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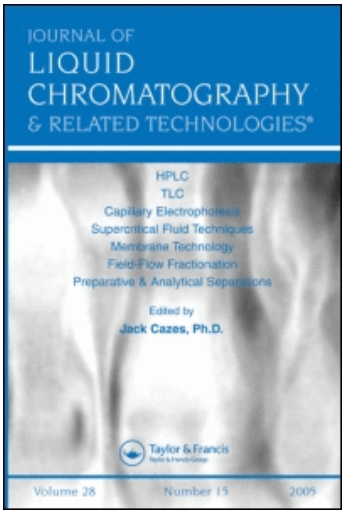

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THE ROLE OF THE LATERAL ANALYTE-ANALYTE INTERACTIONS IN THE PROCESS OF TLC BAND FORMATION

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ABSTRACT

An attempt has been made to investigate intermolecular hydrogen-bonding interactions among adsorbed analyte molecules (i.e. the so-called lateral interactions) and their real impact on the retention process. To this effect, two different models (Models 1 and 2) were elaborated, taking into the account the aforementioned interactions. Model 1 is based on the Langmuir adsorption isotherm, implemented with a very simple assumption about the tendency of an analyte to form linear associative *n*-mers. This kind of intermolecular interaction is most characteristic of aliphatic alcohols, although it can also be observed for a wide

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variety of the other classes of chemical compound. Model 2 is considerably more sophisticated and makes a clear distinction between the formation of a monolayer of adsorbed analyte and the accumulation of further layers of adsorbed analyte on the original monolayer. Model 2 makes use of the Langmuir and Langmuir–Freundlich isotherms and is well suited to the description of fairly subtle molecular-level effects accompanying the adsorption of carboxylic acids.

The validity of Models 1 and 2 was checked experimentally with three higher fatty acids (dodecanoic, tetradecanoic, and hexadecanoic) as test solutes. TLC was performed with cellulose powder and decalin, respectively, as stationary and mobile phases. The results obtained fully confirmed the practical usefulness of the two approaches.

The traditional definition of the R_F coefficient was also re-examined and its irrelevance for analytes participating in lateral interactions was demonstrated, as was the use of densitograms (rather than flat overall pictures of TLC chromatograms). We have proposed two novel (and optional) definitions of the R_F coefficient, which make use of the concentration profiles of analytes and have compared the practical performance of each approach.

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INTRODUCTION

The aim of this study was:

to provide reliable experimental proof from TLC that lateral analyte–analyte interactions have a measurable impact on chromatographic band shape and, thus, considerably affect the entire chromatographic process;

to develop a physicochemical model able to furnish theoretical foundations of the aforementioned and experimentally proven phenomenon of lateral analyte–analyte interactions; and

to re-examine the traditional definition of analyte R_F coefficient, and the technique used to measure it, when the concentration profile of the chromatographic band is taken into consideration (instead of measuring the respective distances on the freshly visualized chromatogram).

THEORY

We propose two models for describing analyte behavior on the stationary phase surface; both take into account the lateral interactions among adsorbed

analyte molecules. The approach introduced in Model 1 is more general (and also more superficial) and, therefore, seems roughly suitable for all solute classes which readily form linear associative *n*-mers. Model 2 proposes a more sophisticated approach to the phenomenon of intermolecular interactions by hydrogen bonding, and makes a clear distinction between the formation of the adsorbed analyte monolayer and the accumulation on this monolayer of further adsorbed layers. This model seems particularly suited to carboxylic acids, with their tendency to form both cyclic associative dimers and linear associative *n*-mers.

Model 1

Let us assume, that:

Analyte molecules can form a polylayer on the adsorbent surface, or,to put it differently, further molecules of the same type can be added to the adsorbed analyte molecules (i.e., one molecule of a given analyte can adsorb another), and

Adsorption of the $(n + 1)$th layer on the n-th layer can be described by the Langmuir isotherm.

The amount of the analyte adsorbed in layer 1 can be calculated from the equation:

$$q_1 = \frac{q_s K_1 C}{1 + K_1 C} \tag{1}$$

where q_1 denotes the quantity of the analyte adsorbed in layer 1, q_s denotes the total coverage, K_1 is the analyte–adsorbent equilibrium constant, and C is concentration of the analyte in the mobile phase.

