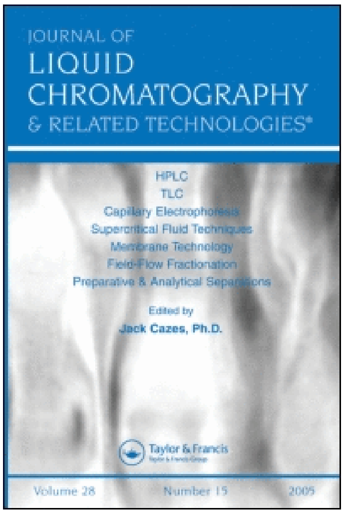

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ADSORPTION OF SOLVENTS AND MOLECULAR INTERACTIONS IN LSC WITH A TERNARY MOBILE PHASE

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ABSTRACT

A modification of Jaroniec equation [1] is proposed. Adsorption of all solvents is taken into account. A physical meaning of the slope of the equation is analysed. The effects of solvents adsorption, solvent-solvent and solute-solvent molecular interactions on the retention in LSC with ternary mobile phase are discussed.

INTRODUCTION

Separations achieved by liquid-solid chromatography are based on the competition for sites on an active adsorbent surface. However, the molecular interactions in the mobile phase play important role in a mechanism of resolution. Theories involving all possible interactions lead to very complicated equations for retention. The solute-solvent and solvent-solvent interactions may be described in terms of a formation of different associates [1].

From this approach follows a simple linear relation:

$$(k'_s x_1)^{-1} = \alpha + \beta x_1. \tag{1}$$

Here k'_s is the capacity ratio of the solute "s", x_1 denotes the mole fraction of the 1-st solvent in the mobile phase, whereas α and β are constants connected with parameters characterizing molecular interactions.

The equation (1) has been derived for a chromatographic system in which almost whole adsorbent surface was covered by molecules of the 1-st solvent. In other words, equation may be used when adsorption of other solvents is assumed negligible. Such condition is frequently difficult to satisfy. However, the usefulness of the relationship (1) to describe of the solute retention was confirmed by numerous experimental studies [2-6].

In this paper the modification of the equation (1) is proposed. New expressions for constant α and β involving the "adsorption correction" are derived.

THEORY

Let us consider chromatographic system with solute "s" and ternary mobile phase. Further assumptions are as follows: (1) adsorbent is energetically homogeneous, (2) stationary phase is ideal, (3) molecular sizes of all sovents and solutes are the same, (4) two types of associates form in the mobile phase - dimers consisting of molecules of the 1-st solvent (1-1) and solvates

(1-s), (5) the ratio of mole fractions of solvents "3" and "2" in the mobile phase is constant:

$$x_3/x_2 = w = \mathrm{const} \tag{2}$$

According to the paper [7] the capacity ratio of the solute "s" is given by:

$$k'_s = q(1+Cx)^{-1}(y_1/x_{1(1)}) \tag{3}$$

where y_1 is the mole fraction of the 1-st solvent in the stationary phase, C is the solvatation constant, $x_{1(1)}$ denotes the mole fraction of monomer of the solvent "1" in the mobile phase, q is constant connected with a chromatographic bed [8]. The real adsorption of the 1-st solvent from ternary solution may be calculated from the formula [7]:

$$y_1 = K_{13}x_{1(1)}\left(\sum_{i=1}^{3} K_{i3}x_{i(1)}\right)^{-1} \tag{4}$$

where K_{i3} is thermodynamic adsorption constant for the binary mixture (i,3), $x_{i(1)}$ denotes the mole fraction of monomer of the i-th solvent; $x_{i(1)} = x_i$ for i = 2,3 because these solvents do not form any associates. When the assumption (2) is fulfilled adsorption isotherm (4) may be rewritten in the form analogous to that derived for binary solution, namely

$$y_1 = K^* x_{1(1)}\left(1-x_1+K^* x_{1(1)}\right)^{-1} \tag{5}$$

Here K^* is constant characterizing adsorption of the 1-st solvent from mixed solvent (2,3):

$$K^{*} = K_{13}(w+1)/(w+K_{23}) \tag{6}$$

The mole fraction of monomer of the 1-st solvent depends upon its total concentration: $x_{1(1)} = x_{1(1)}(x_1)$. An analytical form of this function has been discussed in the paper [7]. However, for small association effects the Jaroniec's approximation may be used [1]:

$$x_{1(1)} \approx x_1(1-2Lx_1) \tag{7}$$

where L is the association constant.

