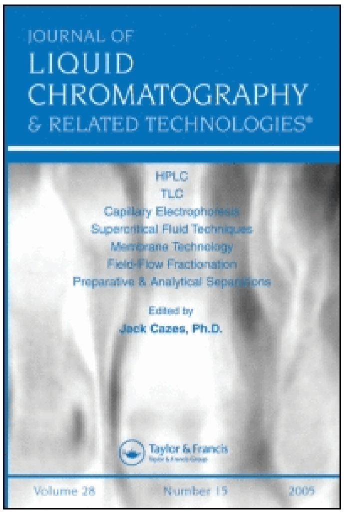

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Borówko, M.(1986) 'A Simple Dependence of the Capacity Ratio on the Composition of the Mobile Phase in Liquid-Solid Chromatography', Journal of Liquid Chromatography & Related Technologies, 9: 9, 1837 — 1847

To link to this Article: DOI: 10.1080/01483918608078746

URL: http://dx.doi.org/10.1080/01483918608078746

JOURNAL OF LIQUID CHROMATOGRAPHY, 9(9), 1837-1847 (1986)

A SIMPLE DEPENDENCE OF THE CAPACITY RATIO ON THE COMPOSITION OF THE MOBILE PHASE IN LIQUID-SOLID CHROMATOGRAPHY

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ABSTRACT

The general dependence of the capacity ratio on the composition of the multicomponent mobile phase is presented. The effects connected with difference of molecular sizes of solutes and solvents are considered. A simple linear dependence for the binary mobile phase is proposed and tested on experimental data.

INTRODUCTION

Significant progress has been made during the last twenty years in the theory of liquid adsorption chromatography. The fundamental results have been summarized in several reviews (1-4). The most general formulation has been proposed by Jaroniec and his coworkers (5-9). Their approach based on the theory of adsorption from multicomponent solutions.

In this paper the effects connected with difference of molecular sizes of solutes and solvents are discussed. The general equation defining the capacity ratio of a given solute chroma-

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tographed in a multicomponent eluant is presented. The special case of this equation for a binary mixed solvent is compared with the relationship of Soczewiński (10). A new linear dependence for a binary mobile phase is proposed. Based on this relationship a simple numerical procedure is presented for evaluating the ratio of molecular areas of the solute and solvents, and the constant characterizing adsorption equilibrium in the mixed eluant. This method is examined by using TLC data for several organic compounds chromatographed in benzene-cyclohexane and chloroform-carbon tetrachloride eluants on alumina.

THEORETICAL

Let us consider a chromatographic process for the substance "s" in n-component mobile phase at the energetically homogeneous surface. Let us assume that molecular sizes of all solvents are equal. This assumption seems to be quite realistic and it has often been used in theoretical considerations (2-4). In this case the chromatographic process may be described by the following series of exchange reactions:

$$(s)^1 + r(i)^\sigma \rightleftharpoons (s)^\sigma + r(i)^1 \qquad (1)$$

where symbols $(j)^1$ and $(j)^\sigma$ $(j=1,2,\ldots,n,s)$ denote molecules of jth component in the ςth phase; the superscripts 1 and σ refer to the mobile and stationary phase, respectively. The stoichiometric coefficient r is defined as a ratio of the partial molar areas of the solute (w_s) and solvents $(w_1=w_2=\ldots=w_n=w)$ (11):

$$r = w_s / w \qquad (2)$$

The equilibrium constant of the reaction 1 is given by (4):

$$K_{si} = F_{si} (x_s^{\sigma} / x_s^{l}) (x_i^{l} / x_i^{\sigma})^{r} \qquad (3)$$

where the function F_{si} is equal to:

$$F_{si} = (f_s^{\sigma} / f_s^{l}) (f_i^{l} / f_i^{\sigma})^{r}, \qquad (4)$$

and f_j^{γ} denotes the activity coefficient of the jth component in the γth phase.

According to the suggestion of Everett (11) the constant K_{si} may be expressed as follows:

$$K_{si} = c_{si} \exp ((E_s - rE_i) / k_B T) \qquad (5)$$

where c_{si} is the entropy factor, E_j denotes the adsorption energy of the jth component and k_B is the Boltzman constant.

