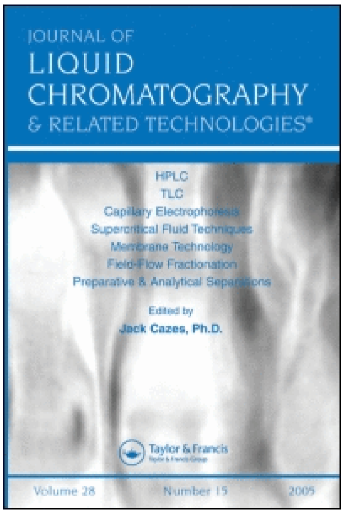

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# Thermodynamic Description of Liquid-Solid Chromatography Process in the Optimization of Separation Conditions of Organic Compound Mixture

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# THERMODYNAMIC DESCRIPTION OF LIQUID-SOLID CHROMATOGRAPHY PROCESS IN THE OPTIMIZATION OF SEPARATION CONDITIONS OF ORGANIC COMPOUND MIXTURE

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## ABSTRACT

Continuous interest in chromatographic methods as analitical techniques of different compounds separation gives rise to studies on theoretical description of chromatographic systems and, at the same way, to the selection of the best way of the prediction of chromatographic separation results.

The main problem of theoretical studies in adsorption chromatography is to describe precisely correlations between retention parameters of given solute and mobile phase composition.

In present paper the effort was made to use thermodynamic description of adsorbent - binary solvent - substance systems for theoretical predictions of analytical separation results in high-performance liquid column and thin-layer chromatography. The attention was paid to the possibility of using thin-layer chtomatography as a method of an initial choice of chtomatographic process optimization.

## INTRODUCTION

The present paper is the continuation of the article (1) studying possibilities of using different chromatographic techniques in the description of adsorption in solid-binary solution systems.

Basing on the previous papers (1,2) the effort was made to theoretical prediction of chromatographic separation results and, at the same way, to the optimization of liquid column chromatography process conditions according to experimental data obtained by thin-layer chromatography.

In agreement with thermodynamic description of adsorbent - binary solution - chromatographed substance systems, there is the following relationship between $R_M$ value of chromatographed substance and mobile phase composition (3,5):

$$R_{M12} = X_1 R_{M1} + X_2 R_{M2} + (X_1^s - X_1)(\Delta R_{M12} + A_{12}) \qquad (1)$$

or the following stright-line relationship (6):

$$\frac{X_1 X_2}{R_{M12} - X_1 R_{M1} - X_2 R_{M2}} = aX_1 + b \qquad (2)$$

The detail derivation of the above equation 1 is presented in previous papers (2,6).

In equations 1 and 2 $R_{M1}$, $R_{M2}$ and $R_{M12}$ values are $R_M$ parameters of given solute obtained for pure solvents 1 and 2, and for their binary mixture 1+2, respectively; $\Delta R_{M12} = R_{M1} - R_{M2}$; $X_1$ and $X_2$ are molar fractions of solvent 1 and 2 in mobile phase; $X_1^s$ is molar fraction of solvent 1 in surface phase; $A_{12}$ parametr describes molecular interactions present in bulk phase; a and b values from equation 2 are stright-line

$$\frac{X_1X_2}{R_{M12} - X_1R_{M1} - X_2R_{M2}} \text{ vs. } X_1 \text{ parameters.}$$

For using equations 1 or 2 for theoretical predictions of chromatographic process conditions, it is necessary to calculate $X_1^s$ and $A_{12}$ values characterizing given system. $R_{M1}$ and $R_{M2}$ values from equations 1 and 2 are obtained experimentally.

According to Everett's equation (7), $X_1^s$ value can be calculated from the following dependence:

$$X_1^s = \frac{X_1K_{12}}{X_2 + X_1K_{12}} \qquad (3)$$

In this equation the $K_{12}$ value is the adsorption equilibrium constant in the given system.

