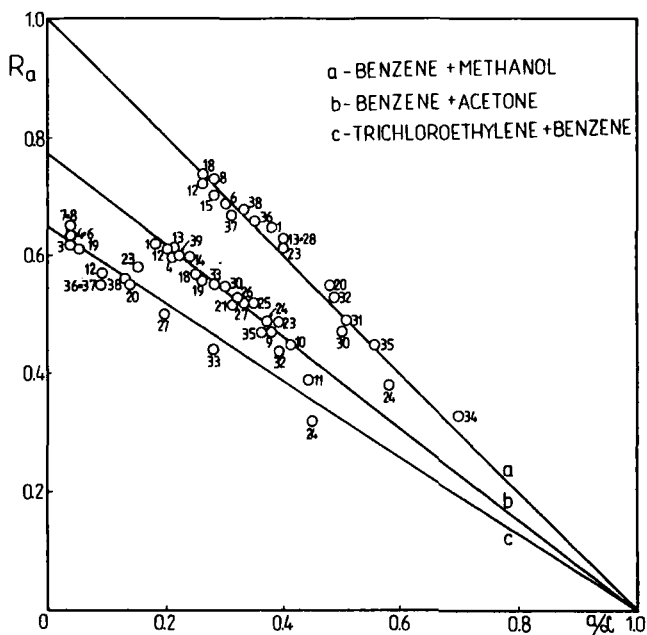


Figure 6. Relationships R_a vs. a/α for three binary mobile phases on silica gel at 293 K. Individual numbers refer to solutes from Table 2.

system with binary mobile phase permits to evaluate not only the differences in equilibrium constants of association, R_a , but also separately values of both constants (C_1 and L_2). These problems will be studied in future.

SUMMARY

The results of investigations of great number of chromatographic systems have permitted to answer the questions formulated in this paper:

- the linear relationships between α and β parameters of eq.(1) for all binary mobile phases have been obtained;

- all binary mobile phases may be divided into two groups taking into account values of parameters a and b of eq.(4) (Table 3);
- eq.(6) correlates all equilibrium constants (C_1 , L_2 and $K_{s1} \sim 1/\alpha$) characterizing the molecular interactions determining the chromatographic process;
- analysis of boundary conditions of eq.(6) creates the interesting possibilities of description of molecular mechanism of chromatographic process performed in the systems containing binary mobile phases. In the case of strong polar component of this phase not only the differences of equilibrium constants, R_a , can be evaluated but also the separately values of both constants (C_1 and L_2).

The above ascertainments and conclusions show, that the proposed model of the chromatographic process performed in the systems with binary mobile phases creates the great possibilities of the interpretation of experimental data. This model opens also the further possibilities in investigations of such complex systems.

REFERENCES

1. Jaroniec M., Jaroniec J.A., A model of liquid adsorption chromatography involving solute-solvent interaction in the mobile phase, energetic heterogeneity of the adsorbent and differences in molecular sizes of the solute and solvents, *J.Liq.Chromatogr.*, 4, 2121, 1981.
2. Jaroniec M., Jaroniec J.A., Theoretical description of association effects in liquid adsorption chromatography with a mixed mobile phase, *J.Chromatogr.*, 295, 377, 1984.
3. Jaroniec M., Jaroniec J.A., Theoretical foundations of liquid adsorption chromatography with mixed eluent, *J.Liq.Chromatogr.*, 7, 393, 1984.
4. Jaroniec M., Różyło J.K., Ościk-Mendyk B., Determination of association effects in TLC data for different solutes chromatographed in methanol-acetone on silica gel, *J.Liq.Chromatogr.*, 5, 1033, 1982.

5. Ościk-Mendyk B., Różyło J.K., Jaroniec J.A., Studies of association effects in liquid adsorption chromatography with ternary mobile phases, *J.Liq.Chromatogr.*, 10, 2845, 1987.
6. Ościk-Mendyk B., Różyło J.K., Molecular interactions in adsorption liquid chromatography with mixed mobile phases, *Chromatographia* 25, 300, 1988.
7. Ościk-Mendyk B., Molecular interactions in liquid adsorption chromatography with mixed mobile phase. Solvation of the chromatographed substance in a ternary mobile phase, *Chromatographia* 28, 151, 1989.
8. Ościk-Mendyk B., Effect of the surface phase composition on retention mechanism in solid-liquid chromatography with binary mobile phases, *J.Planar Chromatogr.*, 3, 322, 1990.
9. Ościk-Mendyk B., Mechanism of liquid adsorption chromatography in thin-layer chromatography with ternary mobile phase, *J.Chromatogr.*, in press.
10. Pimentel G.C., McClellan A.L., *The hydrogen bond*, Freeman, San Francisco, 1960.
11. Różyło J.K., Ościk-Mendyk B., Problems related to the optimum separation conditions in liquid adsorption chromatography, *Chromatographia* 19, 371, 1984.