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J. K. Roźyło<sup>a</sup>; M. Jaroniec<sup>a</sup>; J. A. Jaroniec<sup>a</sup>

<sup>a</sup> Institute of Chemistry M. Curie-Skłodowska University, Lublin, Poland

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## EFFECTS OF SOLUTE-SOLVENT INTER-ACTIONS IN LIQUID ADSORPTION CHROMATOGRAPHY WITH MIXED MOBILE PHASE

J. K. Rożyło, M. Jaroniec, and J. A. Jaroniec

*Institute of Chemistry  
M. Curie-Skłodowska University  
20031 Lublin, Poland*

### ABSTRACT

Two simple equations, involving formation of the multimolecular solvates in the mobile phase, are discussed. These equations define the dependence of the capacity ratio upon mobile phase composition. The LC data, available from the literature, for different alcohols chromatographed in binary mixtures of n-heptane with alkyl acetate and tetrahydrofuran on Partisil 10 at 298 K are used to examine these equations.

### INTRODUCTION

The competitive solute and solvent adsorption is one of the most important phenomena determining the liquid/solid chromatography (LSC) process and it was considered by several authors (1-4). This phenomenon is represented by the phase exchange reaction describing the displacement of solvent molecules from the stationary (surface) phase by solute molecules contained in the mobile phase. The displacement

process in question may be strengthened or weakened by solute-solvent and solvent-solvent interactions in the mobile and surface phases. The non-specific interactions between molecules of solute and solvents may be described by means of the activity coefficients (5). However, the strong specific interactions between solute and solvent molecules cause the formation of multimolecular complexes in the mobile phase (6). The process of their formation may be represented by quasi-chemical reactions occurring in the mobile phase. In the case of LSC on strongly polar adsorbents, e.g., silica gel, these complexes can be destroyed in the surface phase because of strong interactions of solute and solvent molecules with the active centers of the adsorbent (e.g., silanol groups of the silica surface), which compete with the solute-solvent interactions.

In this paper the effects due to the specific solute-solvent interactions in the mobile phase are discussed. The LC data for different alcohols chromatographed in binary mixtures of *n*-heptane with alkyl acetate and tetrahydrofuran on Partisil 10 at 298 K (7) are applied to examine two simple equations involving formation of the multimolecular solvates in the mobile phase.

#### THEORETICAL

Some important factors determining the LSC process have been mentioned in the introduction. They are: competitive character of solute and solvent adsorption, and specific solute-solvent and solvent-solvent interactions in the mobile and surface phases. The elaboration of the theoretical description of the LSC process, involving the

majority factors determining this process, is very difficult because of its great complexity. Therefore, the simplifying assumptions are usually used to formulate the LSC models. The models considered here are based on the following assumptions: (a) only unassociated solute and solvent molecules participate in the displacement process, (b) solute and solvent molecules form solvates in the mobile phase, which are destroyed in the surface phase because of strong solute-adsorbent interactions, (c) solute and solvent molecules have spherical shapes of different molecular sizes, (d) the molecular sizes of all solvents are identical, (e) the total number of all solvent molecules in the surface phase is constant and independent of the presence of solute molecules because of their infinitely low concentration, (f) the adsorbent surface is energetically homogeneous. Taking into account the above assumptions and limiting theoretical considerations to the mobile phase containing the double solvates only, we have (6):

$$k'_s = \beta K_{s1}(y_1/x_1)^r(1 + C_1x_1)^{-1} \quad (1)$$

where  $k'_s$  is the capacity ratio of the  $s$ -th solute chromatographed in the binary eluant "1+2",  $K_{s1}$  is the equilibrium constant describing the displacement process of 1-st solvent molecules from the surface phase by the  $s$ -th solute molecules contained in the mobile phase,  $y_1$  and  $x_1$  are mole fractions of 1-st solvent in the surface and mobile phases, respectively,  $C_1$  is the equilibrium constant describing formation of double solvates in the mobile phase,  $r$  is the ratio of solute and solvent molecular sizes, and  $\beta$  is the proportionality factor

characteristic for a given adsorbent and independent upon the eluant nature in a good approximation (1).