So, according to thermodynamic considerations, adsorbent - binary solution - chromatographed substance system is characterized by $K_{12}$ and $A_{12}$ values.

As it was described previously (2,6), $K_{12}$ and $A_{12}$ values can be calculated from the linear dependence (equation 2) from the following relationships:

$$K_{12} = \frac{a}{b} + 1 \qquad (4)$$

and

$$A_{12} = \frac{1}{a} - \Delta R_{M12} \qquad (5)$$

In previous article (1) the effect of chromatographic technique on $K_{12}$ and $A_{12}$ values obtained from equations 4 and 5, respectively, was analyzed. From the results that have been obtained seems that retention parameters obtained by using liquid column and thin--layer chromatography measurements describe the adsorption (by $K_{12}$ values) in adsorbent-binary solution systems in the same way.

At the same way, it was stated that there is a good agreement between $A_{12}$ values obtained for the given solute by liquid column and thin-layer chromatography measurements. So, it is possible to use thin-layer chromatography as a pilot technique for high-performance liquid column chromatography method and for the optimization of chromatographic process conditions.

## EXPERIMENTAL

### I. Thin-layer chromatography measurements

Experimental $R_M$ values of studied substances were obtained by using thin-layer chromatography measurements realized in sandwich chambers.

As adsorbent were used precoated plates covered with silica gel Si-60 with the pore diameter $d_p$=5μm (Merck). The following mobile phases were used:

| mobile phase | classification according to (8) |
|---|---|
| hexane - carbon tetrachloride | N - N |
| hexane - benzene | N - N/B |
| hexane - ethylene chloride | N - A |
| heptane- ethylene chloride | N - A |
| hexane - ethyl acetate | N - B |

As chromatographed substances the following model group of organic compounds was used:

| No | solute | classification according to (8) |
|---|---|---|
| 1 | 2,3-dichlorophenol | AB |
| 2 | 2,4-dichlorophenol | AB |
| 3 | 2,5-dichlorophenol | AB |
| 4 | 2,6-dichoorophenol | AB |

Chromatograms were developed at 18±0.5°c temperature.

Table I

$K_{12}$ values (eq. 4) obtained from (a) thin-layer and (b) liquid column measurements for the following mobile phases:

I - hexane - tetrachloride
II - hexane - benzene
III - hexane - ethylene chloride
IV - hexane - ethyl acetate

| Solute | I | | II | | III | | IV | |
|---|---|---|---|---|---|---|---|---|
| | a | b | a | b | a | b | a | b |
| 1 | 1.8 | 1.9 | 5.2 | 5.3 | 8.0 | 8.0 | 9.0 | 9.2 |
| 2 | 1.8 | 1.9 | 5.4 | 5.3 | 8.0 | 8.0 | 9.0 | 9.2 |
| 3 | 1.9 | 1.9 | 5.8 | 5.8 | 8.0 | 8.0 | 8.7 | 9.0 |
| 4 | 1.9 | 1.9 | 5.6 | 5.5 | 8.0 | 8.0 | 9.0 | 9.0 |

Table II

$A_{12}$ values (eq. 5) obtained from (a) thin-layer and (b) liquid column measurements for the following mobile phases:

I - hexane - tetrachloride
II - hexane-benzene
III - hexane - ethylene chloride
IV - hexane - ethyl acetate

| solute | I | | II | | III | | IV | |
|---|---|---|---|---|---|---|---|---|
| | a | b | a | b | a | b | a | b |
| 1 | -0.13 | -0.29 | 0.56 | 0.69 | 0.27 | 0.23 | 0.34 | 0.11 |
| 2 | 0.13 | 0.00 | 0.49 | 0.61 | 0.28 | 0.26 | 0.29 | 0.28 |
| 3 | -0.26 | -0.22 | 0.50 | 0.53 | 0.23 | 0.17 | -0.17 | -0.12 |
| 4 | -0.17 | -0.30 | 0.43 | 0.39 | 0.27 | 0.27 | -0.44 | -0.17 |

