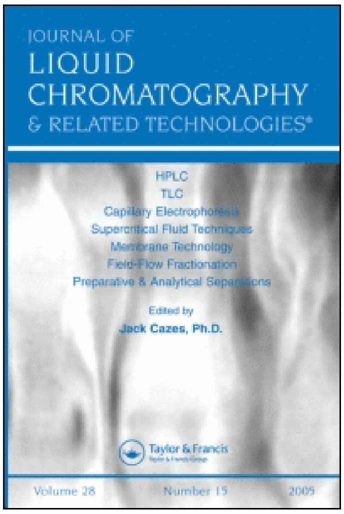

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STUDIES OF ASSOCIATION EFFECTS IN LIQUID ADSORPTION CHROMATOGRAPHY WITH TERNARY MOBILE PHASES

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ABSTRACT

In this paper a model of chromatographic process, which takes into account molecular association in the mobile phase is discussed. This model is applied to study the association effects in liquid adsorption chromatography with ternary mobile phases. Efects of nature of the eluent and structure of the chromatographed substance on the type of association is also investigated. Association effects in the chromatographic system containing ternary mobile phase can be evaluated by means of equations describing chromatographic process with the binary mobile phases.

INTRODUCTION

In the past twenty years a considerable development in the field of adsorption from solutions on solid surfaces and liquid adsorption chromatography is observed. Past investigations were concentrated on studies concerning energetic heterogeneity of adsorbent surface, nonideality of surface and bulk phases as well as evaluation of effects connected with differences in molecular sizes of chromatographed substances and solvents (1-8). Description of intramolecular interactions in the mobile phase based on Ościk (9) conception indicates a great significance of these interactions in the liquid adsorption chromatography process, especially in the reversed phase liquid chromatography, in which the adsorbent heterogeneity may be practically neglected. While the nonspecific interactions in the mobile phase are satisfactory described, the specific interactions causing formation of the molecular complexes associates in the phase require further studies.

In this paper a model of chromatographic process, which takes into account molecular association in the mobile phase is discussed (10-14). This model is applied to study the association effects in liquid adsorption chromatography with ternary mobile phases. Efects of nature of the eluent and structure of the chromatographed substance on the type of association is also investigated.

THEORETICAL CONSIDERATIONS

Chromatographic process in the liquid-solid system is determined by competitive adsorption of solute and solvent molecules. This phenomenon may be represented by the phase exchange reaction consisting in displacement of solvent molecules from the stationary phase by solute molecules contained in the mobile phase. This displacement can be weakened or strenghned in consequence of solute-solvent and solvent-solvent interactions occuring in the surface and bulk phases. Strong specific interactions cause formation of molecular complexes associates in both phases.

In the real chromatographic systems associates of different dimensions and structure can exist (15 - 21). Investigations of many authors (18-21) have been showed that the steric and kinetic effects limit frequently the number of various types of complexes and their dimensions. It appears that in many cases the model assuming existence of double associates is sufficient for a correct description of thermodynamic properties of the bulk and surface solutions (15-17). In the case of liquid chromatography with binary and ternary eluents three most important types of association can be distinguished:

1) association of molecules of the more polar solvent

2) association of the chromatographed substance and molecules of the more polar solvent

3) association of molecules of different solvents.

Multicomponent eluents used in practice contain usually one more polar solvent, which can associate, whereas association of less polar or nonpolar solvents can be neglected. Association of the chromatographed substance influences very slightly on chromatographic process because concentration of this substance is infinitely low. Association of the chromatographed substance with molecules of the more polar solvent affects significantly the chromatographic process. Migration of the chromatographic substance molecules from the bulk phase to the surface phase is then more difficult. Association of molecules of the more polar solvent showed also affect the chromatographic process because of a great concentration of this solvent. Mechanism of formation of various associates in the multicomponent bulk phase (mobile phase) is described theoretically by Jaroniec and Jaroniec (22). Theoretical considerations of these authors are utilized to analyse the chromatographic data. According to this treatment, we can assume that the molecules of the more polar solvent form double pure associates and mixed solute-solvent associates in the mobile phase. The capacity ratio of the s-th solute may be expressed as follows:

$$k_s' = q^{-1} K_{s1} \left(4 L_2\right)^n y_1^n \left[\left(1 + 8 L_2 x_1^o\right)^{1/2} - 1\right]^{-n} \qquad (1)$$

