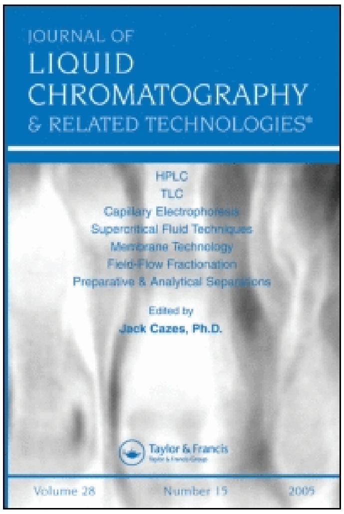

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DETERMINATION OF SOLVATION EFFECTS IN LIQUID ADSORPTION CHROMATOGRAPHY WITH MIXED MOBILE PHASES

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ABSTRACT

A model of chromatographic process, involving formation of multimolecular solute-solvent solvates in the mobile phase, is discussed. This model leads to an equation describing dependence of the capacity ratio upon mobile phase composition. The TLC data for some solutes chromatographed in n-heptane+chloroform on silica gel are interpreted by means of the above equation.

INTRODUCTION

Beginning with the works of Ościk (1) and Snyder (2) almost twenty years ago, theoretical studies in a continuing stream have examined means of evaluating main effects in liquid adsorption chromatography with mixed mobile phases. Reviews of these efforts (3-6) show the extent of these investigations. The main principle of simple chromatographic models is competitive character of adsorption process

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occuring at liquid/solid interface (2-6). Moreover, these models can incorporate additional assumptions - treating such effects as surface heterogeneity of the adsorbent, differences in molecular sizes of solute and solvent molecules, changes of surface phase composition upon mobile phase composition, nonspecific and specific molecular interactions in the surface and bulk solutions.

In many chromatographic systems, in which specific solute-solvent and solvent-solvent interactions are possible, e.g., hydrogen bonding between solute and solvent molecules, the association effects play an important role (7-13). A most general description of liquid adsorption chromatography with mixed mobile phases, involving solute-solvent and solvent-solvent association, has been presented in the previous paper (9). In the case of model assuming formation of double associates in the mobile phase, a simple equation has been proposed to describe dependence of the capacity ratio upon mobile phase composition (7,8). This equation has been used to interpret HPLC (10,12) and TLC (13) data. This interpretation gives answer to the question: what type of association in the bulk solution is dominant, solute-solvent or solvent-solvent association.

In this article we will study a model of chromatographic process, involving formation of multimolecular solute-solvent complexes (solvates) in the mobile phase. This model leads to an equation, which will be examined by using TLC data of some solutes chromatographed in n-heptane+chloroform on silica gel.

THEORY

Let us consider liquid adsorption chromatography with mixed mobile phase, in which strong specific interactions between solute and solvent molecules cause the formation of mixed complexes (solvates). Further assumptions are as follows:

(a) the initial solution is devided into two phases, the surface phase and the mobile phase,

(b) adsorption has a competitive character,

(c) molecules of solute and solvents have different sizes and a spherical shape,

(d) the total number of moles of all solvents in the surface phase is constant and independent upon the presence of solute molecules because of their infinitely low concentration,

(e) the adsorbent surface is supposed to be homogeneous,

(f) the surface phase is ideal and monomolecular,

(g) the solvates are formed in the mobile phase.

Assumptions (a)-(e) are frequently used in the theory of liquid adsorption and liquid adsorption chromatography (6,14,15). The remaining assumptions, (f) and (g), are reasonable for adsorbent surfaces interacting strongly with the solute molecules. In this case the solute-adsorbent interactions are predominant over specific solute-solvent interactions in the solution. As a consequence the solvates break down in the potential field generated by the adsorbent surface. Therefore, there are only monomers in the surface phase.