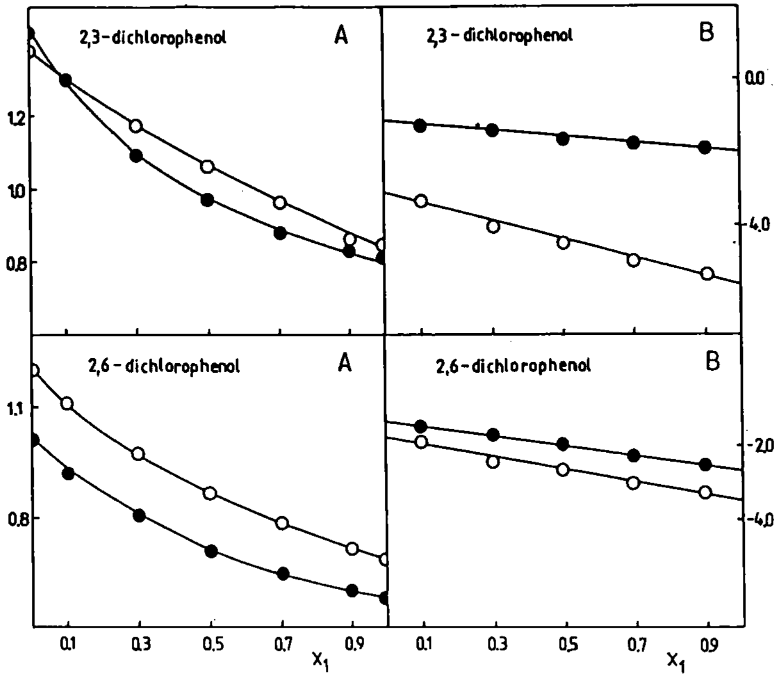

Fig.1

$R_{M12}$ vs $X_1$ (A) and $\left(\dfrac{X_1X_2}{R_{M12} - X_1R_{M1} - X_2R_{M2}}\right)$ vs $X_1$ (B)

relationships obtained for hexane - carbon tetrachloride as mobile phase by:

○ TLC measurements;

● LCC measurements.

## II. Liquid column chromatography measurements

Liquid column chromatograph Type 302 (Techma-Robot, Warsaw) connected with UV detector (Labmim, Budapest) was used in column measurements.

As adsorbent it was used Lichrosorb Si-60 (Merck) with pore diameter $d_p$=5μm.

The same solutes and mobile phases as mentioned above were used in LCC measurements.
Mobile phase flow rate was v=1 ml/min.

Detailed informations about liquid column and thin-layer chromatography measurements were described in previous papers (1,9).

## RESULTS

Tables I and II presented in paper summarize $K_{12}$ (equation 4) and $A_{12}$ (equation 5) values calculated according to experimental data obtained by thin-layer and liquid columnchromatography. These values refer to the group of four dichlorophenols and different binary mobile phases. These $K_{12}$ and $A_{12}$ values were calculated from chromatographic parameters presented as $R_{M12}$ vs $X_1$ relationships (Figs 1-4 A) or

$$\frac{X_1X_2}{R_{M12} - X_1R_{M1} - X_2R_{M2}} \text{ vs } X_1$$

relationships (Figs 1-4 B).

According to theoretical dependence between $R_M$ parameter and k' (capacity factor) value of given solute described by the following relationship:

$$R_M = \log k' \qquad (6)$$

equation 1 can be written as follows:

$$\log k'_{12} = X_1 \log k'_1 + X_2 \log k'_2 + (\log \frac{k'_1}{k'_2} + A_{12}) \qquad (7)$$

where

$\log k'_1 = R_{M1}$; $\log k'_2 = R_{M2}$ and $\log k'_{12} = R_{M12}$.