It follows from equation 3 that:

$$x_i^{\sigma} = k^{1/r} (F_{si} / K_{si})^{1/r} x_i^{l} \qquad (6)$$

where k is the distribution coefficient of the solute "s" defined by:

$$k = x_s^{\sigma} / x_s^{l} \qquad (7)$$

The summation of the mole fractions in the stationary phase leads to:

$$\sum_{i=1}^{n} x_i^{\sigma} = k^{1/r} \sum_{i=1}^{n} (F_{si} / K_{si})^{1/r} x_i^{l} \approx 1 \qquad (8)$$

After a simple transformation we obtain

$$k = (\sum_{i=1}^{n} (F_{si} / K_{si})^{1/r} x_i^{l})^{-r} \qquad (9)$$

When $F_{si}=1$ $(i=1,2,...,n)$ we have:

$$k' = \left(\sum_{i=1}^{n} x_i^l/(k_i')^{1/r} \right)^{-r} \tag{10}$$

where k' and k_i' denote the capacity ratios of the solute "s" in the mixed solvent and a pure solvent "i", respectively; $k'=\bar{q}\ k$ ($\bar{q}$ is the constant characteristic for the chromatographic bed) (1).

It is easy to prove that for $F_{si}=1$ and $c_{si}=1$ $(i=1,2,...,n)$ the following equalities are satisfied:

$$K_{si} = k_i \quad \text{and} \quad K_{ij} = (k_j/k_i)^{1/r} = (k_j'/k_i')^{1/r} \tag{11}$$

where K_{ij} is the constant characterizing adsorption from binary solution (i,j) (12).

Let us discuss the dependence of the capacity ratio upon the mobile phase composition for a binary mixed eluant. In this case equation 10 becomes a simple linear form:

$$(k')^{-1/r} = a\ x_1^l + b \tag{12}$$

where

$$a = (k_1')^{-1/r} - (k_2')^{-1/r} \quad \text{and} \quad b = (k_2')^{-1/r}. \tag{13}$$

When molecular areas of the solute and solvent are equal (r=1) equation 12 is identical with that proposed by Jandera and Churacek (13), and strictly derived in terms of Snyder's approach by Narkiewicz et al (14):

$$(k')^{-1} = \left((k_1')^{-1} - (k_2')^{-1} \right) x_1^l + (k_2')^{-1} \tag{14}$$

In order to compare equation 12 with the well-known relationship of Soczewiński (10):

$$\ln k' = \ln k_1' - r \ln x_1^l , \quad (15)$$

we discuss the function ln k′ vs. ln x_1^l calculated according to equation under consideration. For high values of mole fractions x_1^l this function may be approximated by the following linear relationship:

$$\ln k' = \ln k_1' - n \ln x_1^l \quad . \quad (16)$$

The coefficient n may be calculated by using of equation 12:

$$n = -\lim_{x_1^l \to 1} (d \ln k' / d \ln x_1^l) = r (1 - 1 / K_{12}) \quad (17)$$

Let us notice that when the 1st solvent is very strongly adsorbed ($K_{12} \to \infty$) the coefficient $n \approx r$, and equations 12 and 15 give the same results for high values of mole fraction x_1^l.

In Figure 1 an comparison of the functions ln k′vs. ln x_1^l calculated from equation 12 with the linear relationship of Soczewiński is presented. This figure shows these curves plotted for r=2 and different values of the constant K_{12} characterizing adsorption in the binary solution (1,2). When K_{12} are sufficiently high the functions ln k′vs. ln x_1^l may be approximated by stright lines 16 even for comparatively low concemtrations of the 1st solvent. The slopes of these lines vary according to equation 17, and they tend to r when K_{12} increases. It means that an interpretation of the coefficient n determined from experimental linear dependence ln k′ vs. ln x_1^l requires the knowledge of adsorption properties of both solvents. Analogous results have been obtained by Borówko and Jaroniec (15) which proved that the coefficient n depended upon several different parameters characterizing adsorbent-adsorbate and adsorbate-adsorbate interactions.