The amount of the analyte adsorbed in layer 2 can be described by the relationship:

$$q_2 = \frac{q_1 K_2 C}{1 + K_2 C} \tag{2}$$

where K_2 is the equilibrium constant between the analyte in layers 1 and 2. Similarly, the amount of the analyte can be calculated for the consecutive layers.

The total amount (q) of substance adsorbed can thus be given by the equation:

$$q = \sum_{i=1}^{n} q_i = \frac{q_s K_1 C}{1 + K_1 C}\left(1 + \frac{K_2 C}{1 + K_2 C} + \frac{K_3 C}{1 + K_3 C} \cdot \frac{K_2 C}{1 + K_2 C} + \ldots\right) \tag{3}$$

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The magnitudes K_2, K_3, etc., can be treated as the dynamic equilibrium constants for intermolecular associates (i.e., for the associative dimers, trimers, and higher *n*-mers) of a given analyte. If persistent bi-molecular aggregates or dimers are formed (possible only if K_2 tends to infinity), eq. (3) would take the simpler form:

$$q = \frac{2 \cdot q_s K_1 C}{1 + K_1 C} \tag{4}$$

For associates composed of *n* molecules (i.e., associative *n*-mers), eq. (3) becomes:

$$q = \frac{n \cdot q_s K_1 C}{1 + K_1 C} \tag{5}$$

For very low concentrations of analyte, the following relationship is fulfilled:

$$q = n \cdot q_s K_1 C \tag{6}$$

The retention coefficient *k* is then given by:

$$k = \frac{1 - \varepsilon_t}{\varepsilon_t} n \cdot q_s K_1 \tag{7}$$

where ε_t denotes the total porosity of the investigated solid bed, and the R_F coefficient is given by the relationship:

$$R_F = \frac{1}{1 + \frac{1 - \varepsilon_t}{\varepsilon_t} n \cdot q_s K_1} = \frac{1}{1 + n \cdot A}, \text{ where } A = \frac{1 - \varepsilon_t}{\varepsilon_t} \cdot q_s K_1 \tag{8}$$

From the physicochemical relationship given by eq. (8), it is easily deduced that the numerical value of the R_F coefficient ought to decrease substantially as the number (*n*) of analyte molecules in a given *n*-mer increases.

If we assume $K_2 = K_3 = \ldots = K_n = K$, eq. (3) will be reduced to:

$$q = \sum_{i=1}^{n} q_i = \frac{q_s K_1 C}{1 + K_1 C}\left(1 + \frac{KC}{1 + KC} + \left(\frac{KC}{1 + KC}\right)^2 + \ldots\right) = \frac{q_s K_1 C}{1 + K_1 C}\left(1 + \sum_{i=1}^{n-1}\left(\frac{KC}{1 + KC}\right)^i\right) \tag{9}$$

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or

$$q = \frac{q_s K_1 C}{1 + K_1 C}\left(\sum_{i=0}^{n-1}\left(\frac{KC}{1+KC}\right)^i\right) = \frac{q_s K_1 C}{1 + K_1 C}\left(\frac{1-\left(\frac{KC}{1+KC}\right)^n}{1-\left(\frac{KC}{1+KC}\right)}\right) \tag{10}$$

If K tends to infinity, a simplified relationship can be obtained:

$$q = \frac{q_s K_1 C}{1 + K_1 C}\left(\sum_{i=0}^{n-1}\left(\frac{KC}{1+KC}\right)^i\right) = \frac{q_s K_1 C}{1 + K_1 C} \cdot n \tag{11}$$

where n denotes the number of the adsorbed analyte layers (which is equivalent within the framework of our model to the number of the associated molecules in a given associative n-mer).

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Model 2

Let us introduce the following assumptions:

In the solution applied to stationary phase, the analyte occurs as an associative dimer;

On the stationary phase surface, the dimers dissociate to form monomers and the monomers are adsorbed by the surface;

Cyclic analyte dimers will then be adsorbed by the first layer of adsorbed analyte monomers; they change their initial configuration, and linear associative multimers are formed;

Adsorption of layer 1 is described by the Langmuir isotherm [see eq. (1)];

Adsorption of cyclic dimers as successive layers fulfils the Langmuir–Freundlich equation with a power exponent of 2. The equilibrium constant, K, assumes the same numerical values for successive adsorbed layers.