Let s denotes s-th solute chromatographed in multicomponent eluent, in which solvents are numbered successively beginning from the most efficient eluting solvent to the weakest solvent. Thus, 1-st solvent is the most efficient one. Similarly as in the previous paper (9) the chromatographic process may be represented by quasi-chemical reactions describing competitive character of solute adsorption and solvation phenomenon in the mobile phase. Thus, the solute adsorption is represented by the phase-exchange reversible reaction (6,9):

$$s_{(m)} + r\, 1_{(s)} \rightleftharpoons s_{(s)} + r\, 1_{(m)} \qquad (1)$$

where the subscripts (m) and (s) refer to the mobile and surface phases, respectively, s and 1 denote molecules of the s-th solute and 1-st solvent, and r is the ratio of molecular sizes of the s-th solute and 1-st solvent. The solvation phenomenon, occuring in the mobile phase, may be represented by the following reaction:

$$s_{(m)} + q\, 1_{(m)} \rightleftharpoons 1_q s_{(m)} \qquad (2)$$

where $1_q s_{(m)}$ denotes (q+1)-molecular complex in the mobile phase composed of one solute molecule and q molecules of 1-st solvent. The equilibrium constants describing reactions 1 and 2 may be expressed as follows:

$$K_{s1} = (y_s/x_s)\cdot(x_1/y_1)^r \qquad (3)$$

and

$$C_q = z_q/[\, x_s(x_1)^q] \qquad (4)$$

where y_s and y_1 are mole fractions of the s-th solute and 1-st solvent in the surface phase, x_s and x_1 are mole fractions of the s-th solute and 1-st solvent in the mobile phase, and z_q is the mole fraction of the solvate $1_q s$ in the mobile phase defined as the ratio of the number of solvates $1_q s$ to the total number of molecules in the mobile phase. The mole fractions y_s , y_1 , x_s and x_1 define concentrations of unassociated molecules of the s-th solute and 1-st solvent.

The total mole fractions of the s-th solute and solvents in the mobile phase are expressed by :

$$x_s^o = x_s + \sum_{q=1}^{p} z_q = x_s \, [\, 1 + \sum_{q=1}^{p} C_q (x_1)^q \,] \tag{5}$$

$$x_1^o = x_1 + \sum_{q=1}^{p} q \, z_q = x_1 + x_s \sum_{q=1}^{p} q \, C_q (x_1)^q \approx x_1 \tag{6}$$

$$x_i^o = x_i \quad \text{for} \quad i > 1 \tag{7}$$

Since the mole fraction x_s is infinitely low in comparison to the solvent concentration (c.f., assumption d), the total mole fraction x_1^o is in a good approximation equal to x_1 . According to the assumption (g) the surface phase contains only monomers of solute and solvents. Therefore, the total mole fractions y_s^o and y_1^o are equal to y_s and y_1 , respectively. The distribution coefficient k_s , defined as the ratio of the total mole fractions of the s-th solute in the surface and mobile phases, respectively, i.e.,

$$k_s = y_s^o / x_s^o \quad , \tag{8}$$

in the case of the model under considerations assumes the following form:

$$k_s = y_s/x_s^o = (y_s/x_s)[1 + \sum_{q=1}^{p} C_q(x_1)^q]^{-1} \quad (9)$$

Taking into account the proportionality between distribution coefficient k_s and capacity ratio k'_s, we have:

$$k'_s = \beta\, k_s = \beta\, (y_s/x_s)[1 + \sum_{q=1}^{p} C_q(x_1)^q]^{-1} \quad (10)$$

where β is characteristic for a given adsorbent and independent upon the eluent nature in a good approximation (2). The ratio y_s/x_s may be determined from equation 3 and then equation 10 assumes the following form:

$$k'_s = \beta\, K_{s1}\, (y_1/x_1)^r\, [1 + \sum_{q=1}^{p} C_q(x_1)^q]^{-1} \quad (11)$$

In the case of one-component eluent (solvent 1), x_1 is equal to unity and the capacity ratio of the s-th solute chromatographed in the pure solvent 1 is expressed as follows:

$$k'_{s1} = \beta\, K_{s1}(1 + \sum_{q=1}^{p} C_q)^{-1} \quad (12)$$

Thus, if solvent forms associates with the solute, the capacity ratio of the solute chromatographed in this pure solvent depends on the phase-exchange equilibrium constant K_{s1} and association (solvation) constants C_1, C_2, ..., C_p.