K_{s1} denotes the therodynamic equilibrium constant for the phase exchange reaction between molecules of the s-th solute and solvent "1", q is the ratio of the total number of moles of the s-th solute and solvents in the mobile phase to the total number of moles of these substances in the surface phase. Snyder (23) has showed that the coefficient q is characteristic for a given adsorbent and not depends on the nature of the mobile phase. L_2 denotes the association constant describing formation of double associates of the more polar solvent (1-1), x_1^o is the total mole fraction of the more polar solvent in the mobile phase, n is the ratio of the surface area occupied by one solute molecule to the surface area occupied by one solvent molecule, y_1 is the mole fraction of the more polar solvent in the surface phase. For smaller values of L_2, n=1 and y_1=1 equation 1 can be transformed into linear form (24-26):

$$1/x_1^o k_s' = a + b x_1^o \qquad (2)$$

where

$$a = \left(K_{s1}/q\right)^{-1} \qquad b = -2L_2 \left(K_{s1}/q\right)^{-1}$$

Since the thermodynamic constants K_{s1} and L_2 are always non-negative, the straight line slope is negative. Thus, presentation of chromatographic data according to equation 2 permits to conclude about association of the more polar solvent in the mobile phase (22). Mixed association i.e association between molecules of the chromatographed substance and the more polar solvent molecules plays an important role in many chromatographic systems. Formation of these types of associates makes difficult, as mentioned above, migration of the solute molecules from the mobile phase to the surface phase. The simplest mixed associates formed in the mobile phase are double associates consisting of one molecule of the more polar solvent and one solute molecule. For this type associates the capacity coefficient k'_s may be expressed by:

$$k'_s = K_{s1} q^{-1} \left(y_1/x_1^o\right)^n \left(1 + C_1 x_1^o\right)^{-1} \qquad (3)$$

where C_1 denotes equilibrium constant for mixed associates. For n=1 and y_1=1 this relation can be presented in the linear form (22):

$$1/x_1^o k'_s = a' + b' x_1^o \qquad (4)$$

where

$$a' = q/K_{s1} \qquad b' = C_1 q/K_{s1}$$

It appears that equation 2 for n=1 and y_1=1 derived for model assuming association of the more polar solvent is identical with equation 4 derived for mixed association. In this connection we can write in general that:

$$1/k'_s x_1^o = \alpha_1 + \beta_1 x_1^o \qquad (5)$$

where

$$\alpha_1 = \begin{cases} a > 0 & \text{for association of 1-1 type} \\ a' > 0 & \text{for association of s-1 type} \end{cases}$$

$$\beta_1 = \begin{cases} b < 0 & \text{for association of 1-1 type} \\ b' > 0 & \text{for association of s-1 type} \end{cases}$$

Thus equation 5 can be utilized to study the type of association in the chromatographic systems.

Using the well-known dependence

$$k' = 10^{R_{Ms}}$$

we can utilize the above equation in thin layer chromatography. Presenting experimental data in the $(k'_s x_1^o)^{-1}$ vs. x_1^o coordinates we can conclude on the basis of equation 5 , which type of association predominates in the given chromatographic system. In real chromatographic systems both types of association occurs simultaneously. Depending on the nature of solvent and solute one of these types can predominate. Thus, the capacity coefficient is determined by K_{s1} or C_1 and L_2 values. This fact can be illustrated by following equation:

$$k'_s = K_{s1} q^{-1} \left[y_1/x_1^o \left(1-2L_2 x_1^o\right) \right]^n \left[1/1+C_1 x_1^o \left(1-2L_2 x_1^o\right) \right] \qquad (6)$$

For n=1 equation 6 assumes a very useful linear form:

$$y_1/k'_s x_1^o = \alpha'_1 + \beta'_1 x_1^o \qquad (7)$$

where $y_1/k'_s x_1^o$ is linear function of the mole fraction of the more polar solvent, whereas constants α'_1 and β'_1 are defined as follows:

$$\alpha'_1 = q / K_{s1} \qquad \beta'_1 = \left(C_1 - 2L_2\right) q / K_{s1} \qquad (8)$$

The constants K_{s1}, C_1 and L_2 may be evaluated from the straight line parameters. When the C_1-value is greater than $2L_2$ the straight line has a positive slope and then association of solvent and solute molecules predominates. If C_1 is smaller than $2L_2$ then association of solvent molecules is predominating although weak association of s-1 type cannot be excluded.