In tables III-VI are presented experimental k' values obtained for studied substances by using high-performance liquid column measurements and theoretical k' values of these substances calculated from equation 7.

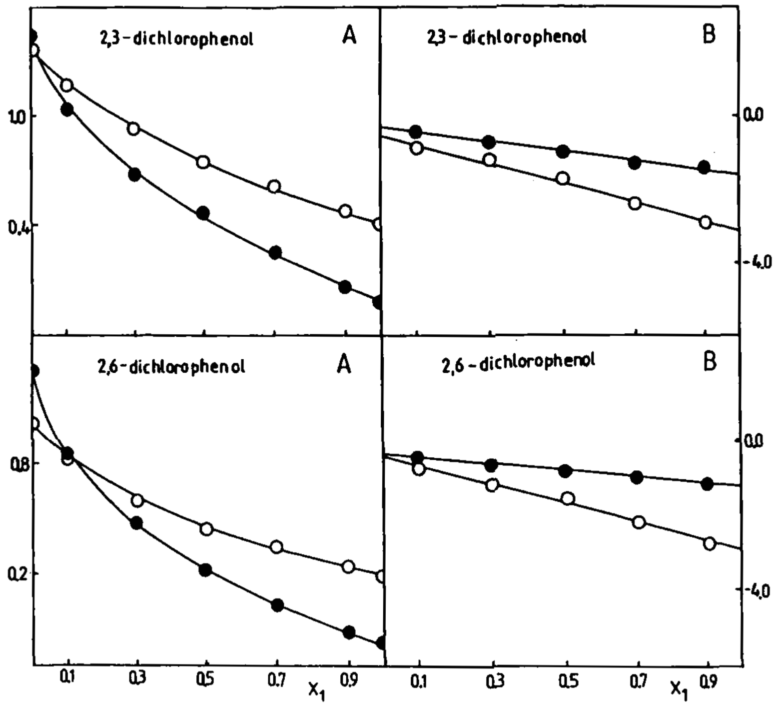

Fig.2
$R_{M12}$ vs $X_1$ (A) and $\left(\frac{X_1X_2}{R_{M12} - X_1R_{M1} - X_2R_{M2}}\right)$ vs $X_1$ (B) relationships obtained for hexane - benzene as mobile phase by:

○ TLC measurements;

● LCC measurements.

Theoretical k' values were calculated using $K_{12}$ (Table I) and $A_{12}$ (Table II) values obtained from equations 4 and 5 according to thin-layer and liquid column measurements.

From the results that have been obtained (Tables III-VI) seems that, in all cases, with no regard