Combining equations 11 and 12 we have:

$$k'_s = k'_{s1} (y_1/x_1)^r \frac{1 + \sum_{q=1}^{p} C_q}{1 + \sum_{q=1}^{p} C_q (x_1)^q} \qquad (13)$$

Equation 11 and its another form, equation 13, describe dependence of the capacity ratio upon mobile phase composition for the eluent, in which 1-st solvent can form different multimolecular solvates $1_q s$ for $q=1,2,\ldots,p$. In many systems one type of solvates is dominant, e.g., (q+1)-molecular solvates; then, equations 11 and 13 assume simpler forms:

$$k'_s = \beta K_{s1} (y_1/x_1)^r [1 + C_q (x_1)^q]^{-1} \qquad (14)$$

$$k'_s = k'_{s1} (y_1/x_1)^r \frac{1 + C_q}{1 + C_q (x_1)^q} \qquad (15)$$

Another simplifications of equations 11 , 13 , 14 and 15 are possible for $r=1$ (identical molecular sizes of solute and solvent molecules) and/or $y_1=1$ (this assumption is valid for the whole concentration region except the low concentrations of x_1 and for very strong adsorption of 1-st solvent in comparison to adsorption of other solvents). The mole fraction y_1 may be determined from the excess adsorption data measured for 1-st solvent or calculated by means of the theoretical isotherm equations (6).

The equilibrium constants K_{s1} and C_q may be evaluated from the chromatographic data by using another forms of equations 11 and 14 :

$$(y_1/x_1)^r(k_s')^{-1} = \sum_{q=0}^{p} C_q'(x_1)^q \tag{16}$$

$$(y_1/x_1)^r(k_s')^{-1} = C_0' + C_1'(x_1)^q \tag{17}$$

where

$$C_0' = (\beta\ K_{s1})^{-1} \tag{18}$$

$$C_q' = C_q/(\beta\ K_{s1}) \text{ for } q = 1,2,\ldots,p \tag{19}$$

For $r=1$ and $y_1=1$ equations 16 and 17 become:

$$(k_s'\ x_1)^{-1} = \sum_{q=0}^{p} C_q'(x_1)^q \tag{20}$$

$$(k_s'\ x_1)^{-1} = C_0' + C_1'(x_1)^q \tag{21}$$

According to equation 21 the dependence $(k_s'\ x_1)^{-1}$ vs. $(x_1)^q$ is linear. Equation 21 with $q = 1$ has been examined by using HPLC and TLC data (10,12,13); for many chromatographic systems it gives a good representation. It means that assumption of double associates in the mobile phase gives frequently satisfactory results. In this paper we shall examine equation 21 for $q > 1$ by using TLC data.

EXPERIMENTAL

Chemicals

Chloroform and n-heptane (puriss. grade) were obtained from Polskie Odczynniki Chemiczne (Gliwice, Poland). The silica gel (type 100) was from E.Merck (Darmstadt, FRG).

TLC measurements

The TLC measurements were made under thermostated conditions at 293K. Silica gel was the adsorbent and chloroform+n-heptane was the eluent. The adsorbent layers were 0.3 mm thick and were activated for 2h at 408K. The chromatograms were developed by the ascending technique to a distance of 16 cm. The spots were visualized using the universal reagent (16). The R_F-values have been measured for : p-nitroaniline, o-nitroaniline, 2-nitro-p-toluidine, 4-nitro-p-toluidine, 2,3-dihydroxynaphthalene and o-dinitrobenzene. The R_F-values were converted into R_M-values using the well-known equation:

$$R_M = \log [(1 - R_F)/R_F] \qquad (22)$$

However, the capacity ratio was calculated as follows:

$$k'_s = 10^{-R_M} \qquad (23)$$

The experimental dependence k'_s vs. x_1 for different solutes chromatographed in chloroform+n-heptane was examined by using equation 21 .