METHODS

Chromatographic data are obtained by thin layer chromatography measurements. Silica gel 60 H (Merck Darmstadt FRG) was used as adsorbent. Following solvent systems were used as ternary mobile phases:

- heptane + cyclohexane + chloroform	N + N + A
- heptane + cyclohexane + ethyl acetate	N + N + B
- heptane + toluene + acetone	N + N/B + B
- heptane + toluene + ethyl acetate	N + N/B + B

Two less polar components of the mobile phase were mixed always in the 1:1 mole fraction ratios and the mole fraction of third solvent has changed in the range of 0.1 - 0.9 . Chromatograms were developed at the distance of 16 cm at temperature of 293K. R_F-values obtained for given substance have differed between them by 0.02 R_F unit. The measurements were carried out for substances presented in Table I.

RESULTS AND DISCUSSION

In the theoretical part of this paper it has showed that in the case of molecular association in the mobile phase it should take into account formation of mixed double associates formed by solute and solvent molecules and also formation of associates of the more polar solvent. Since the mobile phases used consisted of one more polar solvent of A or B class according to Pimentel - McClellan (24) classification, and two solvents of N class it should to assume that association in these ternary mobile phases may be described by equation derived for the model assuming formation of associates in the binary mobile phase. For simplification of our consideration we have assumed that in equation 7 $y_1=1$. Thus

$$1/k'x_1^o = \alpha_1' + \beta_1' x_1^o \qquad (9)$$

Table I

Solute	Class according to Pimentel and McClellan
2.3-dichlorophenol	AB
2.5-dichlorophenol	AB
3.4-dichlorophenol	AB
2.4.6-trichlorophenol	AB
o-nitrophenol	AB*
2-naphthol	AB
4-nitro-o-toluidine	AB
o-nitroaniline	AB
p-nitroaniline	AB
2.3-dihydroxynaphthalene	AB
2.7-dihydroxynaphthalene	AB
8-hydroxyquinoline	AB
isoquinoline	B
O-dinitrobenzene	B
p-dinitrobenzene	B
anthracene	N
pyrene	N

Assumption that $y_1=1$ denotes that molecules of the more polar component of the mobile phase fill completely the surface phase because concentration of the solute is very small in comparison to the concentration of solvents. Such assumption is fulfilled in the case of the mobile phases containing components of very different adsorption energies; then $y_1=1$ almost in the whole concentration range. In the region of low concentration of the more polar component a small deviation of the y_1-values from unity are observed. When differences in adsorption energies of components of the mobile phase are small then concentration range in which $y_1=1$ narrows. The above considerations prove that experimental relationship $1/k'x_1^o$ vs. x_1^o can show deviations from the straigh line in the range of small concentration of the component "1". These deviations can be due among other by neglect of changes in surface phase composition.

In the course of our investigations the relation 9 was plotted for several substances in the following mobile phase systems: heptan + cyclohexane + chloroform heptan + cyclohexane + ethyl acetate, heptan + toluene + acetone and heptan + toluene + ethyl acetate. Because of great number of experimental data only small part of linear relationship 9 is prasented on figures 1-3. It should to emphasise that in all cases the linear

