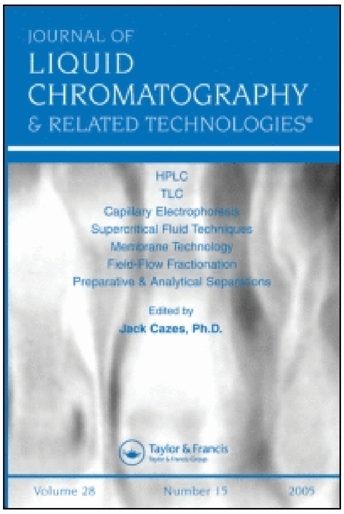

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Retention Process in Normal-Phase TLC Systems

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Retention Process in Normal-Phase TLC Systems

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ABSTRACT

The influence of mobile phase composition on the retention of selected test analytes in different normal-phase TLC systems has been studied. A novel adsorption model for an accurate prediction of the analyte retention in the thin-layer chromatography with binary mobile phase has been proposed. The performance of the model was compared with the retention models reported in the literature. All the models were verified for different TLC systems by three criteria: the sum of squared differences between the experimental and theoretical data, the approximation of the standard deviation, and the Fisher test.

Key Words: Mobile phase composition; Polar bonded stationary phases; Retardation factor; Retention models; TLC.

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INTRODUCTION

Different methods of optimization of chromatographic separations usually require the use of equations relating retention parameters to mobile phase composition (e.g., modifier concentration are pH). The existing retention vs. mobile phase composition equations were derived from some simplified models of interactions within surface active sites of a stationary phase, solute molecules being chromatographed, and mobile phase components. Partition and adsorption mechanisms of solute retention are the two most universal mechanisms of chromatographic separation, both operating on a physical principle. In fact, practically all solutes can adsorb on a microporous solid surface or be partitioned between two immiscible liquids.

The basic principle of solute retention in normal-phase (adsorption) chromatography is its distribution between the sorbent and the mobile phase. To characterize such chromatographic systems, the following models can be taken into consideration.[1,2]

The retention model derived from Snyder–Soczewiński theory assumes monolayer adsorption of a polar component of the eluent on the adsorbent surface and their displacement by molecules of the chromatographed compounds.[3–6]

The second model proposed by Scott and Kucera assumes bilayer adsorption of solvent, sorption of solute molecules without displacement, as well as dispersive interactions between eluent components and solute molecules.[7–9]

The model of Jaroniec and co-workers, which deals with self-association of more polar component of binary mobile phase and association of solute molecules with this component of the eluent.[10,11]

The relationship between retardation factor and the mobile phase composition for the normal-phase chromatographic modes proposed by Kowalska.[12–14]

The application of the most important retention models for different TLC systems has been thoroughly analyzed in the previous papers.[1,2,15] The earliest models were mainly the straight-line relationships. However, with the progress of modern computational techniques there is no need to adhere to such simplistic approaches, since a good number of curvilinear and non-linear retention models have already been devised. Such retention models dedicated to the analysis of the retention process in normal-phase chromatographic systems have been recently proposed by Kaczmarski and co-workers:[16,17]

$$k = \frac{1}{p_1\varphi + p_2(1-\varphi)} \tag{1}$$

Nikitas and Pappa-Louisi:[18,19]

$$k = \exp\left[p_1 - \ln(1 + p_2\varphi) - \frac{p_3\varphi}{1 + p_2\varphi}\right] \tag{2}$$

Zapala and co-workers:[1]

$$\ln k = p_1 - p_2\varphi^{p_3} \tag{3}$$

where φ is the mole or volume fraction of the modifier contained in the binary eluent and p_1, p_2, and p_3 are the equation constants.

Equations 1–3 were successfully tested for a set of the different test solutes, and a large variety of the TLC and HPLC systems.[1,20]

In this paper, we present a new adsorption model of solute retention, valid basically for normal-phase liquid chromatography systems with chemically bonded stationary phases. To verify experimentally the correctness of the proposed model, we applied the results from TLC measurements obtained by use of various model compounds in systems: polar bonded stationary phases (CN–, NH_2–, and Diol–silica) – nonaqueous eluent (*n*-heptane with polar modifier in different concentrations).[2] Despite that there are many models available in almost all areas of science, there are still being performed investigations to find more universal, useful, and precise models, which has also been the aim of this work.