Thus the adsorption isotherm for dimers on layer 1 can be described by the relationship:

$$q_2 = \frac{q_1 KC^2}{1 + KC^2} \tag{12}$$

Eq. (12) results from assuming the adsorption kinetics:

$$k_{adsorption} \cdot C \cdot C \cdot (q_1 - q_2) - k_{desorption} \cdot q_2 = \frac{\partial q_2}{\partial t} \tag{13}$$

If the adsorption–desorption process is assumed to be infinitely rapid, the following relationship is obtained:

$$\frac{k_{adsorption}}{k_{desorption}} \cdot C \cdot C \cdot (q_1 - q_2) - q_2 = 0 \tag{14}$$

and, hence, eq. (12) results.

In agreement with assumption 3, dimers form, with the analyte from layer 1, a linear multimer comprising three molecules.

The total amount of the adsorbed analyte (q) is thus given by:

$$q = \sum_{i=1}^{n} q_i = \frac{q_s K_1 C}{1 + K_1 C}\left(1 + \frac{KC^2}{1 + KC^2} + \left(\frac{KC^2}{1 + KC^2}\right)^2 + \ldots\right) \tag{15}$$

In this particular instance the total number of adsorbed analyte layers can be regarded as equal to $1 + 2\,(n - 1) = 2n - 1$. The numerical value of the R_F coefficient can be calculated by use of a relationship analogous with eq. (8).

Eq. (15) can finally be transformed to a form analogous with that of eq. (10):

$$q = \frac{q_s K_1 C}{1 + K_1 C}\left(\frac{1 - \left(\frac{KC^2}{1 + KC^2}\right)^n}{1 - \left(\frac{KC^2}{1 + KC^2}\right)}\right) \tag{16}$$

EXPERIMENTAL

Working Conditions

Stationary phase: cellulose (cellulose-coated TLC plates manufactured by E. Merck, Darmstadt, Germany, Cat. # 1.05730). Mobile phase: decalin.

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Visualization of the chromatograms was achieved by spraying with a solution of bromocresol green in alcohol, prepared in accordance with a procedure described elsewhere.[1]

Densitograms were obtained by use of the Shimadzu (Columbia, MD USA) CS9301 PC model scanning densitometer, by using a rectangular-cross-section light beam (wavelength λ = 625 nm, rectangle dimensions 0.05 mm × 0.5 mm). The detector used in this densitometer can only detect analytes active in the visible or ultraviolet range, i.e. the absorption or fluorescence of the analyte is quantified. In our experiment, the analytes were optically inactive and it was, therefore, necessary to visualize them. The visualizing procedure, however, spoils the quality of the densitogram, basically because of noise originating as a result of uneven distribution of the visualizing agent (in our experiments, bromocresol green dye) on the stationary phase surface. Thus, interpretation of the densitograms obtained was possible only after preliminary de-noising; this was achieved by approximation, by use of a smoothing spline fit.[2]

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The Ability of Test Analytes to Self-Associate by Hydrogen-Bonding

Higher fatty acids can form associative multimers by hydrogen-bonding. This is because of the presence of the negatively polarized oxygen atom from the carbonyl group and the positively polarized hydrogen atom from the carboxyl group.

It seems that direct contact of higher fatty acids with an adsorbent results in opening of most of the rings of the cyclic dimers (e.g., because of the inevitable intermolecular interactions which result from hydrogen-bonding with the hydroxyls of the cellulose), thus considerably shifting the self-association equilibrium towards linear associative multimers. The numerical value of n in our model denotes both the number of the adsorbed carboxylic acid layers and number of the acid molecules in the associative multimer.

Determination of the Numerical Values of Analyte R_F Coefficients from the Densitograms

The traditional (and so far only) method of determination of the numerical values of analyte R_F coefficients quasi-automatically assumes the following preconditions:

a) circular chromatographic band, and

b) Gaussian mass distribution of the analyte in the concentration profile of this band.

On the basis of these assumptions, the position of a band on the chromatogram is defined by measuring the distance between the origin and the geometrical center of the band. Despite the considerable imprecision of this definition for asymmetric (i.e., 'tailing') and non-Gaussian bands, the following features of the definition are very important:

(i) The traditional definition regards the center of a chromatographic band as the point at which the local concentration of the analyte is highest;

(ii) Simultaneously, the traditional definition regards the center of the chromatographic band as the center of gravity of the mass distribution of the analyte in the band.