RESULTS AND DISCUSSION

In the paper (17) the TLC data for many solutes of different chemical structure were measured by using the following binary mobile phases: methanol, ethanol, n-propanol, n-butanol with benzene, ethyl acetate, acetone and ethylmethylketone with toluene, ethyl acetate and chloroform with n-heptane.

Analysis of TLC data for solutes chromatographed in alcohol+benzene and ketone+toluene shown that effects connected with association of 1-st solvent are dominant. However, for many solutes chromatographed in ethyl acetate

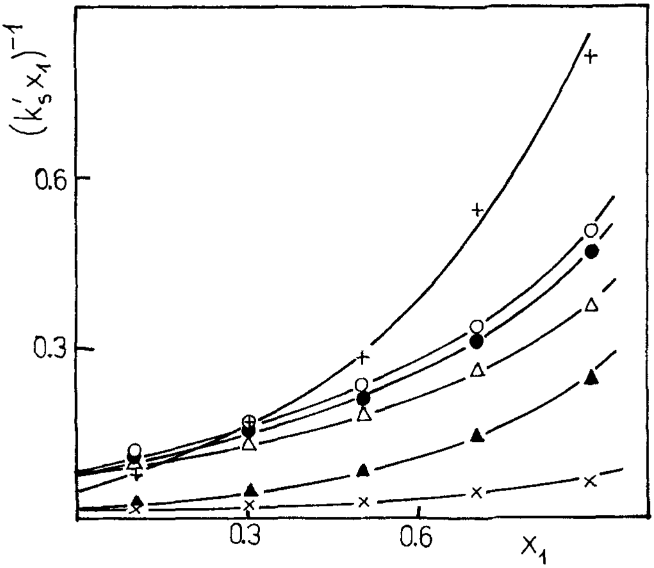

FIGURE 1 . Dependence $(k'_s\ x_1)^{-1}$ vs. x_1 for six solutes chromatographed in chloroform+n-heptane on silica gel. Solutes: p-nitroaniline (▲), o-nitroaniline (○), 2-nitro-p-toluidine (●), 4-nitro-p-toluidine (△), 2,3-dihydroxynaphthalene (×) and o-dinitrobenzene (+).

and chloroform with n-heptane the solvation effects play an important role. For majority solutes chromatographed in these eluents the model assuming formation of double associates in the mobile phase gives a good representation of TLC data in question (17). However, this model (equation 21 with q=1) is not suitable to interpret the TLC data presented in the experimental part. Experimental points does not fulfil equation 21 with q=1 (see Figure 1). Plotting these data according to equation 21 with q=2 , we observe a good linear behaviour of $(k'_s\ x_1)^{-1}$ vs.$(x_1)^2$;Fig.2 . It follows from Figure 2 that the model assuming formation

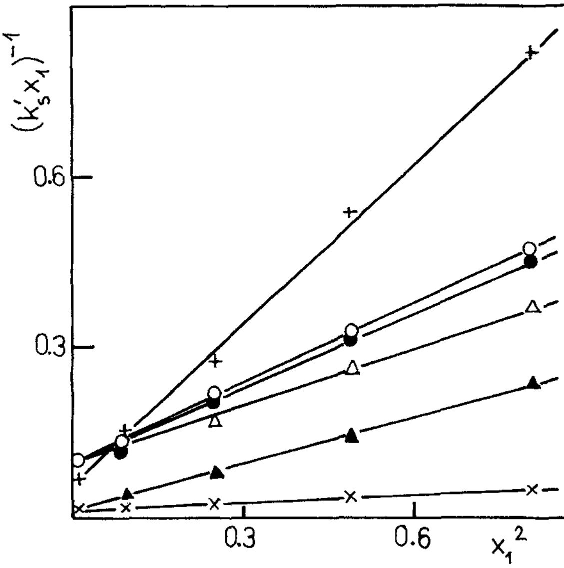

FIGURE 2 . Dependence $(k'_s\ x_1)^{-1}$ vs. $(x_1)^2$ for the solutes presented in Figure 1.

of solvates (one solute molecule + two solvent molecules) in the mobile phase gives a reasonable representation of TLC systems in question.

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