THEORY

In the previous work,[20] a new adsorption model was proposed for description of the retention coefficient, *k*, of a given solute, as a function of the mixed mobile phase composition. The model proposed[20] was formulated on the basis of the following assumptions:

For chemically bonded stationary phases, the isotherm equation $\Gamma_1(c)$, describing adsorption of the constituents of the liquid phase can be written as follows:

$$\Gamma_1 = \Gamma_1' + \Gamma_1'' \tag{4}$$

where Γ_1' describes a linear interaction between the components and chemically bonded organic ligands:

$$\Gamma_1' = Kc_1 \tag{5}$$

The equation constant, K, depends on the mole or volume fraction, φ, of the mobile phase modifier, according to the Langmuir-type model proposed by Row and co-workers:[15,21]

$$K = p_1'' + \frac{p_2''}{\varphi} \tag{6}$$

where p_1'' and p_2'' are the experimental coefficients.

Γ_1'' is the sorption of the same components on the free actives sites of the silica matrix.

Function Γ_1'' describes the adsorption on the free active sites of the silica matrix. The relationship between the amount of the substance adsorbed on the free active sites of the sorbent and its concentration in the bulk solution can be given by the competitive Langmuir isotherm:

$$\Gamma_1'' = \frac{K_1 \Gamma^{\infty} c_1}{1 + K_1 c_1 + K_2 c_2 + K_3 c_3} \tag{7}$$

The parameters c_1, c_2, c_3 are the concentrations of the solute and the components of the mixed mobile phase, respectively, Γ^{∞} is the saturation capacity of solid phase, and K_1, K_2, K_3 are the equilibrium constants. For low numerical values of c_1, Eq. (7) can be given as follows:

$$\Gamma_1'' = \frac{K_1 \Gamma^{\infty} c_1}{1 + K_2 c_2 + K_3 c_3} \tag{8}$$

On the basis of the ideal chromatographic column model,[22] the retention coefficient, k, equals the ratio of the derivative of the solute concentration in the bulk mobile phase and the derivative of the solute concentration in the surface mobile phase:

$$k = \frac{1 - \varepsilon_t}{\varepsilon_t} \frac{\partial \Gamma_1}{\partial c_1} \tag{9}$$

where ε_t, total bed porosity:

Where, from Eqs. (4)–(6) and (8):

$$\frac{\partial \Gamma_1}{\partial c_1} = K + \frac{K_1 \Gamma^{\infty}}{1 + K_2 c_2 + K_3 c_3} = p_1'' + \frac{p_2''}{\varphi} + \frac{K_1 \Gamma^{\infty}}{1 + K_2 c_2 + K_3 c_3} \tag{10}$$

Combining Eqs. (9) and (10), we can obtain:

$$k = \frac{1-\varepsilon_t}{\varepsilon_t}\left(p_1'' + \frac{p_2''}{\varphi} + \frac{K_1\Gamma^\infty}{1+K_2c_2+K_3c_3}\right) \tag{11}$$

The mixed mobile phase can be considered as the ideal mixture. Equation (11) can be given in the following form:

$$k = p_1' + \frac{p_2'}{\varphi} + \frac{1}{p_3' + p_4'\varphi + p_5'(1-\varphi)} \tag{12}$$

After simple mathematical transformations, the final relationship between the retention coefficient k and modifier concentration in the binary mobile phase φ takes the following form:

$$k = \frac{p_1(1+p_2\varphi+(p_3/\varphi))}{1+p_4\varphi} \tag{13}$$

where p_1, p_2, p_3, p_4, model parameters.

Model (13) was thoroughly tested in the HPLC experiments with the use of many different analytes, columns, and sorbents with chemically bonded ligands.[20] All the computation results obtained confirmed very good performance of the proposed model (13). This model gives good fitting results, accuracy, and great applicability.

The aim of this work was to analyze the applicability of the proposed adsorption model (13) for the description of retention processes in different normal-phase TLC systems. Since the relationship between the retention coefficient, k, and the retardation parameter, R_f, is given by the equation:

$$R_f = \frac{1}{1+k} \tag{14}$$

the proposed relationship for R_f finally takes the form:

$$R_f = \frac{1+P_1\varphi}{P_2(1+P_3\varphi+(P_4/\varphi))} \tag{15}$$

Model parameters, P_i, were estimated by minimization of a sum of the squared differences between the experimental and theoretical data, using the Marquardt method, which was later modified by Fletcher.[23] The accuracy of determination of the model's parameters was assessed using the formulas given in the monograph[24] for the 95% confidence interval of Student's test.