A simple expression may be also obtained for the mobile phases containing multimolecular solvates, i.e., solvates consisting of one solute molecule and one, two, three and so forth molecules of 1-st solvent. It is (8):

$$k'_S = \beta K_{S1}(y_1/x_1)^r(1 - C x_1) \quad (2)$$

where  $C$  is the constant connected with the equilibrium constant  $C_q$  describing formation of multimolecular solvates consisting of one solute molecule and  $q$  molecules of 1-st solvent. The relationship between these constants may be assumed as follows:

$$C_q = C^q \quad (3)$$

Thus, the constant  $C$  is connected with an average interaction energy between one solvent molecule and solute molecule being the kernel of the multimolecular solvate. Equations 1 and 2 may be more simplified. For solvents showing a great difference in their elution parameters, the complete coverage of the surface by 1-st solvent ( $y_1 = 1$ ) is already reached at lower concentrations of this solvent (1). Moreover, for many chromatographic systems the molecular areas occupied by solute and solvent molecules on the adsorbent surface are similar and they may be assumed to be identical ( $r = 1$ ). Taking into account these additional assumptions in equations 1 and 2 we have:

$$\frac{1}{k'_S x_1} = \frac{1}{\beta K_{S1}} (1 + C_1 x_1) \quad (4)$$

and

$$k'_s x_1 = \beta K_{s1} (1 - C x_1) \quad (5)$$

Equation 4 corresponds to equation 1, however, equation 5 relates to equation 2. The linear dependence  $(k'_s x_1)^{-1}$  vs.  $x_1$  shows positive slope for the chromatographic systems with strong solute-solvent interactions in the mobile phase, however, the dependence  $k'_s x_1$  vs.  $x_1$  has negative slope for the chromatographic systems in question. Of course, equation 4 should give better representation of chromatographic data for systems with double solvates in the mobile phase, whereas, equation 5 should be better for describing the systems with multimolecular solvates in the mobile phase.

#### RESULTS AND DISCUSSION

The purpose of this section is the study of utility of equations 4 and 5 for evaluating effects of the solute-solvent interactions in the mobile phase. Equations 4 and 5 were examined by using HPLC data published by Scott and Kucera (7). They measured the corrected retention volume of the  $s$ -th solute  $V'_s$  for different volume fractions of 1-st solvent in the mobile phase (1-st solvent is assumed to be the more efficient eluting solvent). Since equations 4 and 5 relate to  $r = 1$  (identical molecular sizes of solute and solvents), the mole fraction  $x_1$  denotes simultaneously the volume fraction of 1-st solvent in the mobile phase. The corrected retention volume  $V'_s$  is proportional to the capacity ratio  $k'_s$ , where the void volume of the mobile phase in the column  $V_m$  is the proportionality factor. Replacing in equations 4 and 5  $k'_s$  by  $V'_s/V_m$  we obtain:

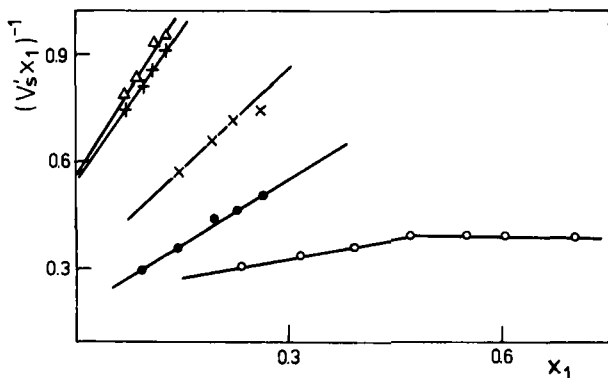


FIGURE 1. Linear plots  $(V'_S x_1)^{-1}$  vs.  $x_1$  for phenyl methyl carbinol chromatographed in binary eluants consisting of n-heptane with dioxane ( $\Delta$ ), tetrahydrofuran (+), and benzyl alcohol chromatographed in n-heptane/tetrahydrofuran (x), 3-phenyl-1-propanol chromatographed in n-heptane/tetrahydrofuran ( $\bullet$ ) and desoxycorticosteron chromatographed in n-heptane/isopropanol (O) on Partisil 10 at 298 K.

$$\frac{1}{V'_S x_1} = \frac{1}{\beta V_m K_{S1}} (1 + C_1 x_1) \quad (6)$$

and

$$V'_S x_1 = \beta V_m K_{S1} (1 - C x_1) \quad (7)$$

Equation 6 has been examined in the reference (9). For the purpose of illustration Figure 1 presents the linear dependence  $(V'_S x_1)^{-1}$  vs.  $x_1$  for phenyl methyl carbinol chromatographed in different binary eluants on Partisil 10 at 298 K. The values of the equilibrium constant  $C_1$  for HPLC systems studied are summarized in Table 1. The same HPLC data have been described by means of equation 7 (see Figures 2 - 4).

