CHROM. 19 111

COADSORPTION EFFECTS IN LIQUID–SOLID SYSTEMS OF THE TYPE SILICA–HEPTANE + DIOXANE

I. THEORETICAL CONSIDERATIONS

EDWARD SOCZEWIŃSKI

Department of Inorganic and Analytical Chemistry, Medical Academy, Staszica 6, 20-081 Lublin (Poland)

(First received July 22nd, 1986; revised manuscript received September 22nd, 1986)

SUMMARY

Relatively stronger adsorption on silica of proton-donor solutes from mobile phases containing 1,4-dioxane as the polar modifier is interpreted as a result of an additional adsorption mechanism for the solutes on the monomolecular layer of dioxane molecules which retains some adsorptive properties owing to the presence of external ether groups. A molecular model of adsorption in systems of this type is given which takes into account three equilibria: competitive adsorption of the solute molecule on the silica surface, adsorption on the dioxane layer and competitive solvation in the bulk phase. A mathematical equation for the relationship between the retention and the modifier concentration is discussed.

INTRODUCTION

In recent years, adsorption models based on the competitive adsorption of solute and modifier molecules on polar adsorbent surfaces[1,2] have become popular. Although elaborated primarily for silica, alumina and Florisil, they have found application also to polar bonded phases such as aminopropyl silica[3-7] and cyanopropyl silica[6] and even for non-polar (RP) bonded phases[8,9].

According to the simplest form of relationship between the retention and the eluent composition which follows from the Snyder–Soczewiński adsorption model[1,10-12], the logarithm of the capacity factor should be a linear function of the logarithm of the concentration of the polar modifier, the slope being related to the molecular mechanism of mutual displacement of the solute and modifier molecules. Such simple relationships (very convenient for description of the retention behaviour of large groups of compounds and the choice of optimum conditions for analysis)[6,7] have been reported by numerous authors. A summary of such relationships has been given[13]; further recent examples for various adsorbent–solvent systems are given in Table I. It is surprising that the simple relationship, derived primarily for mobile phases composed of a non-polar diluent and a polar modifier, is observed also for strongly non-ideal, associated aqueous mobile phases.

TABLE I

EXAMPLES OF SYSTEMS (ADSORBENT–MODIFIER S + DILUENT) FOR WHICH LINEAR LOG k' $vs.$ LOG c_S PLOTS WERE REPORTED (WITH OCCASIONAL DEVIATIONS FROM LINEARITY)

THF = Tetrahydrofuran; TLC = thin-layer chromatography; CC = column chromatography.

Adsorbent	Polar modifier/diluent	Solutes	Method	Ref.
–NH₂	Isopropanol, ethyl acetate/n-heptane	20 phenols	HPLC	3
Silica, –NH₂	Ethyl acetate, dioxane, ethanol/hexane	Steroids	HPLC	6
–CN	Dioxane/hexane	Steroids	HPLC	7
RP-8	Propanol/water + formic acid	Proteins	HPLC	9
–NH₂	THF, tetrachloromethane, dichloromethane, chloroform, acetonitrile, ethyl acetate/hexane	Aromatic hydrocarbons and polar derivatives, oligomers of Triton X-100	HPLC	14
Sephadex	THF, acetone, ethanol, methanol/water, pH 4.0	L-Thyroxine, 3,3′,5-triiodo-L-thyronine	CC	15
	Ethanol/water, pH 2.0	2,3,5-Triiodobenzoic acid	CC	16
		Prostaglandin tyrosine methyl esters	CC	17
	Ethanol/water	Testosterone-3-(O-carboxymethyl)oxime tyrosine methyl ester and its derivative	CC	18
	Ethanol/water	Progesterone succinyl tyrosine methyl ester	CC	19
	Ethanol/water	Estriol and derivative	CC	20
	Ethanol/water	Thyroxins, diiodo- and triiodothyronines	CC	21
Silica	Isopropanol, diethyl ether/heptane	Adamantanones, cyclic ketones	HPLC	22
	Isopropanol, diethyl ether/heptane	Alcohols, adamantane derivatives	HPLC	23
	Diethyl ether, ethyl acetate, acetone, propanol/heptane, benzene, dichloromethane, THF, isopropanol/hexane	3-, 17- and 3,17-substituted androstanes	HPLC	24
	THF, isopropanol/hexane	Santonin derivatives (terpenoid lactones)	HPLC	25
	Chloroform, diethyl ether, ethyl acetate, methyl acetate, ethyl methyl ketone, acetone, dioxane, propanol/benzene	Steroids	TLC	26
	Acetone/chloroform	Sudan IV, steroids	TLC	27
	Acetone/cyclohexane	Dyes	TLC	28
	Acetonitrile + dichloromethane/heptane	Pesticides	HPLC	29
	Acetonitrile + dichloromethane/heptane	Pyrethroid pesticides	HPLC	30
	Dichloromethane/tetradecene			
Alumina	Ethyl acetate/heptane	Azaarenes, aromatic derivatives, azo dyes	TLC	31

