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**A SIMPLE LINEAR DEPENDENCE OF THE
LOGARITHM OF THE CAPACITY RATIO
UPON MOBILE PHASE COMPOSITION IN THE
REVERSED-PHASE LIQUID
CHROMATOGRAPHY**

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ABSTRACT

The linear dependence of the logarithm of the capacity ratio upon mobile phase composition is considered as a special case of a more complex equation describing the chromatographic process. This dependence gives a satisfactory representation of the chromatographic data for phenol derivatives in methanol-water and ethanol-water on LiChrosorb RP-8 at 20°C.

INTRODUCTION

Some theoretical treatments have been proposed to describe the liquid chromatography with mixed mobile phases (1-9). The treatments presented in the papers (1-8) were directed toward liquid adsorption chromatography with unmodified surfaces and in the normal-phase (NP) mode. Recently, Martire and Boehm (9) generalized their earlier treatment (3,4),

so that it may be applied to both normal-phase liquid chromatography (NPLC) and reversed-phase liquid chromatography (RPLC). The development of their treatment is a promising avenue for future progress in the theoretical description of liquid chromatography process.

In the present paper one of the equations derived by Martire and Boehm (9) is discussed in comparison to the Ošćik's equation (10), which was proposed in 1965. This equation has been applied to describe the chromatographic data for phenol derivatives chromatographed in methanol-water and ethanol-water on LiChrosorb RP-8 at 20°C.

THEORETICAL

Martire and Boehm (9) derived equations for a chromatographic system, in which the stationary phase consists of chemically homogeneous, semiflexible chains permanently bonded to a solid surface plus those solvent and solute molecules residing in the same layers as the chain segments. For binary mixtures of the two solvents and completely collapsed chemically bonded chains their formulation gives the following expression (9):

$$\ln k' = \theta_1 \ln k'_1 + \theta_2 \ln k'_2 - A \theta_1 \theta_2 \quad (1)$$

where k' is the capacity ratio of a solute chromatographed in the binary eluent "1+2", k'_i for $i = 1, 2$ is the capacity ratio of this solute in the i -th pure solvent, θ_i for $i = 1, 2$ is the volume fraction of the i -th solvent in the mobile phase and A is the constant connected with the parameters characterizing interactions between solvent molecules and the parameter defining structure of the solute. Moreover,

equation 1 has been derived by assuming the virtual exclusion of the solvents from the surface phase, i.e., their volume fractions in the surface phase are equal to zero, and the reduced film thickness of the chemically bonded phase (CBP) is equal to the fractional surface coverage by the CBP chains. Equation 1, resulting from the rigorous statistico-thermodynamical treatment, has the same form as the corresponding relation for classical partitioning (9).

Since the solute concentration is infinitely low, the sum of the volume fractions of the solvents in the mobile phase is equal to unity, i.e.,

$$\theta_1 + \theta_2 = 1 \quad (2)$$

Substitution of equation 2 into equation 1 gives:

$$\ln k' = \theta_1 \ln k'_1 + \theta_2 \ln k'_2 - A\theta_1 + A\theta_1^2 \quad (3a)$$

or

$$\ln k' = \ln k'_2 + (\ln k'_1 - \ln k'_2 - A)\theta_1 + A\theta_1^2 \quad (3b)$$

For lower values of θ_1 and small parameter A equation 3 can be approximated as follows:

$$\ln k' = \ln k'_2 + (\ln k'_1 - \ln k'_2 - A)\theta_1 \quad (4)$$

Equation 4 predicts the correct value of the capacity ratio at $\theta_1 = 0$; then $k' = k'_2$.

In 1965 Ošćik (10) proposed an equation for thin layer chromatography (TLC) with multicomponent mobile phase. His equation is widely discussed in the review (1) and was widely applied to describe the NP TLC data. Its mathematical form for binary mobile phases, written by means of the capacity ratios, is (11):

$$\ln k' = \theta_1 \ln k'_1 + \theta_2 \ln k'_2 + A'(\theta_1^B - \theta_1) \quad (5)$$

where θ_1^B is the volume fraction of 1-st solvent in the surface phase and A' is the parameter describing molecular interactions in the mobile phase (1,10). Using analogous assumption as that leading to equation 1, i.e., $\theta_1^B = 0$, we have

$$\ln k' = \theta_1 \ln k'_1 + \theta_2 \ln k'_2 - A'\theta_1 \quad (6a)$$

or

$$\ln k' = \ln k'_2 + (\ln k'_1 - \ln k'_2 - A')\theta_1 \quad (6b)$$

Equations 3 and 6 have the same mathematical form. The comparison of equations 1 and 5, giving this same limiting expression, suggests that equation 5 may be used for describing the RPLC data. Moreover, a detailed comparative study of the treatments proposed by Ošcik (10) and Martire and Boehm (9) may be useful for quantitative description of adsorption and partition effects in the RPLC with chemically bonded phases. The theoretical studies of these effects are still expected.

EXPERIMENTAL

The chromatographic measurements were carried out by means of liquid chromatograph Varian Aerograph 4100 equipped with Orlita pompe AF 10-4 (G.F.R.) and 46 K injection system from Waters. As a detector UV - 254 mm spectrophotometer (Varian) was employed. The stainless steel column (250x4 mm) was packed with LiChrosorb RP-8 (7 μ m) from Merck (Darmstadt) by means of a balance density slurry technique.

Ethanol, methanol and their mixtures with water were used as the mobile phases. Flow rate (1 ml/min) was measured

with accuracy 0.01 ml/min. The elution volumes V_e of phenol, p-cresol, 3-aminophenol, 2-nitrophenol and benzene were calculated by extrapolating the experimental dependences $V_e = f(v_g)$ to $v_g = 0$, where v_g is the volume of injected substances in the mobile phase. All measurements were carried out at 20°C.