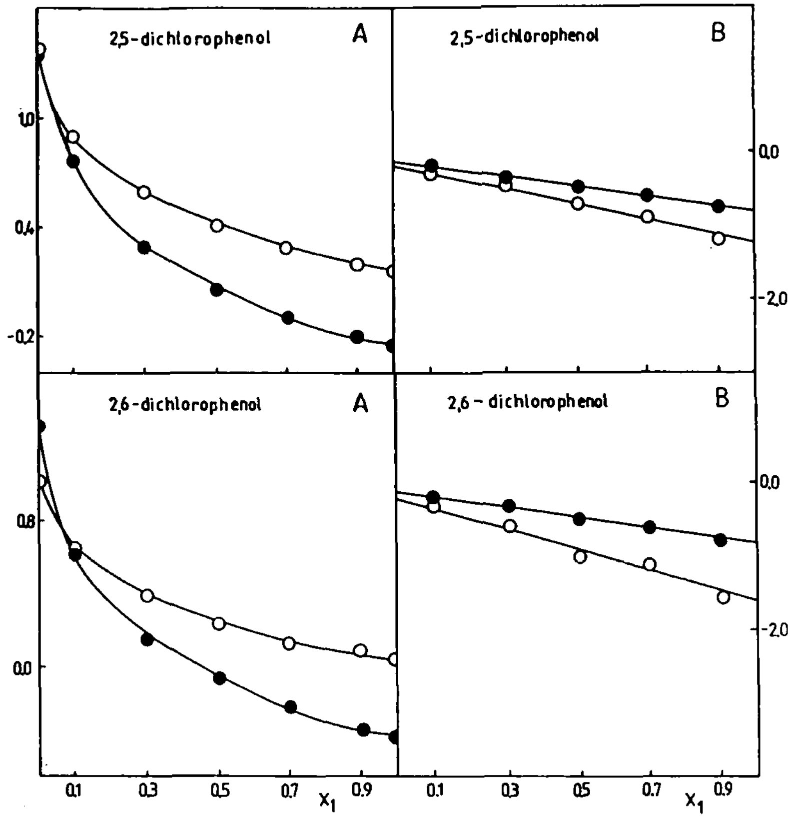

Fig.3

$R_{M12}$ vs $X_1$ (A) and $\left(\frac{X_1X_2}{R_{M12} - X_1R_{M1} - X_2R_{M2}}\right)$ vs $X_1$ (B) relationships obtained for hexane - ethylene chloride mobile phase by:

○ TLC measurements;

● LCC measurements.

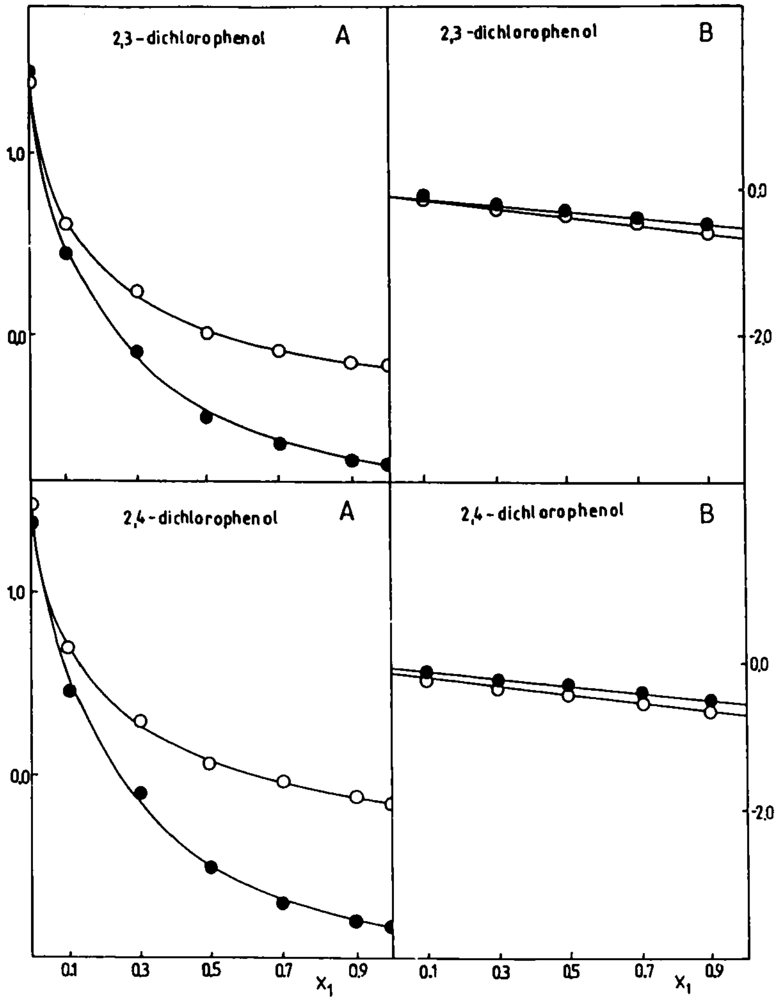

Fig.4
$R_{M12}$ vs $X_1$ (A) and $\left(\dfrac{X_1X_2}{R_{M12} - X_1R_{M1} - X_2R_{M2}}\right)$ vs $X_1$ (B) relationships obtained for hexane - ethyl acetate as mobile phase by:

○ TLC measurements;

● LCC measurements.