The following statistical criteria for the assessment of the proposed model accuracy in different TLC systems were used:

- the sum of squared differences between the experimental and the theoretical retention data:

$$\mathrm{SUM} = \sum_i (R_{\mathrm{f\,exp}}(i) - R_{\mathrm{f\,theor}}(i))^2 \tag{16}$$

- approximation of standard deviation:

$$\mathrm{SD} = \sqrt{\frac{\mathrm{SUM}}{\mathrm{LD} - L}} \tag{17}$$

- Fisher test:

$$F = \frac{\sum_i (R_{\mathrm{f\,exp}}(i) - (\sum_i (R_{\mathrm{f\,exp}}(i)/\mathrm{LD})^2/(\mathrm{LD}-1))}{\sum_i \left(R_{\mathrm{f\,exp}}(i) - R_{\mathrm{f\,theor}}(i)\right)^2/(\mathrm{LD}-L)} \tag{18}$$

where $i = 1 \cdots \mathrm{LD}$, LD, number of experimental points, L, number of estimated parameters.

EXPERIMENTAL

To verify the correctness of the proposed model (15) experimentally, we have applied the results from TLC measurements obtained using a variety of different NP-TLC systems. Thin-layer chromatography was performed on 10 × 10 cm glass Diol F_{254}, CN F_{254}, and NH_2 F_{254} HPTLC precoated plates (E. Merck, Darmstadt, Germany), in horizontal Teflon chambers with an eluent distributor (DS, Chromdes, Lublin, Poland).[25,26] Samples (2 μL) of 2.5% m/v solutions of the solutes in methanol were spotted to the adsorbents layer. Plates were conditioned for 15 min in eluent vapors to eliminate the demixing effect, and developed face-down to a distance of 8 cm from the origin at 20 ± 1°C. Binary mixtures of polar modifiers: 2-propanol, ethyl acetate, ethyl methyl ketone, dioxane, or tetrahydrofuran with *n*-heptane were used as eluents. Solvents were analytical grade from Polish Reagents (POCh, Gliwice, Poland). The location of the spots was determined under UV light ($\lambda = 254$ nm). In all cases, the spots were symmetric and did not exhibit tailing. We used 16 different compounds as test analytes. The chromatographed compounds are listed in Table 1.

Table 1. Example test analytes, mobile phases, ranges of the modifier mole fractions, and the TLC plates used.

Data set	Test analyte	Mobile phase	Range of modifier mole fraction	Chemically bonded stationary phase
1	Phenol	2-Propanol–*n*-heptane	0.05–0.6	–CN
2	2-Nitroaniline	2-Propanol–*n*-heptane	0.05–0.6	–CN
3	4-Nitrophenol	Ethyl acetate–*n*-heptane	0.15–0.6	–CN
4	Quinoline	Ethyl acetate–*n*-heptane	0.15–0.6	–CN
5	4-Aminophenol	Ethyl methyl ketone–*n*-heptane	0.05–0.7	–CN
6	Quinoline	Ethyl methyl ketone–*n*-heptane	0.05–0.7	–CN
7	Hydroquinone	THF–*n*-heptane	0.1–0.7	–CN
8	1,2-Phenylenediamine	THF–*n*-heptane	0.2–0.8	–CN
9	2-Hydroxyquinoline	Ethyl acetate–*n*-heptane	0.1–0.7	–DIOL
10	4-Nitroaniline	Ethyl acetate–*n*-heptane	0.1–0.7	–DIOL
11	Quinoline	Ethyl methyl ketone–*n*-heptane	0.1–0.7	–DIOL
12	1,2-Phenylenediamine	Ethyl methyl ketone–*n*-heptane	0.1–0.7	–DIOL
13	6-Nitroquinoline	THF–*n*-heptane	0.1–0.7	–DIOL
14	2-Iodoaniline	THF–*n*-heptane	0.1–0.7	–DIOL
15	8-Methylquinoline	Dioxane–*n*-heptane	0.1–0.7	–DIOL
16	4-Nitrophenol	Dioxane–*n*-heptane	0.1–0.7	–DIOL
17	4-Nitroaniline	2-Propanol–*n*-heptane	0.1–0.7	$–NH_2$
18	Aniline	2-Propanol–*n*-heptane	0.1–0.7	$–NH_2$
19	8-Methylquinoline	Ethyl acetate–*n*-heptane	0.1–0.7	$–NH_2$
20	1-Aminonaphthalene	Ethyl acetate–*n*-heptane	0.1–0.8	$–NH_2$
21	2-Nitroaniline	Ethyl methyl ketone–*n*-heptane	0.1–0.7	$–NH_2$
22	4-Iodoaniline	Ethyl methyl ketone–*n*-heptane	0.1–0.7	$–NH_2$
23	1,5-Diaminonaphthalene	THF–*n*-heptane	0.1–0.7	$–NH_2$
24	4-Nitroaniline	THF–*n*-heptane	0.1–0.7	$–NH_2$

