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LIQUID ADSORPTION CHROMATOGRAPHY WITH MIXED MOBILE PHASES

IV. A NEW EQUATION FOR THE CAPACITY RATIO INVOLVING THE SOLUTE–SOLVENT INTERACTIONS

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SUMMARY

A new equation for the capacity ratio has been derived on the basis of Snyder's assumption concerning the additivity of the capacity ratio in liquid chromatography with multicomponent mobile phase. This equation involves the heterogeneity of interactions of all adsorbed molecules with adsorbent surface (adsorbent heterogeneity) and solute–solvent interactions. The effects of solute–solvent interactions have been included in the modified Snyder equation according to the Ościk approach to liquid chromatography with multicomponent mobile phase.

INTRODUCTION

Increasing interest in gradient liquid chromatography (LC) as a rapid method of analysis requires further theoretical studies on isocratic liquid adsorption chromatography. These studies are necessary for exact description of the gradient elution chromatography[1]. One of the main quantities used in LC is the capacity ratio. The most important problem in LC with multicomponent mobile phase is evaluation of the capacity ratio by means of the capacity ratios characterizing the LC with pure solvents. Many attempts have been made to solve this problem. The most advanced investigations have been reported and compared in ref. 2.

In this paper we shall continue the theoretical considerations presented in the previous parts of this series[3–5]. The result of these considerations will be a new equation for the capacity ratio taking into account the solute–solvent interactions. This equation will be derived by applying Snyder's assumption concerning the additivity of the capacity ratio in LC with multicomponent mobile phase[2,6] and the Ościk expression determining the contribution of the solute–solvent interactions to the capacity ratio[7].

THEORETICAL

LC with multicomponent mobile phase

It has been shown in ref. 4 that the capacity ratio $k'_{(\eta)s}$ for s-th chromatographed solute in n-component mobile phase on heterogeneous solid surfaces of quasi-gaussian energy distribution may be expressed as follows:

$$k'_{(\eta)s} = \sum_{i=1}^{n} k'_{(i)s} y_i^{1/m} \tag{1}$$

where $k'_{(i)s}$ is the capacity ratio for sth solute in the i-th pure solvent, y_i is the mole fraction of the ith solvent in the adsorbed phase, $\eta = (1,2,\ldots,n)$ is an n-dimensional vector used to denote the capacity ratio for s-th solute in n-component mobile phase, and m is the heterogeneity parameter defining the shape of the quasi-gaussian energy distribution. The physical meaning of the parameter m is explained in ref. 4. This parameter characterizes mainly the system adsorbent–solvent mixture; however, its dependence on the kind of solute may be neglected for many adsorption systems.

For $m = 1$, eqn. 1 becomes the Snyder equation for homogeneous adsorbents[2-6]:

$$k'_{(\eta)s} = \sum_{i=1}^{n} k'_{(i)s} y_i \tag{2}$$

For many experimental systems, the theoretical values of $k'_{(\eta)s}$ calculated according to eqn. 2. differ from the experimental ones. For description of such systems, Snyder[6] introduced the following modification of eqn. 2:

$$k'_{(\eta)s} = \sum_{i=1}^{n} k'_{(i)s} y_i + \varDelta \tag{3}$$

where $\varDelta$ is the parameter characterizing the deviation of $k'_{(\eta)s}$ values, predicted by eqn. 2, from experimental ones. Comparing eqn. 3 with Ościk's relationship[7,8], we can express $\varDelta$ by the following equation:

$$\varDelta = \sum_{i=1}^{n-1} A_{is}(y_i - x_i) \tag{4}$$

where x_i is the mole fraction of the ith solvent in the mobile phase, and A_{is} is the constant characterizing the interactions of solute "s" with the binary solvent mixture "$i-n$". The physical meaning of this constant is more exactly explained in the papers[7,8]. If eqn. 4 is added to eqn. 1, we have

$$k''_{(\eta)s} = \sum_{i=1}^{n} k'_{(i)s} y_i^{1/m} + \sum_{i=1}^{n-1} A_{is}(y_i - x_i) \tag{5}$$

Eqn. 5 defines the capacity ratio for sth solute in n-component mobile phase by means of the capacity ratios $k'_{(i)s}$, the heterogeneity parameter m, and the parameters A_{is} determining the solute–solvent interactions. For $m=1$, eqn. 5 reduces to that describing LC with homogeneous adsorbent. Eqn. 5 contains the mole fractions of all

solvents in the adsorbed phase, which may be determined according to the following equation[4,9]:

$$y_i = (x_i/k'_{(i)s})^m / \sum_{j=1}^{n} (x_j/k'_{(j)s})^m \quad \text{for} \quad i = 1, 2, ..., n$$

This eqn. was derived in ref. 9 by applying the theory of adsorption from liquid mixtures on heterogeneous solid surfaces. However, in ref. 4 this equation has been applied to determine the capacity ratio for LC with multicomponent mobile phase.