Taking into account the fact that association and solvation effects are small we obtain the following relationship from equations (3) - (7):

$$(k_s'x_1)^{-1} = (qK_{s1})^{-1}\left[\left(K^{*}x_1\right)^{-1}+I_sx_1+1-\left(K^{*}\right)^{-1}\right] \tag{8}$$

where

$$I_s = C-2L \tag{9}$$

and it may be called "interaction parameter".

The expression on the right side of eq. (8):

$$f(x) = (qK_{s1})^{-1}\left[\left(K^{*}x_1\right)^{-1}+I_sx_1+1-\left(K^{*}\right)^{-1}\right] \tag{10}$$

may be linearized for $x_1 \longrightarrow 1$:

$$f(x) \approx \alpha + \beta x_1 \tag{11}$$

where

$$\beta = \left.\frac{d\ f(x_1)}{d\ x_1}\right|_{x_1=1} \tag{12}$$

Finally, from equations (8) - (12) we obtain the relationship (1) with new values of parameters α and β. Equation (12) gives:

$$\beta = (qK_{s1})^{-1}\left(I_s - \left(K^*\right)^{-1}\right) \qquad (13)$$

The constant α may be calculated from the condition $f(1) = (k'_{s(1)})^{-1}$ where $k'_{s(1)}$ is the capacity ratio for the pure solvent "1" given by eq. (3) for $(y_1/x_{1(1)}) = 1$. Hence

$$\alpha = (qK_{s1})^{-1}\left(1 + \left(K^*\right)^{-1}\right) \qquad (14)$$

Equations (13) and (14) may be written in alternative forms:

$$\beta = I_s(qK_{s1})^{-1} - (k_s^*)^{-1} \qquad (15)$$

$$\alpha = (qK_{s1})^{-1} - (k_s^*)^{-1} \qquad (16)$$

where k_s^* is the capacity ratio of the solute "s" in the mixed binary eluant (2,3) (for $x_1 = 0$). Term $(k_s^*)^{-1}$ in the above equations may be treated as "adsorption correction". When it tends to zero parameters α and β becomes values provided by Jaroniec [1].

The eq. (1) with parameters given by expressions (15), (16) allow us to involve as well specific molecular interactions in the liquid mixture as adsorption of all solvents in the quantitative description of the retention process.

RESULTS AND DISCUSSION

In Figure 1 theoretical functions $(k'_s x_1)$ vs. x_1, calculated from general equation derived for ideal

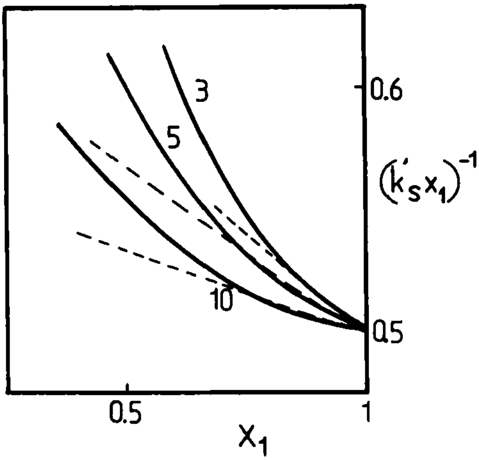

FIGURE 1. Theoretical curves $(k'_s x)^{-1}$ vs x_1 calculated from equations (3), (5), (7) for the ideal mobile phase (C = L = 0, solid lines) and approximated linear dependences (1) (dashed lines). Parameters: K^* = 3, 5, 10.