RESULTS AND DISCUSSION

The results of investigations in different TLC systems are presented in example Figs. 1–3 and in Table 2. Table 2 specifies the values of estimated model parameters, P_i, and related sums of the squared differences between experimental and theoretical data, SDs, and the Fisher test values obtained as results of the comparison between the newly proposed model [Eq. (15)] and the experimental data. The presented results of investigations prove the four-parameter model proposed in this study [Eq. (15)] to represent an excellent agreement between the experimental and theoretical data for most NP-TLC systems studied.

To verify the correctness of the proposed model theoretically, the comparison of Eq. (15) with literature-known adsorption models developed by Kaczmarski and co-workers [Eq. (1)][16,17] and Nikitas and Pappa-Louisi[18,19] [Eq. (2)] has been conducted. All models were compared in different TLC systems, which are presented in Table 1. Table 2 specifies the values of the sums of the squared differences between experimental and theoretical data, SDs, and the Fisher test values obtained as a result of the comparison between Eqs. (15), (1), and (2) and the experimental data.

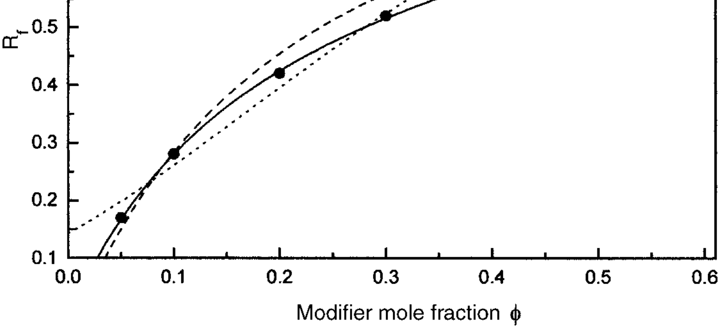

Figure 1. Comparison of retention values (R_f) of solutes of data set 1 with theoretical data. Solid curve has been calculated from proposed model, Eq. (15), dashed curve has been calculated from Eq. (1) and dotted curve has been calculated from Eq. (2).

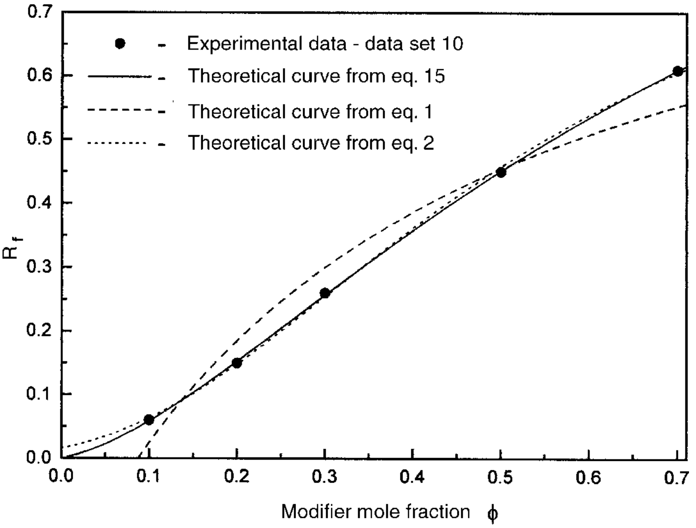

Figure 2. Comparison of retention values (R_f) of solutes of data set 10 with theoretical data. Solid curve has been calculated from proposed model, Eq. (15), dashed curve has been calculated from Eq. (1), and dotted curve has been calculated from Eq. (2).