For ideal, circular bands with a Gaussian analyte concentration profiles, the band centers described by assumptions (i) and (ii) are, in fact, identical.

For densitograms obtained from non-circular (i.e., 'tailing') bands with non-Gaussian concentration profiles, it can be stated that:

The numerical value of the R_F coefficient for a given chromatographic band can be determined for the maximum value of the concentration profile of the band (which is the point at which the local concentration of the analyte is highest). In our study, the R_F coefficient determined according to this definition was denoted $R_{F(max)}$.

Alternatively, the numerical value of the R_F coefficient can be determined from the center of gravity of the distribution of analyte mass in the band; in our particular experiment (i.e., with non-symmetrical chromatographic bands), this value should not be identical with that originating from the maximum of the analyte concentration profile. In our study, the R_F coefficient determined in this manner was denoted as $R_{F(int)}$.

We adopted the following procedure to determine the center of gravity of analyte mass distribution in the chromatographic band. After having established the baseline, de-noised the densitogram, and subtracted the baseline signal, the beginning ($i = 0$) and end ($i = k$) of the chromatographic band were defined and the position of its center of gravity was determined from the relationship:

$$d_{sr.} = \frac{1}{S} \cdot \sum_{i=1}^{k} I\left(\frac{d_i + d_{i-1}}{2}\right) \cdot \frac{d_i + d_{i-1}}{2} \cdot \left(d_i - d_{i-1}\right) \qquad (17)$$

where S denotes the chromatographic band surface, and $I(d_i)$ is the detector signal at the distance d_i.

RESULTS AND DISCUSSION

The first part of this section will be devoted to discussion of the results obtained in the context of Model 1. Figs 2a and 2b show the processed densi-

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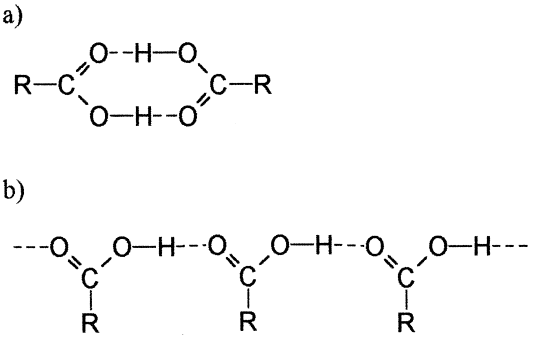

Figure 1. Schematic representation of the self-association of higher fatty acids as a result of intermolecular hydrogen bonding: a) cyclic associative dimer (the predominant structure for pure acids and solutions of these in low-polarity solvents); b) linear associative multimer (complementary structure for pure acids and solutions of these in low-polarity solvents).

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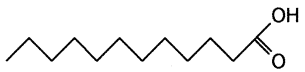
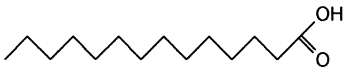
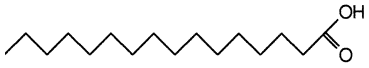
tograms (de-noised, and after subtraction of the baseline) obtained by scanning chromatograms of dodecanoic acid (C_{12}), spotted on to the chromatographic plates as solutions in carbon tetrachloride (10 μL). The initial spot diameter was always constant at 3 mm. The results obtained for tetradecanoic acid and hexadecanoic acid (C_{14} and C_{16}) were fully analogous with those in Fig 2 and, therefore, for conciseness, are not included in this paper.