LC with binary mobile phase

In practical applications, chromatographic systems with two-component mobile phases are of great importance. For such systems eqn. 5 assumes the following form:

$$k'_{(12)s} = k'_{(1)s}y_1^{1/m} + k'_{(2)s}y_2^{1/m} + A_{12}(y_1 - x_1) \tag{6}$$

where

$$y_1 = K_{12}^m x_1^m / (x_2^m + K_{12}^m x_1^m) \tag{7}$$

and

$$K_{12} = k'_{(2)s}/k'_{(1)s} \tag{8}$$

For homogeneous adsorbents eqn. 6 reduces to the simpler form:

$$k'_{(12)s} = k'_{(1)s}y_1 + k'_{(2)s}y_2 + A_{12}(y_1 - x_1) \tag{9}$$

where

$$y_1 = K_{12}x_1/(x_2 + K_{12}x_1) \tag{10}$$

Eqn. 9 may be transformed to the following linear form:

$$G(x_1) = [(K_{12} - 1)(\beta + A_{12})]^{-1} + (\beta + A_{12})^{-1} x_1 \tag{11}$$

where

$$G(x_1) = x_1 x_2 / (k'_{(12)s} - k'_{(1)s}x_1 - k'_{(2)s}x_2) \tag{12}$$

and

$$\beta = k'_{(1)s} - k'_{(2)s} \tag{13}$$

The parameters A_{12} and K_{12} may be calculated from the slope and ordinate of the straight line $G(x_1)$ vs. x_1.

Below, we shall examine eqns. 9, 6 and 11 by using TLC data obtained for different solutes.

RESULTS AND DISCUSSION

Eqn. 6 is a simple sum of two following expressions:

$$F_1 = k'_{(1)}y_1^{1/m} + k'_{(2)}y_2^{1/m} \tag{14}$$

and

$$F_2 = A_{12}(y_2 - x_1) \tag{15}$$

The theoretical curves, calculated according to eqn. 14, were presented in ref. 4. Usually, they are decreasing functions or show a minimum. The function 15 is an excess adsorption isotherm for the first solvent multiplied by the constant A_{12}. For small values of A_{12} the contribution of the expression 15 in the capacity ratio (eqn. 6) is small. However, for higher values of A_{12} the expression 15 strongly influences the shape of eqn. 6. For many mobile phases often used in TLC and LC, the excess adsorption isotherm $(y_1 - x_1)$ shows a maximum (see ref. 10, in which the basic types of adsorption isotherms from liquid mixtures are presented).

For $m = 1$ the function 14 is a decreasing one. Then, the function 6 can shows a minimum for $A_{12} < 0$ and a maximum for $A_{12} > 0$.

For $m < 1$ the function 14 can shows a minimum[4]. Thus, this minimum will be greater for $A_{12} < 0$ and smaller for $A_{12} > 0$. Since the modified Ościk equation[8] is formally analogous to eqn. 6, the theoretical curves from eqn. 6 are similar to those presented in refs. 7, 8 and 11.

For illustrative purposes, the TLC data investigated experimentally by Różyło[12] have been used for examination of eqns. 1, 6, 9 and 11. Numerical calculations have been made for four solutes: o-nitrophenol, quinoline, 2-methylquinoline
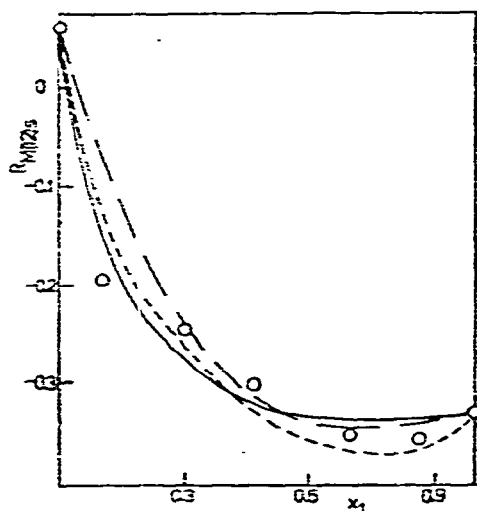

Fig. 1. Dependences $R_{M(2)s}$ vs. x_1 plotted according to eqn. 6 (solid line), eqn. 9 (short dashes) and eqn. 1 (long dashes) for o-nitrophenol in benzene–acetone on silica gel. The mole fraction x_1 refers to acetone.

and 4-methylquinoline in benzene–acetone (2:1) on silica gel at 25°. Other details concerning the chromatographic measurements are given in ref. 12.