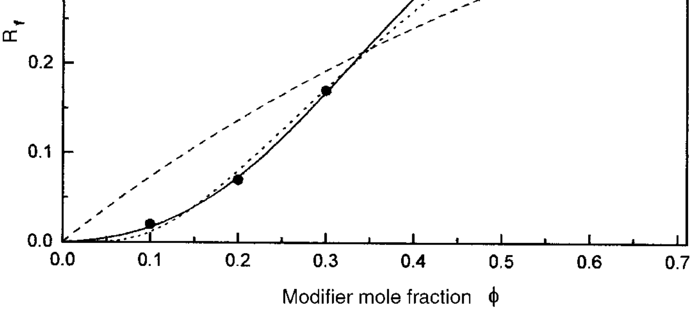

Figure 3. Comparison of retention values (R_f) of solutes of data set 23 with theoretical data. Solid curve has been calculated from proposed model, Eq. (15), dashed curve has been calculated from Eq. (1), and dotted curve has been calculated from Eq. (2).

Table 2. Estimated numerical values of Eq. (15) parameters and values of statistical criteria with the aid of Eqs. (1) and (2).

Data	Model Eq. (15)						
set	P_1	P_2	P_3	P_4	SUM	SD	F
1	-1.54 ± 0.6	0.79 ± 0.01	-2.32 ± 0.2	0.31 ± 0.01	4.9×10^{-5}	0.005	2,460
2	-0.86 ± 0.1	1.30 ± 0.4	-1.71 ± 0.4	0.35 ± 0.05	0.0001	0.0072	933.6
3	-19.0 ± 0.1	0.63 ± 0.05	-44.3 ± 1.1	-2.04 ± 0.8	0.0001	0.0076	564
4	19.7 ± 1.2	20.2 ± 1.8	1.3 ± 0.9	-0.01 ± 0.01	1.1×10^{-6}	0.001	6,089
5	-1.8 ± 0.6	8.1 ± 0.9	-3.8 ± 0.54	0.47 ± 0.1	2.2×10^{-6}	0.0015	6,881
6	-22.45 ± 2	-13.7 ± 4	2.16 ± 0.1	-0.05 ± 0.4	2.8×10^{-5}	0.0037	1,185
7	0 ± 0	-5.5 ± 0.73	-0.86 ± 0.4	-0.47 ± 0.1	0.0006	0.018	223.5
8	3.78 ± 0.85	0.55 ± 0.12	-74.3 ± 6	57.54 ± 5	2.6×10^{-5}	0.0051	1,907
9	5.99 ± 1.1	0.14 ± 0.01	108.7 ± 11	57.71 ± 2.1	0.00019	0.0099	88
10	16.93 ± 4.6	8.17 ± 1.5	1.34 ± 0.23	0.45 ± 0.2	2.210^{-5}	0.005	2,290
11	-10.7 ± 2.3	-7.8 ± 1.1	1.3 ± 0.86	-0.11 ± 0.5	0.00071	0.019	47.55
12	1 ± 0.0	9.17 ± 1.45	-1.18 ± 0.6	0.17 ± 0.1	6.52×10^{-5}	0.006	774.6
13	-0.76 ± 0.1	0.09 ± 0.00	-8.2 ± 1.1	9.12 ± 1.3	7.2×10^{-5}	0.0085	619.4
14	3.1 ± 0.8	3.2 ± 0.2	0.35 ± 0.2	0.02 ± 0.001	4.9×10^{-7}	0.0007	6.2×10^{4}
15	-0.8 ± 0.7	-1.1 ± 0.8	-1.0 ± 0.5	-0.62 ± 0.3	0.04	0.142	3.94
16	4.04 ± 0.5	-3.8 ± 1.2	-2.27 ± 1.8	-0.73 ± 0.5	3.7×10^{-5}	0.0061	1,491
17	-0.49 ± 0.1	-2.34 ± 0.8	-0.9 ± 0.5	-0.62 ± 0.4	6.1×10^{-5}	0.008	620.8
18	$7.1 \times 10^{6} \pm 9$	$2 \times 10^{6} \pm 99$	2.9 ± 1.5	-0.05 ± 0.01	0.0002	0.01	143.6
19	2.4 ± 1.1	2.45 ± 0.5	1.09 ± 0.8	0.03 ± 0.01	9.4×10^{-5}	0.0097	103.4
20	-0.95 ± 0.1	0.003 ± 0.0	-361.4 ± 9	359.4 ± 26	0.0011	0.024	65.26
21	16.5 ± 4	-20.5 ± 2	-1.65 ± 0.9	-0.73 ± 0.3	2.4×10^{-8}	0.0002	1.7×10^{6}
22	16.21 ± 5	-38.8 ± 2	-1.6 ± 0.6	-0.43 ± 0.2	5.2×10^{-5}	0.007	630.2
23	52.25 ± 8	-104 ± 15	-1.72 ± 0.8	-0.43 ± 0.05	2.3×10^{-5}	0.005	1,420
24	16.54 ± 4	-20.53 ± 8	-1.65 ± 0.9	-0.73 ± 0.1	2.4×10^{-8}	0.00015	1.72×10^{6}