TABLE 1

The constants  $C_1$  and  $C$  for different solutes chromatographed in n-heptane (2)/solvent (1) on Partisil 10 at 298 K.

Solute	Solvent †	$C_1$	$C$
$\alpha$ -phenethyl alcohol	ethyl acetate	3.4	2.6
benzyl alcohol	ethyl acetate	7.8	2.6
n-octanol	ethyl acetate	3.1	2.4
n-pentanol	ethyl acetate	2.8	2.3
n-butanol	ethyl acetate	1.7	1.7
benzyl alcohol	tetrahydrofuran	6.3	1.4
3-phenyl-1-propanol	tetrahydrofuran	7.2	1.6
desoxycorticosteron alcohol	isopropanol	1.4	0.5
phenyl methyl carbinol	tetrahydrofuran	5.4	3.0
phenyl methyl carbinol	methyl acetate	7.4	2.9
phenyl methyl carbinol	ethyl acetate	7.0	2.7
phenyl methyl carbinol	propyl acetate	7.1	2.4
phenyl methyl carbinol	butyl acetate	4.4	2.2

It follows from Figures 2 - 4 that the linear equation 7 gives satisfactory representation of the HPLC data published by Scott and Kucera (7). The small deviations of some points from linearity (e.g., Figure 4) may be caused by assumption of equality of molecular sizes of solute and solvents ( $r = 1$ ), ideality of the surface phase and neglect of molecules of 2-nd solvent in the surface phase ( $y_1 = 1$ ). The constant  $C$  has been calculated from the linear dependences shown in Figures 2-4 and its values are given in Table 1.



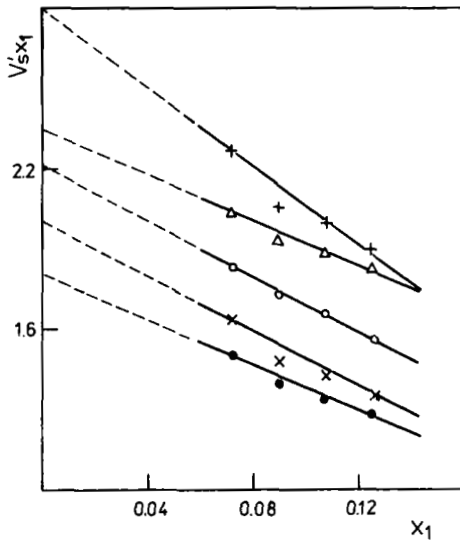


FIGURE 2. Linear plots  $V'_g x_1$  vs.  $x_1$  for  $\alpha$ -phenethyl alcohol ( $x$ ), benzyl alcohol ( $+$ ), *n*-octanol ( $\bullet$ ), *n*-pentanol ( $O$ ) and *n*-butanol ( $\Delta$ ) chromatographed in *n*-heptane/ethyl acetate on Partisil 10 at 298 K.

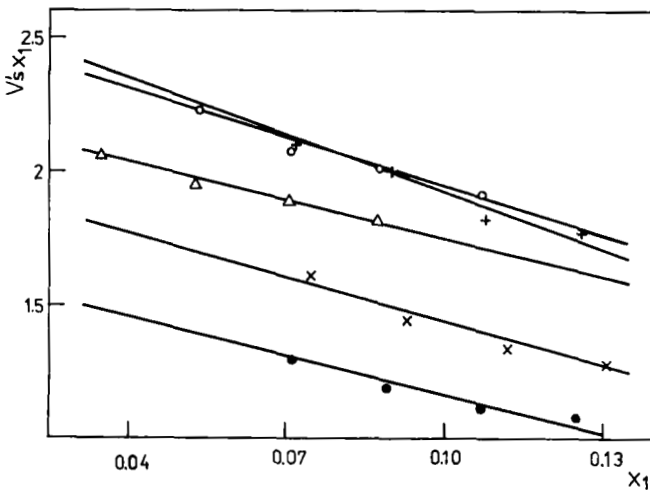


FIGURE 3. Linear plots  $V'_g x_1$  vs.  $x_1$  for phenyl methyl carbinol chromatographed in binary eluents consisting of *n*-heptane with tetrahydrofuran ( $\bullet$ ), methyl acetate ( $x$ ), ethyl acetate ( $+$ ), propyl acetate ( $O$ ) and butyl acetate ( $\Delta$ ) on Partisil 10 at 298 K.