Table III

Experimental (k'exp) and theoretical (k'th) values obtained from:

I Thin-layer measurements,

II Liquid column measurements.

Mobile phase: hexane - carbon tetrachloride

| solute | $X_1$ | k'exp | k'th(I) | k'th(II) |
|---|---|---|---|---|
| 1 | 0.1 | 20.0 | 19,9 | 20.0 |
| | 0.3 | 12.3 | 12.6 | 12.6 |
| | 0.5 | 9.3 | 10.0 | 9.4 |
| | 0.7 | 7.7 | 7.9 | 7.7 |
| | 0.9 | 6.8 | 6.3 | 6.8 |
| 2 | 0.1 | 23.4 | 24.2 | 23.7 |
| | 0.3 | 16.6 | 16.6 | 15.9 |
| | 0.5 | 11.7 | 12.4 | 11.9 |
| | 0.7 | 9.3 | 9.5 | 9.4 |
| | 0.9 | 7.9 | 7.9 | 7.9 |
| 3 | 0.1 | 17.8 | 17.3 | 17.4 |
| | 0.3 | 11.5 | 11.2 | 11.3 |
| | 0.5 | 8.5 | 8.4 | 8.5 |
| | 0.7 | 6.8 | 6.7 | 6.8 |
| | 0.9 | 5.9 | 5.9 | 6.0 |
| 4 | 0.1 | 15.5 | 15.6 | 15.7 |
| | 0.3 | 10.0 | 10.2 | 10.3 |
| | 0.5 | 7.4 | 7.7 | 7.8 |
| | 0.7 | 6.2 | 6.2 | 6.2 |
| | 0.9 | 5.3 | 5.4 | 5.4 |

Table IV
Experimental (k'exp) and theoretical (k'th) values obtained from:
I Thin-layer measurements,
II Liquid column measurements.
Mobile phase: hexane - benzene

| solute | $X_1$ | k'exp | k'th(I) | k'th(II) |
|---|---|---|---|---|
| 1 | 0.1 | 11.0 | 11.0 | 12.0 |
| | 0.3 | 4.8 | 4.4 | 4.9 |
| | 0.5 | 3.0 | 2.5 | 2.8 |
| | 0.7 | 1.8 | 1.6 | 1.7 |
| | 0.9 | 1.1 | 1.1 | 1.2 |
| 2 | 0.1 | 12.6 | 12.1 | 12.9 |
| | 0.3 | 5.6 | 5.0 | 5.6 |
| | 0.5 | 3.3 | 3.0 | 3.3 |
| | 0.7 | 2.1 | 2.0 | 2.1 |
| | 0.9 | 1.5 | 1.4 | 1.5 |
| 3 | 0.1 | 8.7 | 9.5 | 9.7 |
| | 0.3 | 4.2 | 4.1 | 4.2 |
| | 0.5 | 2.5 | 2.5 | 2.5 |
| | 0.7 | 1.6 | 1.6 | 1.6 |
| | 0.9 | 1.2 | 1.2 | 1.2 |
| 4 | 0.1 | 6.9 | 7.2 | 7.1 |
| | 0.3 | 3.0 | 2.7 | 2.6 |
| | 0.5 | 1.6 | 1.6 | 1.5 |
| | 0.7 | 1.0 | 1.0 | 1.0 |
| | 0.9 | 0.8 | 0.7 | 0.7 |

Table V
Experimental (k'exp) and theoretical (k'th) values obtained from:
I Thin-layer measurements,
II Liquid column measurements.
Mobile phase: hexane - ethylene chloride.