It is clearly apparent that the densitogram peak areas obtained for different concentrations of the same analyte (Figs 2a and 2b) are not proportional to the respective initial sample concentrations. This phenomenon undoubtedly results from the mode of visualization employed; the scanned signal depends (at least to some extent) on the amount of visualizing agent applied to the chromatographic plate. We can, on the other hand (owing to even application of the visualizing

Table 1. The Applied Test Solutes

Test solute	Schematic structure	Symbol
Dodecanoic (lauric) acid		C_{12}
Tetradecanoic (myristic) acid		C_{14}
Hexadecanoic (palmitic) acid		C_{16}

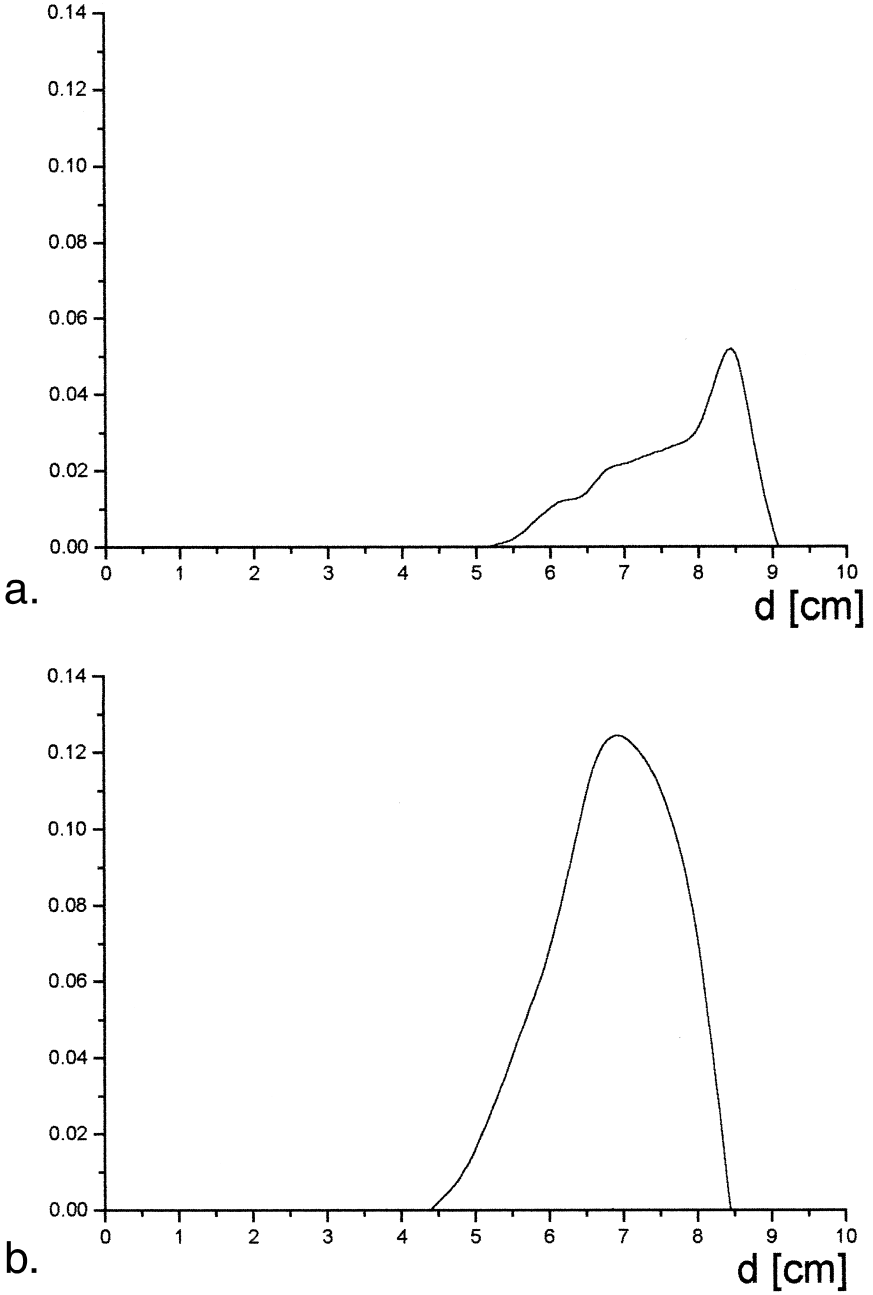


Figure 2. Densitograms obtained for dodecanoic acid (C_{12}). Sample concentrations: a) 0.010 mol L^{-1}, and b) 0.100 mol L^{-1}.

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dye to the entire chromatographic plate surface), expect that the qualitative picture of concentration distribution in the analyte band profiles is correct.