RESULTS AND DISCUSSION

The RPLC data discussed in the experimental section were used to examine the linear dependence (equation 1) of the logarithm of the capacity ratio upon the volume fraction of alcohol. Figure 1 shows this dependence for solutes chromatographed in methanol-water, whereas, Figure 2 presents this same dependence for solutes chromatographed in ethanol-water. The experimental points lie on the straight lines of the following type:

$$\ln k' = a + b \theta_1 \quad (7)$$

where θ_1 is the volume fraction of alcohol, a and b are constants. The parameter a is equal to $\ln k'$ at $\theta_1 = 0$, whereas, the expression $(a+b)$ is equal to $\ln k'$ at $\theta_1 = 1$. Comparing equations 3 and 7 we have: $a = \ln k'_2$ and $a+b = \ln k'_1$. The values of $(a+b)$ and a , obtained from the straight lines shown in Figures 1 and 2, are summarized in Table 1 in comparison to the values of $\ln k'_1$ and $\ln k'_2$ obtained from experiment.

The agreement between a and $\ln k'_2$, $(a+b)$ and $\ln k'_1$ is satisfactory. The observed divergences between these values may be caused by experimental errors of measurement of very low and very high values of the capacity ratio. The values

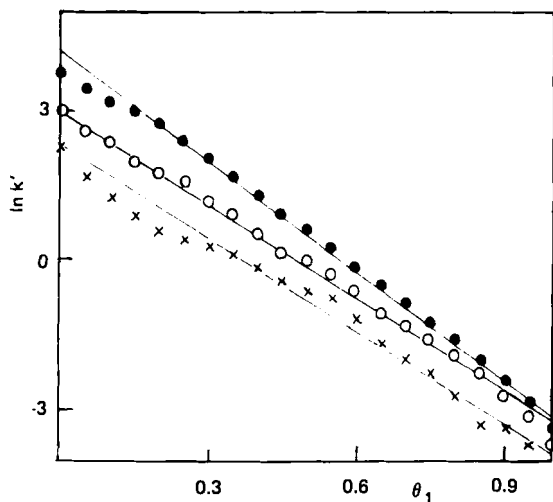


FIGURE 1. Linear dependence $\ln k'$ vs. θ_1 for phenol (o), p-cresol (e) and 3-aminophenol (x) chromatographed in methanol (1) - water (2) on LiChrosorb RP-8 at 20°C.

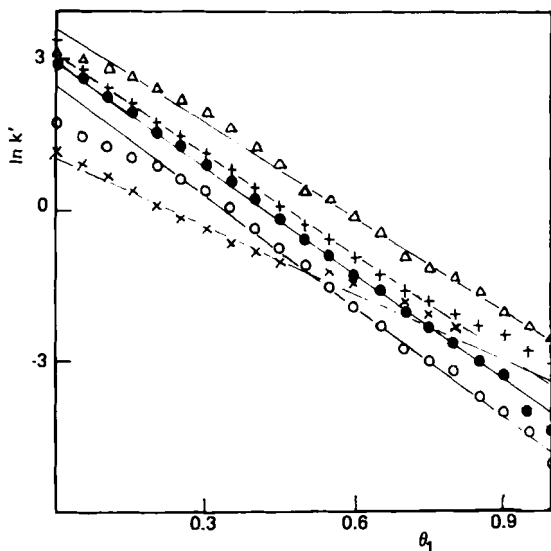


FIGURE 2. Linear dependence $\ln k'$ vs. θ_1 for phenol (o), p-cresol (e), 3-aminophenol (x), 2-nitrophenol (+) and benzene (Δ) chromatographed in ethanol (1) - water (2) on LiChrosorb RP-8 at 20°C.

TABLE 1

Parameters a and $(a+b)$ calculated from the straight lines shown in Figures 1 and 2 in comparison to the values of $\ln k'_2$ and $\ln k'_1$, respectively.

Solute	$\ln k'_1$	$(a+b)$	$\ln k'_2$	a
mobile phase: methanol - water				
phenol	-3.7	-3.2	3.0	3.0
p-cresol	-3.4	-3.1	3.8	4.2
3-aminophenol	-3.7	-3.8	2.3	2.3
mobile phase: ethanol - water				
benzene	-2.5	-2.5	3.2	3.6
phenol	-5.1	-4.8	1.8	2.5
p-cresol	-4.4	-4.0	3.0	3.0
3-aminophenol	-	-3.4	1.2	1.1
2-nitrophenol	-3.1	-3.5	3.3	3.1

of the capacity ratio of the solutes given in Table 1, measured in pure alcohol or in the mobile phase of great concentration of alcohol, are very low. However, the capacity ratios of these solutes in pure water are high. Therefore, they are measured with a greater error.

The results presented in Figures 1 and 2, and Table 1 show that equation 4 gives a good representation of the chromatographic data discussed in the experimental section. Similarity of $\ln k'_1$ and $(a+b)$, $\ln k'_2$ and a shows that the term $A\theta_1\theta_2$ in equation 1 is negligible for the systems in question.

It means that the logarithm of the capacity ratio of the solute in the mixed mobile phase is a simple sum of the logarithms of the capacity ratios of this solute in the pure solvents multiplied by the volume fractions of the solvents (two first terms of equation 1). This additivity of the logarithms of k'_1 and k'_2 , giving the linear dependence of the type 7, is frequently observed for many chromatographic systems (12). Equations 1 and 5 give theoretical foundations for the linear dependence in question, which is frequently treated as a semi-empirical relationship.

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