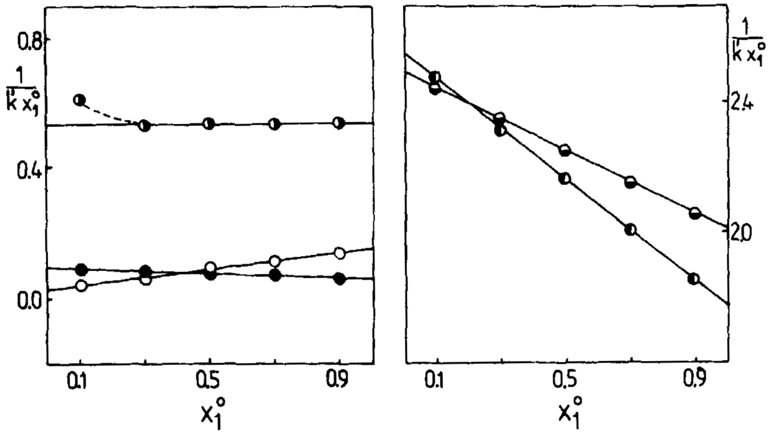

Fig.1

$1/k'x_1^0$ vs. x_1^0 for ○ -p-nitroaniline, ● -isoquinoline, ◑ -2.5-dichlorophenol, ◐ -pyrene and ⊖ -anthracene in heptane + cyclohexane + chloroform system.

course of the relation 9 is observed; small deviations of experimental points from the straigh line are observed for x_1^0=0.1. For the systems investigated either association effects of solute molecules and molecules of the polar solvent s-1 (positive slope) or associations of molecules of the more polar component of the mobile phase 1-1 (negative slope) are observed. It have noticed also that change of nature of the more polar component of the mobile phase causes the changes in association type of some substances. The comparison of such systems as heptene + cyclohexane +

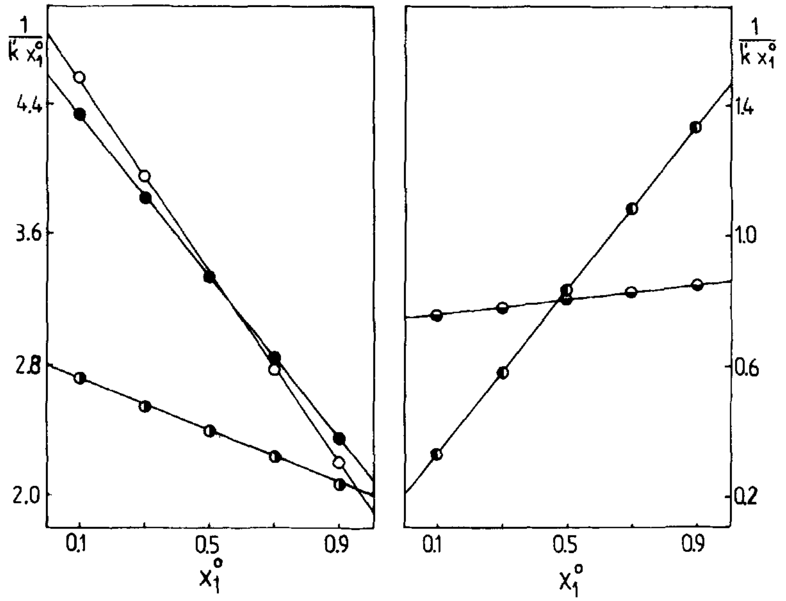

Fig.2

1/k′x_1^0 vs. x_1^0 for ● -pyrene, ○ -anthracene, ◐ -para-nitroaniline, ◑2.5-dichlorophenol and ⊖ -isoquinoline in heptane + cyclohexane + ethyl acetate system.

chloroform and heptane + cyclohexane + ethyl acetate shows that in the first system association of the solute molecules and molecules of chloroform predominate however replacement of chloroform by ethyl acetate causes change of the association type (Fig. 1,2 and table II) . A predominant effect is association of ethyl acetate molecules. Association of the s-1 type also occurs since existence of 1-1 association not