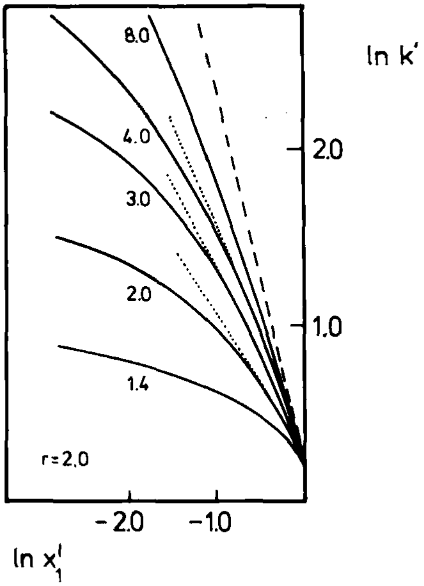

FIGURE 1. Theoretical functions ln k'vs. ln x_1^1 calculated from equation 12 (——) and linear dependences 16 (...) for $\bar{q}$ = 1, r = 2 and different values of the constant K_{12}. The weakely dashed line corresponds to Snyder-Soczewiński relationship.

Thus, the physical meaning of the experimental slope n should be very carefully analysed.

The relationship of Soczewiński may be applied to describe of the chromatographic system in which the 2nd solvent is practically absent in the stationary phase. However, the Snyder treatment leading to equation 14, involves the adsorption of the 2nd solvent but it neglectes the difference in molecular sizes of the solute and solvents.

Concluding, it should be pointed out that model culminating in equation 12 involves both adsorption of the 2nd solvent as the difference in molecular areas of the solute and solvents.

ANALYSIS OF EXPERIMENTAL DATA

Equation 12 was applied to describe the experimental data measured by Ościk and Chojnacka (16). Calculations have been performed for two mobile phases: benzene-cyclohexane and chloroform-carbon tetrachloride. For these mixed eluants the molecular areas of both solvents are equal (1). The following solutes were considered: 6-methylquinoline (A), isoquiniline (B), acridine (C) and 5,6,-benzoquinoline (D).

TABLE 1

Parameters r^*, K_{12}^*, K_{12}, r and n determined according to the procedure discussed in the paper.

Solute	r^*	K_{12}^*	K_{12}	r	n
Mobile phase: benzene (1) - cyclohexane (2)					
A	2.38	3.10	8.59	1.25	1.11
B	0.83	17.3	8.59	1.11	0.98
C	1.52	8.12	8.59	1.47	1.30
D	0.99	5.83	8.59	0.81	0.72
Mobile phase: chloroform (1) - carbon tetrachloride (2)					
A	4.17	1.56	1.94	2.78	1.35
B	5.00	1.36	1.94	2.33	1.13
C	1.49	3.03	1.94	2.50	1.21
D	3.33	1.80	1.94	2.94	1.43

When the ratio r is known from the other measurements equation 12 may be immediately used to describe of experimental data. The molecular areas of most popular chromatographic solvents are summarized by Snyder (1). Unfortunately, the area occupied by solute molecules is usually not available in literature. Therefore, the parameters r were determined from chromatographic data.

In this paper the ratios r have been found numerically. The procedure had two steps.

First, optimal parameters r^* have been obtained by minimization of the standard deviation:

$$SD = \left(\sum_{q=1}^{n} \left(k'_{exp}(x^l_{1,q}) - k'(x^l_{1,q}) \right)^2 / (p - 1) \right)^{1/2}$$

where p denotes the number of experimental points whereas $k'_{exp}(x^l_{1,q})$ and $k'(x^l_{1,q})$ are experimental and theoretical values of the capacity ratio for a given $x^l_{1,q}$. The optimal parameter r^* was that for which the dependence SD vs. r reached a minimum. The optimal values r^* and adsorption constants K^*_{12} calculated from equations 11 are summarized in Table 1. As follows from the analysis of the results constants K^*_{12} are not characteristic for a given mixed solvent and they depends upon the solutes. In this situation the second step of an optimization was applied. The constant K_{12} for a given eluant has been calculated as the arithmetic mean of suitable values K^*_{12}. Next, the values r corresponding to this value of adsorption constant were determined from formula 11 ($r = \ln(k'_2 / k'_1) / \ln K_{12}$). These values are also presented in Table 1. The adsorption constant K_{12} for mobile phase benzene-cyclohexane is bigger than for mixed solvent chloroform-carbon tetrachloride. However, values r determined for benzene-cyclohexane are smaller than those calculated for the second solvent.