| solute | $X_1$ | k'exp | k'th(I) | k'th(II) |
|---|---|---|---|---|
| 1 | 0.1 | 5.6 | 5.6 | 5.5 |
| | 0.3 | 2.0 | 1.9 | 1.8 |
| | 0.5 | 1.3 | 1.1 | 1.1 |
| | 0.7 | 0.9 | 0.8 | 0.8 |
| | 0.9 | 0.7 | 0.6 | 0.6 |
| 2 | 0.1 | 6.3 | 6.2 | 6.1 |
| | 0.3 | 2.3 | 2.0 | 2.0 |
| | 0.5 | 1.3 | 1.2 | 1.2 |
| | 0.7 | 0.8 | 0.9 | 0.9 |
| | 0.9 | 0.7 | 0.7 | 0.7 |
| 3 | 0.1 | 4.8 | 4.9 | 4.7 |
| | 0.3 | 1.8 | 1.7 | 1.6 |
| | 0.5 | 1.1 | 1.1 | 1.0 |
| | 0.7 | 0.8 | 0.8 | 0.8 |
| | 0.9 | 0.6 | 0.6 | 0.6 |
| 4 | 0.1 | 4.2 | 4.1 | 4.1 |
| | 0.3 | 1.4 | 1.3 | 1.3 |
| | 0.5 | 0.9 | 0.8 | 0.8 |
| | 0.7 | 0.6 | 0.6 | 0.6 |
| | 0.9 | 0.5 | 0.4 | 0.4 |

Table VI

Experimental (k'exp) and theoretical (k'th) values obtained from:

I Thin-layer measurements,

II Liquid column measurements.

Mobile phase: hexane - ethyl acetate.

| solute | $X_1$ | k'exp | k'th(I) | k'th(II) |
|---|---|---|---|---|
| 1 | 0.1 | 2.8 | 3.1 | 2.5 |
|  | 0.3 | 0.8 | 0.8 | 0.6 |
|  | 0.5 | 0.4 | 0.4 | 0.3 |
|  | 0.7 | 0.3 | 0.3 | 0.3 |
|  | 0.9 | 0.2 | 0.2 | 0.2 |
| 2 | 0.1 | 2.8 | 2.8 | 2.7 |
|  | 0.3 | 0.8 | 0.6 | 0.6 |
|  | 0.5 | 0.3 | 0.3 | 0.3 |
|  | 0.7 | 0.2 | 0.2 | 0.2 |
|  | 0.9 | 0.2 | 0.2 | 0.2 |
| 3 | 0.1 | 1.4 | 1.3 | 1.3 |
|  | 0.3 | 0.4 | 0.3 | 0.3 |
|  | 0.5 | 0.2 | 0.1 | 0.2 |
|  | 0.7 | 0.1 | 0.1 | 0.1 |
|  | 0.9 | 0.1 | 0.1 | 0.1 |
| 4 | 0.1 | 1.0 | 0.9 | 1.2 |
|  | 0.3 | 0.4 | 0.2 | 0.2 |
|  | 0.5 | 0.2 | 0.1 | 0.1 |
|  | 0.7 | 0.1 | 0.1 | 0.1 |
|  | 0.9 | 0.1 | 0.1 | 0.1 |

to mobile phase kind and composition, there is a good agreement between theoretical and experimental k' values for all studied substances.

The present paper shows the new possibilities for the prediction of chromatographic separation results on the base of retention parameters obtained in thin-layer measurements. The article shows simultanously a way for the optimization of chromatographic process conditions. It should be taken into consideration the comparison of chromatographic process in column and sandwich chambers.

It can be statement for certain that both the techniques, i.e. liquid column and thin-layer chromatography performed in sandwich chambers describe the adsorption in studied systems in the same way. Sandwich chambers imitate chromatographic conditions present in the column and it is the base for using thin-layer chromatography as a pilot technique for column chromatography and for the optimization of chromatographic separation conditions.

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