The rôle of solvation effects in the overall adsorption equilibrium has caused some controversy[11,12]; however, in recent years the extreme views have became moderate[32-34]. It should be mentioned that an hybrid "displacement + solvation" mechanism has already been considered[2]; in fact, that study was preceded by systematic investigations of liquid–liquid partition equilibria for systems consisting of water and an organic phase formed by a non-polar diluent and a water-immiscible polar solvent where the formation of definite solvation complexes in the organic phase is expected[35]. The predominance of solvation effects has been assumed[36]. Solvation effects in liquid-solid chromatography (LSC) have been extensively studied by Jaroniec *et al.*[37-43].

More sophisticated theories of adsorption equilibria have recently been elaborated. Martire and Boehm[44,45] and Jaroniec *et al.*[41-43,46] published a series of papers on the adsorption from multicomponent solutions, based on statistical thermodynamics. The multiparameter equations proposed take into account the activity coefficients in both phases, surface heterogeneity and other effects. Upon more or less valid assumptions, the complex equations simplify to the Snyder–Soczewiński equation. Snyder, Glajch and Kirkland[32,47-50] published a series of investigations on the LSC model, considering some complicating effects such as the restricted access and site-competition localization; general principles for the optimization of the eluent composition in the case of binary, ternary and quaternary eluents were formulated. Rudzinski and Narkiewicz-Michalek[51] discussed the effect of surface heterogeneity on retention–eluent composition relationships.

In a recent paper[52], a more complex adsorption mechanism was considered for the system silica–polar bifunctional modifier, dioxane, which can form bridges between surface silanol groups and proton-donor solute molecules. The effect can be called coadsorption because solute–dioxane solvates are adsorbed due to the presence of the second ether oxygen in the dioxane molecule. In the chair conformation, only one oxygen atom can form an hydrogen bond with the surface OH group owing to steric reasons. The mechanism was illustrated for a small group of polyfunctional solutes.

In the present study a mathematical model of the molecular adsorption mechanism is presented and in the following paper (Part II) a study of a larger group of simpler solutes will be reported, the reference modifier being tetrahydrofuran; its monomolecular adsorbed layer should be non-polar in character.

THEORETICAL MODEL

In a previous paper[2] two molecular mechanisms were considered which could be denoted as "displacement" and "displacement + (competitive) solvation". In the dioxane systems investigated recently[52], a third mechanism, that of coadsorption, is presumed. The three situations can be represented by the diagrams in Fig. 1.

The active sites (A), *i.e.*, polar groups on the adsorbent surface, *e.g.*, silanol or aminopropyl groups, are covered by a monomolecular layer of dioxane molecules (S). The retention of solute molecules (Z) is determined by three equilibria: competitive solvation (K_{ZS}) which blocks the polar group of the solute molecule, displacement of solvent molecules (K) and coadsorption of solute molecules by a diox-
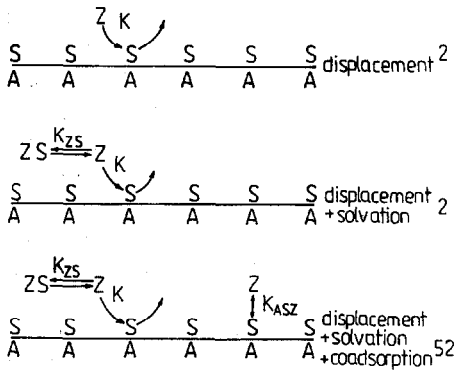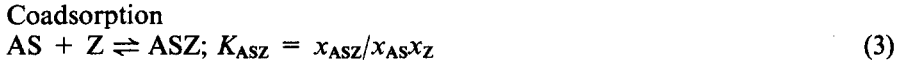
$$\underset{\overline{A}}{S}\quad\underset{\overline{A}}{S}\quad\overset{Z\overset{K}{\curvearrowright}}{\underset{\overline{A}}{S}}\quad\underset{\overline{A}}{S}\quad\underset{\overline{A}}{S}\quad\underset{\overline{A}}{S}\ \text{displacement}\ _2$$