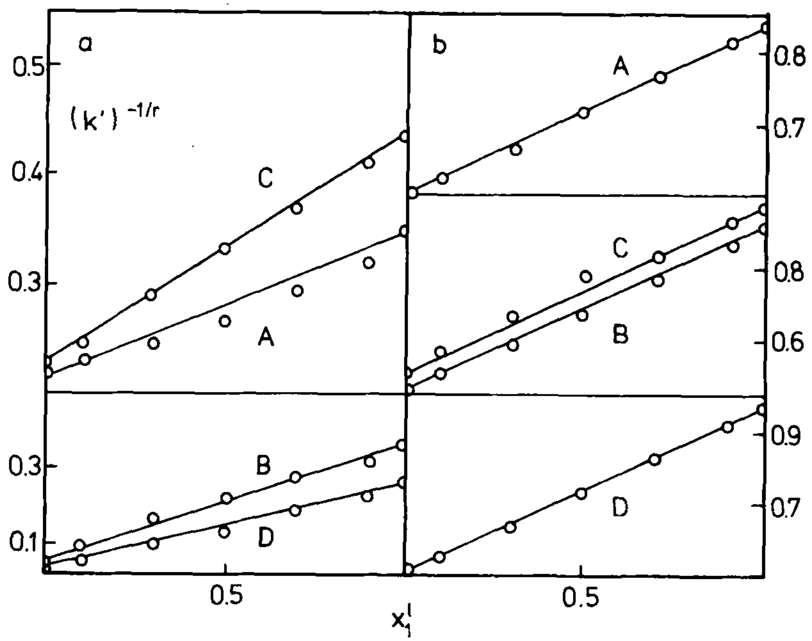

FIGURE 2. Comparison of the experimental points (circles) with linear dependence 12 (solid lines) for 6-methylquinoline (A), isoquinoline (B), acridine (C) and 5,6-benzoquinoline (D) chromatographed in: (a) benzene-cyclohexane, (b) chloroform-carbon tetrachloride on alumina.

Table 1 presents coefficients n calculated by means of equation 17 for the optimal values r and K_{12}. These coefficients are always smaller than r.

Figures 2a and 2b show linear dependence 12 plotted for parameters r and K_{12} summarized in Table 1. The agreement of experimental points with theoretical lines is satisfactory. For one system only (isoquinoline in C_6H_6-C_6H_{12}) a systematic deviation from the linear relationship 12 is observed. In this case the parameter r^* is considerably more useful to approximate of experimental data.

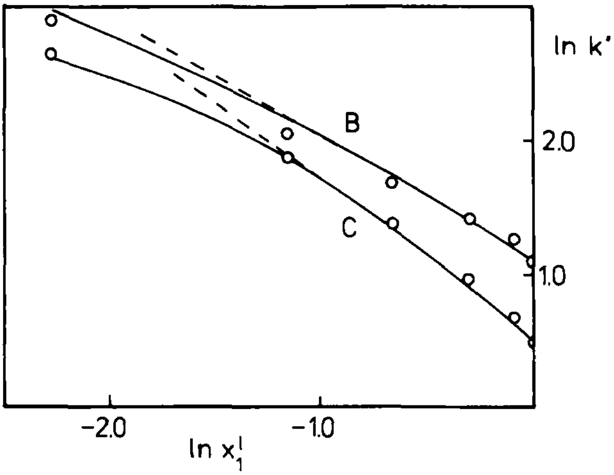

FIGURE 3. Theoretical curves ln k'vs. ln x_1^1 calculated from equation 12 (——), stright lines 16 (---) and experimental points for the solutes B and C chromatogaphed in benzene-cyclohexane on alumina; parameters K_{12} and r are presented in Table 1.

The experimental data were also described by using of the linear dependence 16. Two systems only (isoquinoline(B) and acridine (C) in C_6H_6-C_6H_{12}) may be described by means of equation 16 in the wide concentration region (Figure 3). The coefficients n were determined graphically from experimental curves: $n_B = 0.92$ and $n_C = 1.24$. These values are in a good agreement with theoretical slopes from Table 1.

The presented analysis of the experimental data testifies to a practical usefulnes of the proposed equation 12.

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