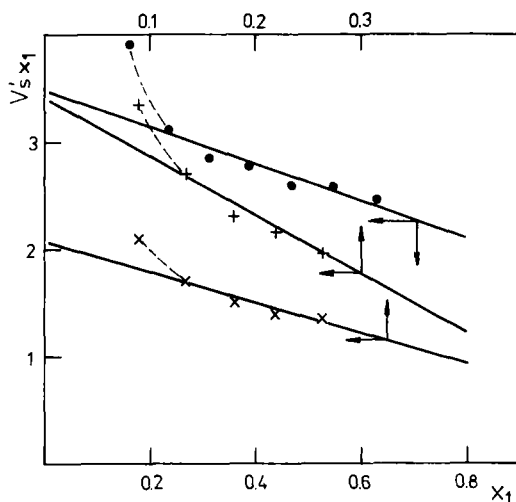


FIGURE 4. Linear plots  $V_g'x_1$  vs.  $x_1$  for benzyl alcohol (x) and 3-phenyl-1-propanol (+) in n-heptane/tetrahydrofuran, and desoxycorticosteron alcohol in n-heptane/isopropanol (●).

The values of the constants  $C_1$  and  $C$  for solutes of smaller molecular sizes referring to n-heptane/ethyl acetate are analogous; it suggests that the model of double solvates in the mobile phase may be used to represent the chromatographic process. However, in the case of solutes of greater molecular sizes, e.g., phenyl methyl carbinol in n-heptane/alkyl acetate, the values of  $C_1$  are greater than the analogous values of  $C$ . On the other hand, the values of  $C$  obtained for phenyl methyl carbinol chromatographed in alkyl acetate/n-heptane eluants are similar to the values of  $C$  evaluated for normal alcohols chromatographed in ethyl acetate/n-heptane eluant. In the both groups of HPLC systems the chemical nature of the interacting molecules is this same, i.e., the alcohol molecules interact with alkyl acetate molecules; it suggests that for

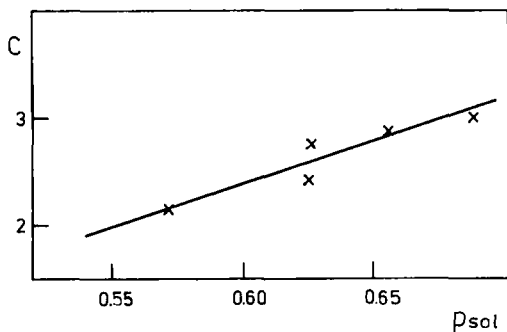


FIGURE 5. Graph of the constant  $C$  against solvent polarizability per unit volume  $p_{sol} = (\epsilon - 1)/(\epsilon + 2)$  for phenyl methyl carbinol chromatographed in binary eluants consisting of *n*-heptane with tetrahydrofuran ( $p_{sol} = 0.687$ ), methyl acetate ( $p_{sol} = 0.654$ ), ethyl acetate ( $p_{sol} = 0.626$ ), propyl acetate ( $p_{sol} = 0.625$ ) and butyl acetate ( $p_{sol} = 0.572$ ) on Partisil 10 at 298 K.

phenyl methyl carbinol chromatographed in alkyl acetate/*n*-heptane eluants the values of  $C$  are more realistic than the values of  $C_1$ . Moreover, these values of  $C$  show a linear dependence upon the polarizability per unit volume of the 1-st solvent defined by  $(\epsilon - 1)/(\epsilon + 2)$ , where  $\epsilon$  is the dielectric constant of the 1-st solvent (c.f., Figure 5). The values of the solvent polarizability were taken from the reference (7). According to Scott and Kucera (7) the contribution to the retention volume from the solute-solvent interactions is proportional to the exponent of the polarizability. Similarly, the constant  $C$  is an exponential function of the solute-solvent interaction energy. Therefore, the values of  $C$  and  $p_{sol}$  fulfils a linear dependence presented in Figure 5. The above facts leads to the conclusion that in the case of phenyl methyl carbinol chromatographed in alkyl acetate/

n-heptane eluants the model of multimolecular solvates is more realistic. Perhaps, the molecules of phenyl methyl carbinol, having greater molecular sizes than the molecules of normal alcohols studied, may annex more than one solvent molecule. It should be pointed out that the values of the constants  $C_1$  and  $C$  may be used for a qualitative description of the solute-solvent interactions effects in HPLC process. The exact explanation of role of the solute-solvent interactions in HPLC process requires a further experimental and theoretical studies.

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