$$ZS\underset{}{\overset{K_{ZS}}{\rightleftharpoons}}Z$$
$$\underset{\overline{A}}{S}\quad\underset{\overline{A}}{S}\quad\overset{Z\overset{K}{\curvearrowright}}{\underset{\overline{A}}{S}}\quad\underset{\overline{A}}{S}\quad\underset{\overline{A}}{S}\quad\underset{\overline{A}}{S}\ \begin{array}{l}\text{displacement}\\ \text{+ solvation}\end{array}\ _2$$

$$ZS\underset{}{\overset{K_{ZS}}{\rightleftharpoons}}Z$$
$$\underset{\overline{A}}{S}\quad\underset{\overline{A}}{S}\quad\overset{Z\overset{K}{\curvearrowright}}{\underset{\overline{A}}{S}}\quad\underset{\overline{A}}{S}\quad\overset{\overset{Z}{\updownarrow}K_{ASZ}}{\underset{\overline{A}}{S}}\quad\underset{\overline{A}}{S}\ \begin{array}{l}\text{displacement}\\ \text{+ solvation}\\ \text{+ coadsorption}\end{array}\ _{52}$$
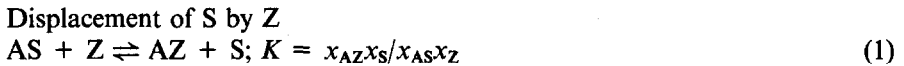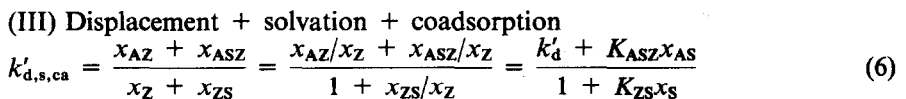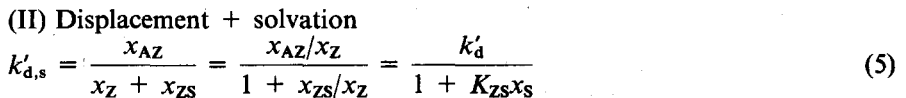
Fig. 1. Molecular mechanisms of adsorption. A = Adsorption site, *e.g.*, silanol group; S = modifier molecule hydrogen bonded to adsorption site; Z = solute molecule.

ane bridge (K_{ASZ}). The equilibrium constants correspond to the reactions:

Displacement of S by Z
$$AS + Z \rightleftharpoons AZ + S; \quad K = x_{AZ}x_S/x_{AS}x_Z \tag{1}$$

Solvation
$$Z + S \rightleftharpoons ZS; \quad K_{ZS} = x_{ZS}/x_Z x_S \tag{2}$$

Coadsorption
$$AS + Z \rightleftharpoons ASZ; \quad K_{ASZ} = x_{ASZ}/x_{AS}x_Z \tag{3}$$

Note that the concentrations (mole fractions) are defined as if the surface sites (A) and adsorbed molecules (AZ, ASZ) form a single solution with the bulk phase[2].

The capacity factor of Z is equal to the ratio of the total concentration of Z in the adsorbed forms to that in the bulk phase. Thus, for the simplest case of a monofunctional solute three situations can be visualized, the first two having already been discussed[2]:

(I) Displacement
$$k'_d = \frac{x_{AZ}}{x_Z} = K \cdot \frac{x_{AS}}{x_S} \tag{4}$$

(II) Displacement + solvation
$$k'_{d,s} = \frac{x_{AZ}}{x_Z + x_{ZS}} = \frac{x_{AZ}/x_Z}{1 + x_{ZS}/x_Z} = \frac{k'_d}{1 + K_{ZS}x_S} \tag{5}$$

(III) Displacement + solvation + coadsorption
$$k'_{d,s,ca} = \frac{x_{AZ} + x_{ASZ}}{x_Z + x_{ZS}} = \frac{x_{AZ}/x_Z + x_{ASZ}/x_Z}{1 + x_{ZS}/x_Z} = \frac{k'_d + K_{ASZ}x_{AS}}{1 + K_{ZS}x_S} \tag{6}$$