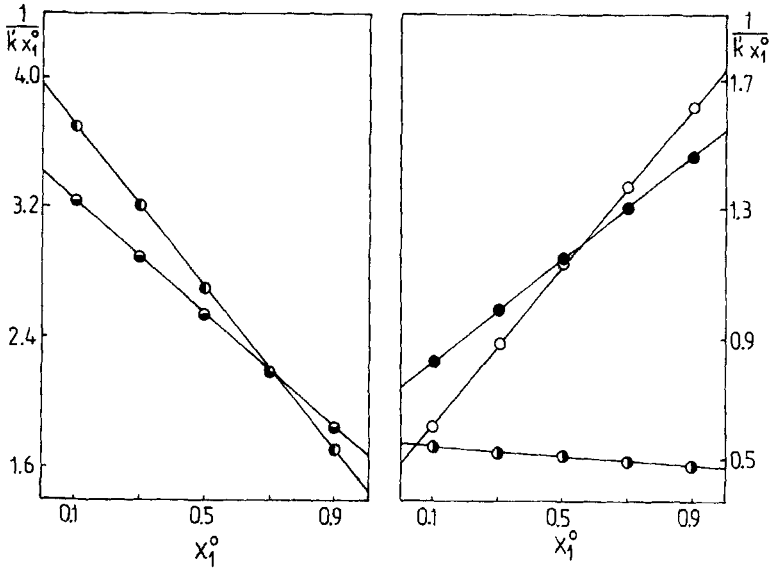

Fig.3

$1/k'x_1^o$ vs. x_1^o for ○2,5-dichlorophenol, ◐ -o-nitrophenol, ◑ -isoquinoline, ◒ -2,3-dihydroxynaphthalene and ● -p-nitroaniline in heptane + toluene + ethyl acetate system.

excludes of other type of association i.e s-1. In further stage of our investigations the $\mathcal{L}_1'$ and β_1' - values defined by equation 7 were determined from these linear relationships. $\mathcal{L}_1'$-values are inversly proportional to the equilibrium constant K_{s1}. $\mathcal{L}_1'$-values for the solutes chromatographed in the system heptane + cyclohexane + ethyl acetate are smaller then those for the system heptane + toluene + ethyl acetate. This

Table II

α_1', β_1' and C_1-$2L_2$ - values for several substances in heptane +cycloheksane + chloroform and heptane + cyclohexane + ethyl acetate systems.

Solute	heptane+ cyklohexane + chloroform			heptane + cyclohexane + ethyl acetate		
	α_1'	β_1'	C_1-$2L_2$	α_1'	β_1'	C_1-$2L_2$
2.5-dichlorophenol	0.53	0.01	0.02	2.79	-0.79	-0.28
2.4.6-trichlorophenol	0.66	0.03	0.05	3.16	-1.21	-0.38
anthrenene	2.48	-0.45	-0.18	4.82	-1.41	-0.29
pyrene	2.55	-0.76	-0.30	4.60	-2.50	-0.54
p-nitroaniline	0.02	0.13	6.50	0.21	1.25	5.95
isoquinoline	0.09	-0.03	-0.33	0.75	0.11	0.15

means that equilibrium constant for heptane + cyclohexane + ethyl acetate system is greater than the K_{s1}-value for heptane + toluene + ethyl acetate system. It means that the less polar component of the mobile phase "2" has a significant influence on $\mathcal{L}_1'$-value (Table III). Exchange of cyclohexane by toluene i.e for solvent of a greater elution power causes an increase in the $\mathcal{L}_1'$-values. This means that chromatographed substance molecules displace molecules of ethyl acetate from the silica gel surface more easily in the presence of cyclohexane than in the presence of toluene. When the component "2" of a greater elution power is used intramolecular interactions in the mobile phase are stronger and the phase exchange between solute molecules and molecules of the solvent "1" is more difficult. The $\mathcal{L}_1'$-values for most solutes in the heptane + cyclohexane + ethyl acetate system are greater than those obtained for the heptane + cyclohexane + chloroform system (TabII). This means that for heptane + cyclohexane + ethyl acetate system the equilibrium constant values K_{s1} are smaller than for the heptane + cyclohexane + chloroform system. Because the logarithm of the equilibrium constant K_{s1} is approximately proportional to the difference in adsorption energies of the s-th solute and solvent "1" the greater K_{s1}-values indicates on greater difference in adsorption

Table III

α'_1 and β'_1-values for several solutes in heptane + cyclohexane + ethyl acetate and heptane + toluene + ethyl acetate systems.