Fig. 3 shows the dependence of R_F on analyte concentration. R_F values determined from the band maxima and from band centers of gravity for different concentrations of the different analytes are compared in Table 2. From these data it is apparent that:

With increasing concentration of solute in the solution applied to the plate, the numerical value of the R_F coefficient decreases; this was confirmed unequivocally by the respective experimental results obtained for the three different higher fatty acids by use of the two independent measuring approaches.

Numerical values of the R_F coefficient, irrespective of the technique used for determination, are similar to each other, although not completely identical. Numerical values of the R_F coefficient obtained by use of the center of gravity are somewhat lower than those obtained from the band maxima. The reason for this difference is the band shape (non-symmetrical distribution of the detector signal). The difference between the R_F values obtained by use of two different approaches evidently depends on the quantity of the test solute applied to the chromatographic plate. As the amount of analyte applied to the stationary phase is increased, the shapes of the resulting chromatographic bands become increasingly non-symmetrical. For very small amounts of analyte, differences between the numerical values of $R_{F(max)}$ and $R_{F(int)}$ should eventually disappear.

The differences, however insignificant, between the numerical values of the R_F coefficients determined in two different ways from the densitometric concentration profiles, indisputably have two causes, which result directly from the technique used for data processing:

(i) For analytes with strongly pronounced lateral interactions, the traditional method of determination of the geometrical center of the chromatographic band as an important reference (without taking the concentration profile into the account) seems an entirely unfounded simplification. Now the real problem emerges, which point ought to be regarded as central for a given chromatographic band. By analogy with column chromatographic techniques (i.e., HPLC and GC), the maximum of the concentration profile of a band can correctly be regarded as its reliable reference point. Alternatively, and in the spirit of the traditional concept of the geometrical center of the chromatographic band, the center of gravity of a band can be assumed to be its central point. It is rather obvious that the two approaches are not equivalent.

(ii) Determination of the maximum of the concentration profile of a band and of its center of gravity are both founded on fairly arbitrary determination of the baseline of the densitogram; the arbitrariness of this determination, however, affects the accuracy of determination of the maximum of the concentration profile of the band or of its center of gravity to somewhat different extents.

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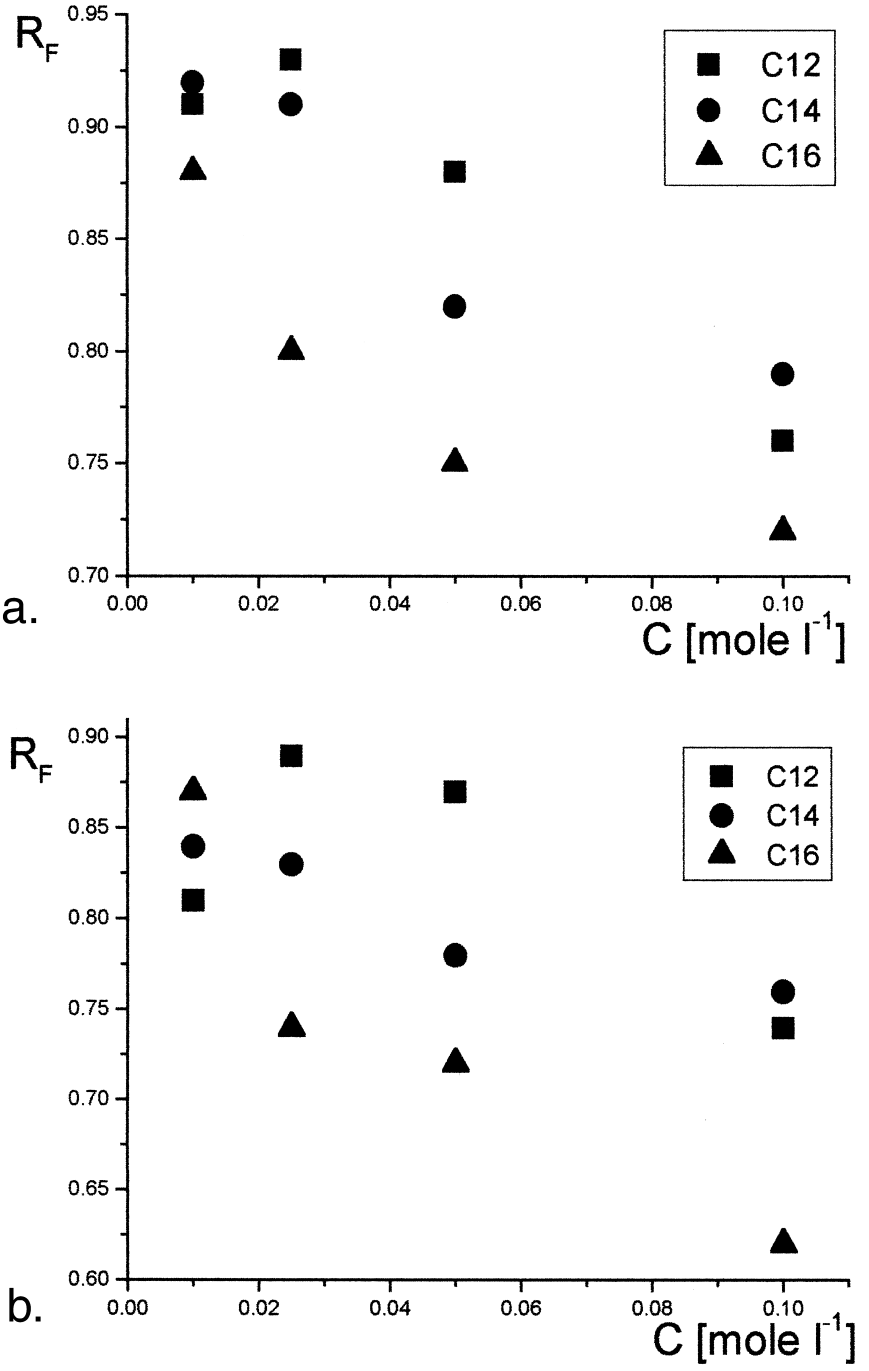