The effect of the molecular structures of the solute (Z), polar modifier (S) and adsorbent sites (A) are here expressed by the equilibrium constants K, K_{ZS} and K_{ASZ}; the relative values of which can be estimated by taking into account the hydrogen-bonding properties. Thus, for Z = pyridine and S = dioxane, $K_{ZS} \approx 0$ and $K_{ASZ} \approx 0$, although some dipole–dipole interactions are expected[53]. For Z = phenol and S = dioxane, hydrogen bonds OH$\cdots$O can be formed and stronger solvation and coadsorption effects are expected.

Comparison of eqn. 4 to eqn. 6 shows that:

(1) Coadsorption tends to increase the observed capacity factor; the effect is stronger for strong solute interactions with the exposed ether oxygens of the adsorbed dioxane molecules (K_{ASZ}) and for adsorbents having large surface areas (x_{AS} is approximately proportional to the adsorbent surface area)

(2) For higher concentrations of the modifier S, coadsorption tends to be counterbalanced by solvation in the bulk phase. However, the decrease in the displacement term, k'_d, with the modifier concentration, x_S, causes the coadsorption and solvation terms to become more important.

Thus, eqn. 6 shows that stronger coadsorption effects are expected for strongly adsorbed modifiers which form a monomolecular adsorbed layer (isotherm plateau) at low concentrations in the bulk phase, when there is least counterbalancing of the solvation ($K_{ZS}x_S$ in the denominator) and coadsorption effects ($K_{ASZ}x_S$ in the numerator).

Several theoretical log k' vs. log x_S curves are presented in Fig. 2 for various values of K, K_{ZS} and K_{ASZ}. For simplicity, it was assumed that $K_{ZS} = K_{ASZ}$, which is equivalent to the presumption that the bonding between the solute molecule Z and a dioxane molecule S is similar in the adsorbed layer and in the bulk solution (see Fig. 1). It was also assumed that the concentration of the modifier molecules in the surface phase, x_{AS}, is 0.5. The analysis of the curves shows that, for strongly adsorbed solutes ($K = 20$, $k'_d > 10$ over the whole concentration range), the effect of coadsorption is negligible in comparison to solvation, unless $K_{ZS} = K_{ASZ} \gg K$ (see upper family of curves). For less strongly adsorbed solutes ($K = 2$, lower lines), more pronounced differences between the k'_d, $k'_{d,s}$ and $k'_{d,s,ca}$ lines are observed, especially for weaker retention ($k' < 10$), i.e., for the range of k' values of interest for high-performance liquid chromatography (HPLC).

The $k'_{d,s,ca}$ values are intermediate between those of k'_d (displacement only) and $k'_{d,s}$ (displacement + solvation).

The net k' value in dioxane systems thus depends on three parallel mechanisms, the relative contributions of which depend on the tendency of the solute molecules to displace dioxane molecules from the adsorbent surface and to form solvation complexes in the bulk phase and in the surface phase. The differentiation of these mechanisms results in the differentiation of k' values of various solutes in dioxane systems, which differs from that observed for "simple" monofunctional modifiers such as alcohols or tetrahydrofuran, the adsorbed monolayers of which are virtually non-polar, cf., ref. 52 and the following paper.