solution [9] are compared with approximated linear dependence (1). Analysis of these results leads to the following conclusions:

- function $(k'_s x_1)^{-1}$ vs. x_1 may be approximated by linear dependence (1) for $x_1 \longrightarrow 1$ and great values of constant K^*,
- the slope β is always negative: $\beta = -(k^*_s)^{-1}$,
- for strong adsorption of the 1-st solvent β tends to zero,
- an increase of adsorption of solvents "2" and "3" brings about decrease of the parameter β.

In non-ideal systems the sign of the slope of relationship (1) depends upon both molecular

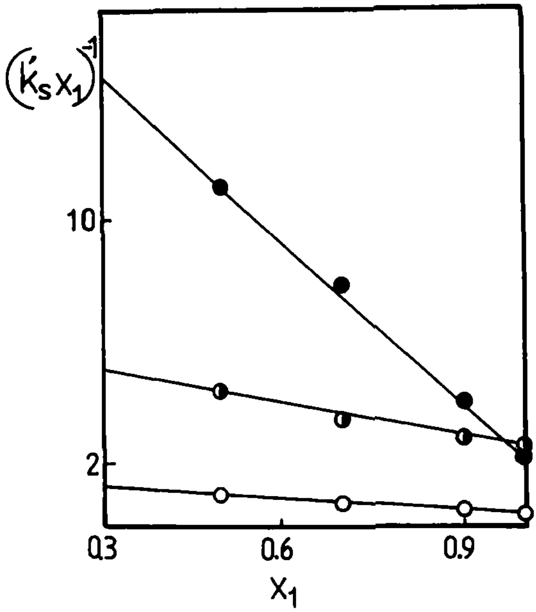

FIGURE 2. Experimental dependences (1) for o-nitrophenol and the ternary mobile phase consisting of the mixing solvent: benzene (2) - carbon tetrachloride (3) (w = 1/3) and: (○) - trichloroethylene, (◑) - acetone, (●) - propanol as the 1-st solvent. Adsorbent - silica gel.

interactions and adsorption effects. Solvation of the solute molecules causes an increase of the constant β whereas association 1-1 and solvent adsorption give an opposite effect.

Some results of an examination of the 1-st solvent effects on the plot $(k'_s x_1)^{-1}$ vs. x_1 are shown in Fig. 2. The experimental data have been measured by using of TLC technique [5,10]. For almost ideal mixed solvent trichloroethylene (1) - benzene (2) - carbon tetrachloride (3) the slope β is near to zero. However, when the mobile phase contains strongly associating

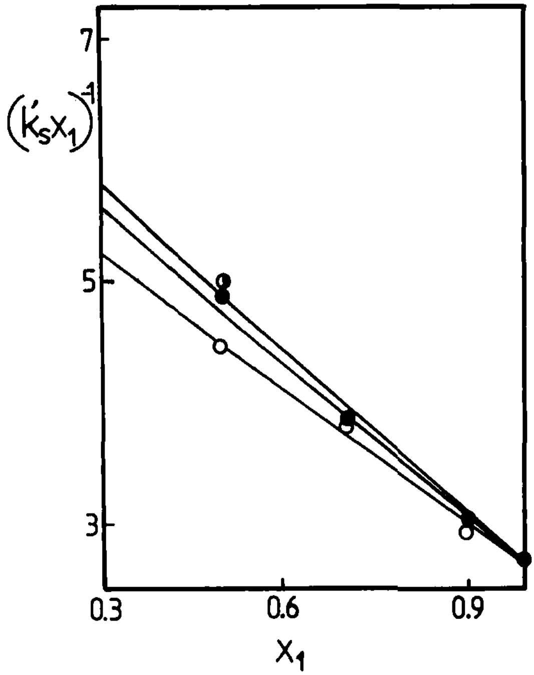

FIGURE 3. Experimental dependences (1) for o-nitrophenol and ternary mobile phase: acetone (1) - benzene (2) - carbon tetrachloride (3) for w = 1/3 (◑), 1 (●), 3 (○). Adsorbent - silica gel.

propanol the parameter β has considerably negative value.