Eqns. 1, 6, 9 and 11 may be used to describe the LC and TLC data. In the case of TLC data, the capacity ratios $k'_{(i)s}$ and $k'_{(12)s}$ should be replaced by the following expressions:

$$k'_{(i)s} = 10^{R_{M(i)s}} \tag{16}$$

$$k'_{(12)s} = 10^{R_{M(12)s}} \tag{17}$$

where $R_{M(i)s}$ is the R_M value for sth solute in the ith pure solvent, and $R_{M(12)s}$ is the R_M value for sth solute in the mobile phase "1–2".

First, we compared the chromatography parameters calculated by means of eqns. 1, 6 and 9 for o-nitrophenol in benzene–acetone (2:1) on silica gel. Fig. 1 presents the curves $R_{M(12)s}$ vs. x_1 plotted according to eqns. 9 (short dashes), 6 (solid line) and 1 (long dashes). Table I summarizes the chromatographic parameters appearing in eqns. 1, 6 and 9. It follows from Table I that the standard deviation (S.D.) is smallest for eqn. 6 and highest for eqn. 9. Eqn. 6 involves both effects: adsorbent heterogeneity (the parameter m) and solute–solvent interactions (the parameter A_{12}). However, eqn. 9 involves the solute–solvent interactions only, whereas eqn. 1 includes the adsorbent heterogeneity. Comparison of eqns. 1 and 9[13] shows that the effects of adsorbent heterogeneity are often greater than the effects of solute–solvent interactions.

TABLE I

PARAMETERS m, A_{12} AND K_{12} CALCULATED FOR FOUR SOLUTES IN BENZENE-ACETONE (2:1) ON SILICA GEL

Solute	Eqn.	m	A_{12}	K_{12}	$R_{M(1)s}$	$R_{M(2)s}$	S.D.
o-Nitrophenol	9	—	−0.35	4.47	−0.33	0.06	0.054
	1	0.64	—	4.47			0.035
	6	0.78	−0.37	4.47			0.03
	11	—	−0.43	4.88			0.052
Quinoline	11	—	−1.37	78.0	−0.37	1.51	0.08
2-Methylquinoline	11	—	−1.36	85.3	−0.50	2.69	0.09
4-Methylquinoline	11	—	−0.87	81.7	−0.33	1.69	0.04

Now we shall discuss the constant K_{12}. According to the theoretical considerations, this constant characterizes the mobile phase only. Usually, it is evaluated by means of the following expression[7,8,12–14]:

$$K_{12} = 10^{-\overline{\Delta R}_{M(12)s}} \tag{18}$$

where $\overline{\Delta R}_{M(12)s} = \overline{R_{M(1)s} - R_{M(2)s}}$ is the average difference of $R_{M(1)s}$ and $R_{M(2)s}$ calculated for a given mobile phase and different solutes. The constants K_{12} and A_{12} may be also evaluated by means of eqn. 11, which is the linear form of eqn. 9. In Table I the parameters K_{12}, A_{12} and S. D., calculated by means of eqn. 11, are summa-

rized for o-nitrophenol and quinoline bases. The constant $K_{12} = 4.88$ is very similar to that obtained from eqn. 18. Interesting results have been obtained for quinoline bases. All constants K_{12} are similar and their average value is 81.6. The analogous value, calculated from eqn. 18, is 81.2^{12}. This close agreement is observed for two reasons: the experimental data for quinoline bases give almost linear plots with eqn. 11 (see Fig. 2), and the interactions of quinoline bases with adsorbent surface and mobile phase are similar.
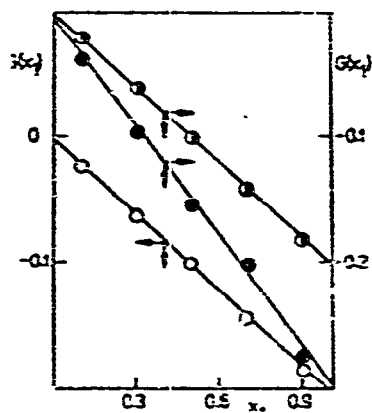

Fig. 2. Linear dependences $G(x_1)$ plotted according to eqn. 11 for quinoline bases in benzene-acetone on silica gel. Quinoline (●), 2-methylquinoline (◑) and 4-methylquinoline (○). The mole fraction x_1 refers to acetone.

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