It should be noted that a double concentration scale is used in Fig. 2: the x_S values are related to the overall composition of the system[2] and cannot exceed 0.5, since the remaining 0.5 units correspond to x_{AS}. On the other hand, x'_{AS} denotes the concentration of the modifier in the eluent itself. Obviously, $x'_S = 2x_S$ and the shapes of the theoretical curves in Fig. 2 are the same for both concentration units owing to the logarithmic scale.
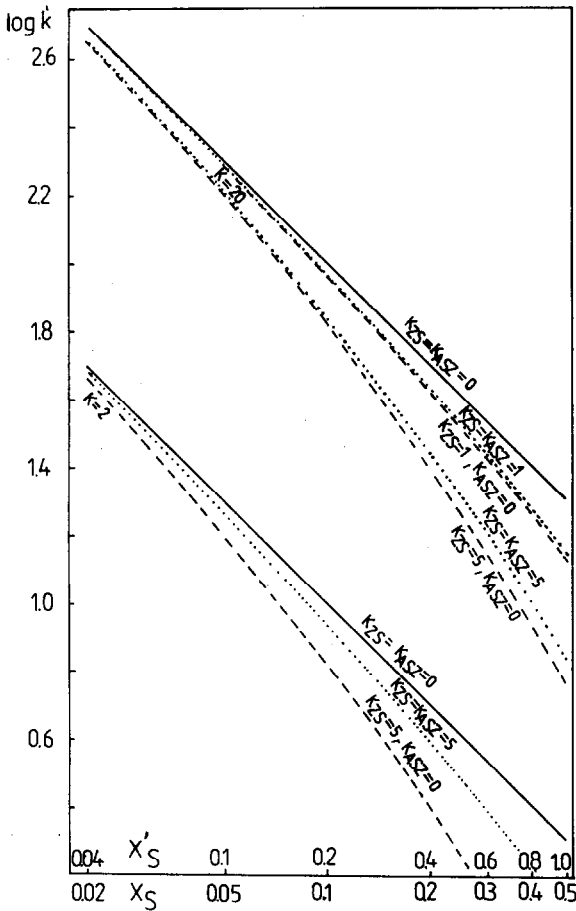
Fig. 2. Theoretical relationships between log k' and log x_S, the concentration of modifier S in the mobile phase relative to the adsorption system as a whole and log x'_S, that in the mobile phase for various values of the displacement, K, solvation, K_{ZS}, and coadsorption, K_{ASZ}, constants (see Fig. 1). The vertical distance between $k'_{d,s}$ and $k'_{d,s,ca}$ represents the difference in log k' values in log k'_{diox} vs. log k'_{THF} correlations. (———) k'_d; (— — —) $k'_{d,s}$; ($\cdots\cdots$) $k'_{d,s,ca}$.

CONCLUSIONS

Coadsorption effects are not infrequent in liquid chromatography, especially in reversed-phase systems. As examples, ion-association and ligand-exchange systems can be mentioned; the adsorption of proton-donor solutes was enhanced by the addition of hydrophobic additives such as tributyl phosphate or trioctylphosphine oxide. Huber and Ziegelmayer[54] have discussed the use of bifunctional modifiers such as diethylamine for modification of the selectivity of silica in LSC.

Owing to the complex liquid–solid distribution mechanism, the dioxane–silica system described in the present paper exhibits, in comparison to simple monofunctional modifiers, an individual selectivity relative to certain groups of solutes. The

differences can also be used to fine-tune the selectivity by the Bakalyar method[55] using a mixed modifier, e.g., dioxane + tetrahydrofuran.

Especially for higher concentrations of the polar modifiers, the retention mechanism can be complicated by multi-layer adsorption and variable contributions from liquid–liquid partition.