Solute	heptane + cyclohexane + ethyl acetate		heptane + toluene + ethyl acetate	
	α'_1	β'_1	α'_1	β'_1
o-nitrophenol	3.64	-1.60	3.96	-1.25
2.3-dichlorophenol	1.67	0.72	2.50	-1.03
2.5-dichlorophenol	2.79	-0.97	3.44	-1.79
p-nitroaniline	0.18	1.28	0.69	0.62
2.3-dihydroxynaphthalene	0.31	1.67	0.51	0.81
isoquinoline	0.45	0.11	0.57	-0.07

energies of "s"-th and "1"-st components. For the heptane + toluene + acetone and heptane + toluene + ethyl acetate systems the α_1'-values are very similar. It takes from this that the values of K_{s1} are also similar for both systems.

Determined values of α_1' and β_1' (Table IV) were then utilized for calculating the following expression:

$$C_1 - 2L_2 = \alpha_1' / \beta_1' \qquad (10)$$

Equation 10 permits to evaluate the predominant type of association in the chromatographic process. The (C_1-2L_2)-values for individual substances are listed in Tables II i V. Analysing the values listed in these Tables according to theoretical considerations it can conclude that predominant effect in the chromatographic systems considered here was association of 1-1 type. Difference in the values of C_1-2L_2 for the same group of compounds in a given chromatographic system indicates that various position of funcional groups in solute molecule affects significantly the association type. This is due probably to intramolecular forces reducing interaction with components of the mobile phase. Smaller values of C_1-2L_2 for most solutes in the systems containing ethyl acetate suggest that ethyl acetate molecules interact with solute molecules more weakly than with molecules of acetone.

Table IV

α'_1 and β'_1 -values for several solutes in heptane + toluene + acetone and heptane + toluene + ethyl acetate systems.

Solute	heptane + toluene + acetone		heptane + toluene + ethyl acetate	
	α'_1	β'_1	α'_1	β'_1
o-nitrophenol	3.03	0.62	3.96	-1.25
2.3-dichlorophenol	2.70	-0.25	2.50	-1.03
2.5-dichlorophenol	3.36	-0.18	3.44	-1.79
2-naphthol	2.30	0.26	2.37	-0.75
isoquinoline	1.04	0.21	0.57	-0.07
2-hydroxyquinoline	0.04	0.92	0.04	0.29
8-hydroxyquinoline	1.54	1.42	2.40	-1.18
2.3-dihydroxynaphthalene	0.19	2.33	0.51	0.81
2.7-dihydroxynaphthalene	0.16	1.65	0.49	0.95
o-nitroaniline	1.84	0.73	2.17	0.81
p-nitroaniline	0.54	1.88	0.69	0.63
4-nitro-o-toluidine	1.10	1.84	1.60	0.36

Table V

(C_1-2L_2)- values for several solutes in heptane + toluene + acetone and heptane + toluene + ethyl acetate systems.

Solute	$C_1 - 2L_2$ heptane + toluene + acetone	$C_1 - 2L_2$ heptane + toluene + ethyl acetate
o-nitrophenol	0.20	-0.31
2.3-dichlorophenol	-0.09	-0.41
2.5-dichlorophenol	-0.03	-0.52
2-naphthol	0.11	-0.32
isoquinoline	0.20	-0.12
2-hydroxyquinoline	23.00	7.25
8-hydroxyquinoline	0.92	-0.49
2.3-dihydroxynaphthalene	12.26	1.59
2.7-dihydroxynaphthalene	10.31	1.94
o-nitroaniline	0.40	0.37
p-nitroaniline	3.48	0.90
4-nitro-o-toluidine	1.67	0.22

CONCLUSIONS

1 For most systems investigated the linear relationships $1/k'_s x_1^o$ vs. x_1^o were observed with a deviation of experimental points at low concentration region

2 In most chromatographic systems association between solute and polar solvent predominates

3 Association effects in the chromatographic system containing ternary phase can be evaluated by means of equations describing chromatographic process with the binary mobile phases

4 Nature of polar component of the mobile phase affects significantly the association type

5 Association type changes with change of position of the functional groups in the solute molecule.

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