Data set	Model Eq. (1)			Model Eq. (2)		
	SUM	SD	*F*	SUM	SD	*F*
1	0.02	0.07	13.06	0.0098	0.057	18.35
2	0.013	0.057	14.7	0.0033	0.033	43.67
3	0.0008	0.016	130.6	0.0004	0.023	62.15
4	2.4×10^{-5}	0.003	837.5	2.4×10^{-5}	0.003	836.4
5	0.0171	0.076	2.7	6.3×10^{-5}	0.006	486.1
6	0.0008	0.015	77.6	0.0008	0.016	63.1
7	0.0633	0.145	3.3	0.0011	0.024	121.6
8	0.105	0.187	1.4	0.0004	0.0139	252.8
9	0.018	0.0245	14.3	0.00022	0.0104	79.5
10	0.028	0.096	5.411	0.000125	0.008	802.5
11	0.002	0.026	25.8	0.0011	0.0233	31.15
12	0.0211	0.084	3.6	0.02	0.082	4.0
13	0.0172	0.076	7.8	0.0006	0.017	153.8
14	0.004	0.035	24.32	0.00015	0.0086	417.1
15	0.83	0.167	2.85	0.045	0.15	3.54
16	0.033	0.105	5.024	0.00023	0.011	484.9
17	0.013	0.065	9.0	0.0008	0.02	93.44
18	0.0004	0.012	105.2	0.0003	0.012	102
19	0.0006	0.014	48.1	0.0006	0.017	32.6
20	0.011	0.052	13.81	0.0022	0.027	50.6
21	0.033	0.105	3.81	1.2×10^{-5}	0.0025	6,945
22	0.02	0.081	5.0	0.001	0.0023	61.62
23	0.02	0.082	4.9	0.00098	0.022	67.6
24	0.03	0.105	3.81	1.2×10^{-5}	0.0025	6,945

In Figs. 1–3, dashed lines show the theoretical curves obtained from Eq. (1) and dotted lines show the theoretical curves obtained from Eq. (2), whereas the solid line depicts the theoretical curves obtained from Eq. (15). In Figs. 4–6, the graphical comparisons of the statistical criteria for analyzed retention models and data sets have been presented. It can be observed, that for most of the analyzed chromatographic systems, the newly proposed model [Eq. (15)] gives better fitting results and accuracy than remaining Eqs. (1) and (2).

It should also be noticed that the proposed model fits much better to experimental results than linear equations derived from the theories of Snyder–Soczewiński and Scott–Kucera. The above equations were fitted to experimental results and the accuracy of the fit was analyzed.[2] It was found that the linear logarithmic equation fits well to the experimental results. However, from the analysis of statistical coefficients *F* and SD, much better accuracy of fit of the proposed Eq. (15) can be observed. SD values were significantly lower in all cases when model (15) was fitted to the experimental results. Simultaneously, *F* values were higher in most cases (in 16 of 24 cases) than the same coefficients for linear logarithmic equations. Similar observations may be made when *F* and SD coefficients for four parameter Eq. (15) and Scott-Kucera linear equations are compared. The higher *F* statistic values for Eq. (15) were obtained in 20 out of 24 cases. It seems that four-parameter Eq. (15) proposed in this paper thoroughly describes the

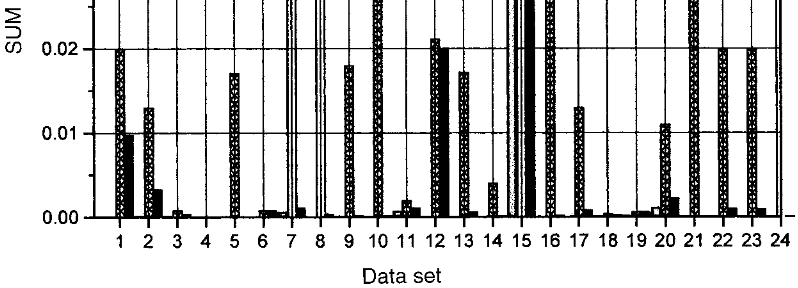

Figure 4. Graphical comparison of the sums of the squared differences between experimental and theoretical retention data.