REFERENCES

1 L. R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.
2 E. Soczewiński, *Anal. Chem.*, 41 (1969) 179.
3 R. J. Hurtubise, A. Hussain and H. F. Silver, *Anal. Chem.*, 53 (1981) 1993.
4 M. C. Hennion, C. Picard, C. Combellas, M. Caude and R. Rosset, *J. Chromatogr.*, 210 (1981) 211.
5 W. E. Hammers, M. C. Spanjer and C. L. De Ligny, *J. Chromatogr.*, 174 (1979) 291.
6 S. Hara and S. Ohnishi, *J. Liq. Chromatogr.*, 7 (1984) 59.
7 S. Hara and S. Ohnishi, *J. Liq. Chromatogr.*, 7 (1984) 69.
8 H. Colin, C. Eon and G. Guiochon, *J. Chromatogr.*, 122 (1976) 223.
9 X. Geng and F. R. Regnier, *J. Chromatogr.*, 296 (1984) 15.
10 E. Soczewiński, *J. Chromatogr.*, 130 (1977) 23.
11 L. R. Snyder, *Anal. Chem.*, 46 (1974) 1384.
12 L. R. Snyder and H. Poppe, *J. Chromatogr.*, 184 (1980) 363.
13 E. Soczewiński and J. Jusiak, *Chromatographia*, 4 (1981) 23.
14 L. R. Snyder and T. C. Schunk, *Anal. Chem.*, 54 (1982) 1764.
15 G. Toth, *Radiochem. Radianal. Lett.*, 29 (1977) 207.
16 G. Toth, *J. Chromatogr.*, 172 (1979) 524.
17 G. Toth, I. Mucha and B. Tanács, *J. Chromatogr.*, 189 (1980) 433.
18 G. Toth, *J. Chromatogr.*, 238 (1982) 476.
19 G. Toth, W. Weber and F. Kling, *J. Chromatogr.*, 213 (1981) 511.
20 G. Toth, *J. Chromatogr.*, 267 (1983) 420.
21 G. Toth, *Radioanal. Chem.*, 46 (1978) 201.
22 L. Vodička, D. Prušova, J. Kříž and J. Burkhard, *J. Chromatogr.*, 200 (1980) 238.
23 L. Vodička, J. Kříž, D. Prušova and J. Burkhard, *J. Chromatogr.*, 198 (1980) 457.
24 S. Hara and S. Miyamoto, *Anal. Chem.*, 53 (1981) 1365.
25 S. Hara, N. Yamauchi, K. Yamakawa and K. Nishitani, *Anal. Chem.*, 57 (1985) 1780.
26 S. M. Petrović, L. A. Kolarov, E. Traljić and J. A. Petrović, *Anal. Chem.*, 54 (1982) 934.
27 D. Nurok, R. M. Becker and K. A. Sassic, *Anal. Chem.*, 54 (1982) 1955.
28 D. Nurok and M. J. Richard, *Anal. Chem.*, 53 (1981) 563.
29 E. Papadopoulou-Mourkidou and Y. Iwata, *Chromatographia*, 17 (1983) 695.
30 E. Papadopoulou-Mourkidou, F. A. Gunther and Y. Iwata, *J. Agric. Food Chem.*, 32 (1984) 800.
31 R. Wawrzynowicz and J. Kuczmierczyk, *Chem. Anal. (Warsaw)*, 30 (1985) 63.
32 L. R. Snyder, in Cs. Horváth (Editor), *High-Performance Liquid Chromatography*, Vol. 3, Academic Press, New York, 1983, pp. 157–223.
33 R. P. W. Scott, *Adv. Chromatogr. (N.Y.)*, (1982) 167–196.
34 H. Engelhardt and H. Elgass, in Cs. Horváth (Editor), *High Performance Liquid Chromatography*, Vol. 2, Academic Press, New York, 1980, pp. 57–111.
35 E. Soczewiński and G. Matysik, *J. Chromatogr.*, 111 (1975) 7.
36 E. Soczewiński, W. Gołkiewicz and H. Szumiło, *J. Chromatogr.*, 45 (1969) 1.
37 M. Jaroniec and J. A. Jaroniec, *J. Chromatogr.*, 210 (1981) 130.
38 M. Jaroniec and J. Piotrowska, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 257.
39 M. Jaroniec and J. A. Jaroniec, *J. Liq. Chromatogr.*, 4 (1981) 2121.
40 M. Borówko, J. Goworek and M. Jaroniec, *Monatsh. Chem.*, 113 (1982) 669.
41 M. Borówko and M. Jaroniec, *Adv. Colloid Interface Sci.*, 19 (1983) 137.
42 M. Jaroniec, *Adv. Colloid Interface Sci.*, 18 (1983) 149.
43 M. Jaroniec, D. E. Martire and M. Borówko, *Adv. Colloid Interface Sci.*, 22 (1985) 177.
44 R. E. Boehm and D. E. Martire, *J. Phys. Chem.*, 84 (1980) 3620.
45 D. E. Martire and R. E. Boehm, *J. Liq. Chromatogr.*, 3 (1980) 753.
46 M. Jaroniec and D. E. Martire, *J. Chromatogr.*, 351 (1986) 1.

47 L. R. Snyder and J. L. Glajch, *J. Chromatogr.*, 214 (1981) 1.
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 J. L. Glajch, J. J. Kirkland and L. R. Snyder, *J. Chromatogr.*, 238 (1982) 269.
51 W. Rudzinski and J. Narkiewicz-Michalek, *J. Chem. Soc., Faraday Trans. 1*, 81 (1965) 553.
52 E. Soczewiński and T. Dzido, *Chromatographia*, 21 (1986) 25.
53 E. Soczewiński, *Chromatographia*, 11 (1978) 534.
54 J. F. K. Huber and A. Ziegelmeyer, *9th Internat. Symp. on Column Liquid Chromatography, Edinburgh, July, 1985*.
55 S. R. Bakalyar, R. McIlwrick and E. Roggendorf, *J. Chromatogr.*, 142 (1977) 353.