In Figure 3 experimental relationships (1) are plotted for the mixed solvent acetone (1) - benzene (2) - carbon tetrachloride (3) and different values of the ratio w. An influence of the ratio w on the slope β may be explained by "solvent adsorption effects" which has been taken into account when equation (15) was derived.

In order to determine parameters I_s experimental results published in the papers [5,10] have been

TABLE 1

Values of the Interaction Parameter I_s for the Following Solutes: 1 - o-nitrotoluene, 2 - o-bromonitrobenzene, 3 - nitroaniline, 4 - nitrophenol. Adsorbent - Silica Gel.

S	I_s			$\bar{I}_s$
	w=1/3	w=1	w=3	
trichloroethylene - benzene - carbon tetrachloride				
1	-0.34	-0.41	-0.48	-0.44
2	-0.35	-0.32	-0.48	-0.38
3	-0.17	-0.51	-0.49	-0.39
4	-0.52	-0.43	-0.49	-0.46
acetone - benzene - carbon tetrachloride				
1	-0.53	-0.54	-0.51	-0.53
2	-0.47	-0.43	-0.48	-0.46
3	-0.46	-0.46	-0.25	-0.39
4	-0.50	-0.58	-0.49	-0.53

analysed. It follows from equations (15), (16) that

$$I_s = \left(\beta+\left(k_s^*\right)^{-1}\right)/\left(\alpha-\left(k_s^*\right)^{-1}\right) \qquad (17)$$

The results obtained for two ternary mobile phases are summarized in Table 1. The mean values of interaction parameters ($\bar{I}_s$) for a given solute are shown in the last column. In all investigated systems the interaction parameters I_s are negative. It means that