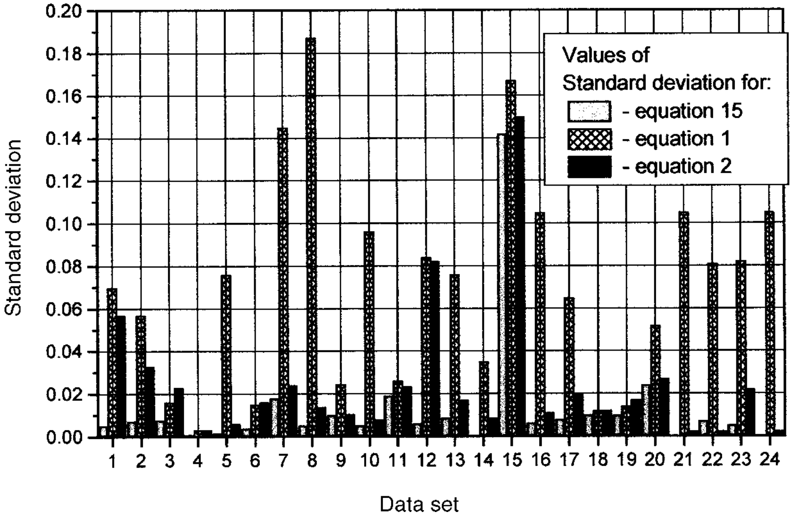

Figure 5. Graphical comparison of the numerical values of the standard deviation for analyzed retention models and data sets presented in Table 1.

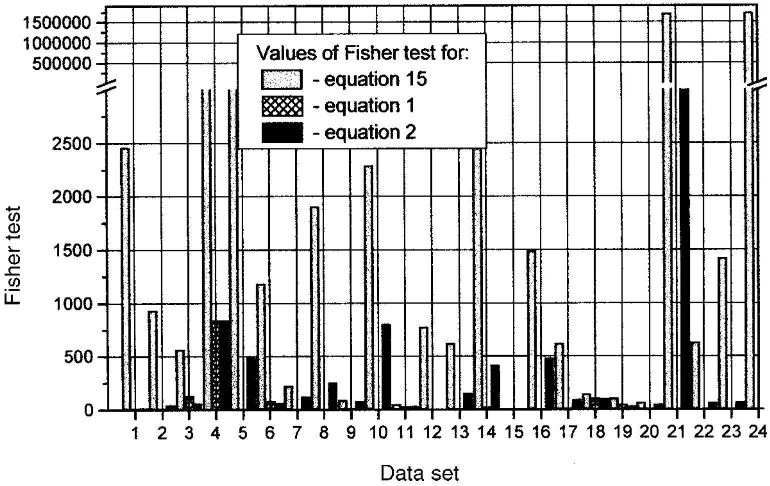

Figure 6. Graphical comparison of the numerical values of the Fisher test for analyzed retention models and data sets presented in Table 1.

retention—eluent composition relationships for chromatographed compounds on polar bonded stationary phases in normal-phase systems.

CONCLUSION

From the study reported here, the following conclusions can be drawn:

- A new adsorption model was proposed for description of the retardation factor, R_f, of a given solute as a function of the mixed mobile phase composition. This model was thoroughly tested in the experiments with the use of many different analytes and sorbents with chemically bonded ligands (only selected results are presented in this study).
- All the computation results obtained confirm excellent performance of the proposed model (15). This model gives good fitting results, accuracy, and great applicability.
- The model (15) was compared with literature-known adsorption models (1), (2) and linear equations of Snyder–Soczewiński and Scott–Kucera. The results of this comparisons show, that especially in the strong nonlinear $R_f = f(\varphi)$ dependence the newly proposed adsorption model (15) gives the most accurate results of computation.
- In comparison with literature-known adsorption models presented in this paper, adsorption models (Eqs. 13 and 15) describe much better HPLC[20] and TLC retention data.

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