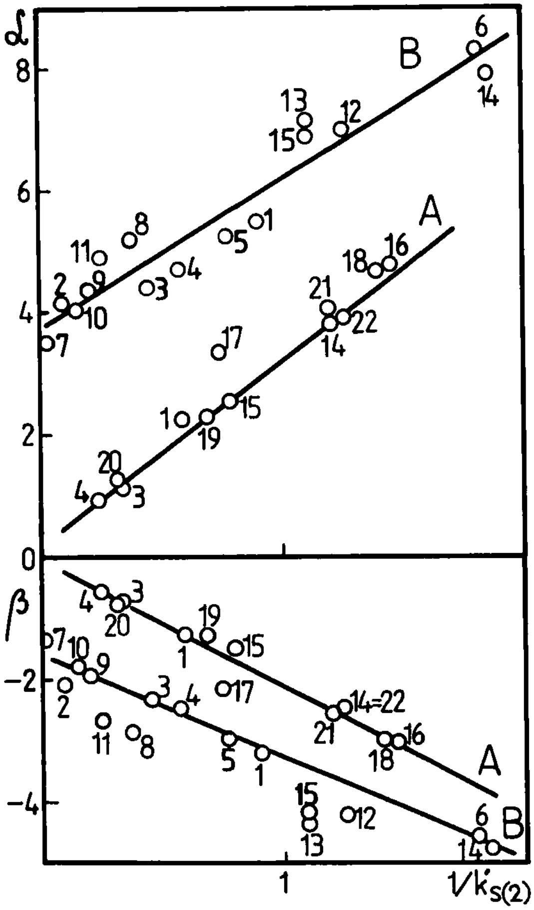

FIGURE 4. Correlations between parameters α, β and the reciprocal of capacity ratio $k'_{s(2)}$ for two mixed mobile phases: A - trichloroethylene (1) - benzene (2), B - acetone (1) - benzene (2) and the following solutes: 1 - o-nitrophenol, 2 - p-nitrophenol, 3 - 2,3-dichlorophenol, 4 - 2,5-dichlorophenol, 5 - 2,6-dichlorophenol, 6 - 2-methylnaphthalene, 7 - 2,7-dihydroxynaphtalene, 8 - o-nitroaniline, 9 - m-nitroaniline, 10 - p-nitroaniline, 11 - 4-nitro-o-toluidine, 12 - o-nitrotoluene, 13 - m-nitrotoluene, 14 - chrysene, 15 - p-bromonitrotoluene, 16 - naphtalene, 17 - N-phenyl-1-naphtylamine, 18 - 1,3-dimethylnaphthalene, 19 - o-bromonitrobenzene, 20 - o-chlorophenol, 21 - pyrene, 22 - phenanthrene. Adsorbent - silica gel.

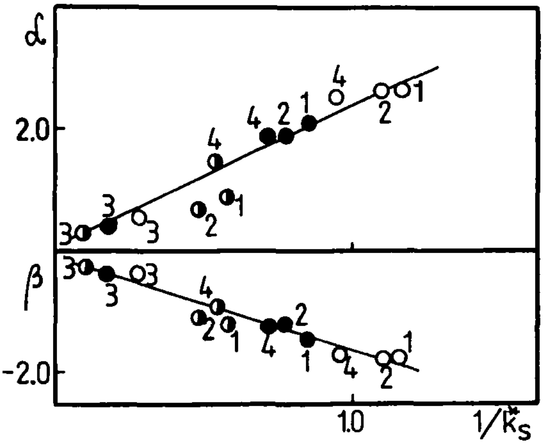

FIGURE 5. Correlations between parameters α, β and the reciprocal of capacity ratio k_s^* for ternary mobile phase: trichloroethylene (1) - benzene (2) - carbon tetrachloride (3) for w = 1/3 (○), 1 (●), 3 (◑). The solutes and adsorbent the same as in the Table 1.

association of the 1-st solvent is stronger than solute solvation. Based on the obtained values I_s we concluded that tendency to form 1-1 type associates is higher for acetone than for trichloroethylene. This conclusion is consistent with another informations about these solutions. However, when adsorption of solvents "2" and "3" was neglected the opposite result has been obtained [5]. The "adsorption correction" have a very importance for mobile phase containing trichloroethylene because its adsorption is smaller than adsorption of benzene.

Figure 4 shows correlations between parameters α, β and the reciprocal of capacity ratio in a pure 2-nd solvent for different solutes. In the case of ternary mobile phase: trichloroethylene - benzene - carbon tetrachloride similar dependences are observed for constants α, β and the capacity ratio k_s^* (Fig. 5). As follows from these plots there is the strict connection between parameters α, β and solvents adsorption effects which may be characterized by the capacity ratio k_s^* (see equations (15), (16)).

CONCLUSIONS

The modified Jaroniec relationship (1) may be used for interpreting experimental data measured in chromatographic system in which stationary phase contains all solvents (e.g. $y_1 \neq 1$). In this case eq. (1) may be applied for ternary mobile phase when the ratio of both less polar solvents is constant.

A physicochemical interpretation of the slope of the line (1) (β) is difficult because it is a complex function of different parameters characterizing chromatographic system.

As follows from discussion presented in previous sections the slope β is:

1^o negative when adsoption of the second and third solvents cannot be neglected($y_1 \neq 1$) or when there is strong association 1-1 in the mobile phase,
2^o positive for strong solvation 1-s.

The parameter I_s calculated from eq. (17) seems to be more useful for characterizing molecular interactions than the slope β because it is independent on solvent adsorption.

Finally, one can concluded that eq. (1) may be applied for determining of the effect of solvent adsorption, solute-solvent and solvent-solvent interactions in LSC with binary and ternary mobile phases. However, a physical meaning of the slope (1) should be very carefully analysed for a definite chromatographic system.

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