Figure 3. Dependence on the concentration of the test analyte solution of numerical values of R_F calculated from (a) the signal maximum and (b) the center of gravity of the band.

Table 2. Numerical Values of the R_F Coefficient, Determined from the Maximum (max) and from the Center of Gravity (int) of the Chromatographic Bands

Test Solute	C_{12}		C_{14}		C_{16}	
Acid Conc. in a Sample [mol L^{-1}]	$R_{F(max)}$	$R_{F(int)}$	$R_{F(max)}$	$R_{F(int)}$	$R_{F(max)}$	$R_{F(int)}$
0.010	0.91	0.81	0.92	0.84	0.88	0.87
0.025	0.93	0.89	0.91	0.83	0.80	0.74
0.050	0.88	0.87	0.82	0.78	0.75	0.72
0.100	0.76	0.74	0.79	0.76	0.72	0.62

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Qualitative Comparison of the Densitograms with Simulated Concentration Distributions

This part of 'Results and Discussion' directly refers to Model 2. Figs 4a and 4b show selected results from simulations of the concentration distribution of analyte C_{12} on the chromatographic plates, as obtained from the adsorption isotherm [eq. (16)] and from solving the differential equation of the mass balance, given below:

$$\frac{\partial C}{\partial t} + w\frac{\partial C}{\partial x} + F\frac{\partial q}{\partial t} = D_x\frac{\partial^2 C}{\partial x^2} + D_y\frac{\partial^2 C}{\partial y^2} \qquad (18)$$

where w is the average flow velocity of the mobile phase, 0.00185 cm s^{-1} (calculated from the chromatogram development time), C and q are the concentrations [mol dm^{-3}] of the analyte in the mobile phase and on the adsorbent surface, respectively, D_x and D_t are, respectively, the effective diffusion coefficients lengthwise (x) and perpendicular to the plate (y), and F is the so-called phase ratio (i.e., the ratio of the volume of stationary phase to that of the mobile phase), which in our experiments was assumed, somewhat arbitrarily, to be 0.25.

It seems worthy of note, that expression of Model 2, by use of eq. (18), shows it to have a distinct resemblance to the widely applied equilibrium-dispersive model.[3]

Constants from the adsorption isotherm equation and the effective diffusion coefficients were chosen to obtain shapes of lengthwise cross-sections of the chromatographic bands and their respective surface areas similar to those from the experimental densitograms. It was assumed, that:

$D_x = 2\cdot10^{-5}$, $D_t = 2\cdot10^{-6}$ [cm^2 s^{-1}],
$q_s = 0.01$ [mol dm^{-3}],

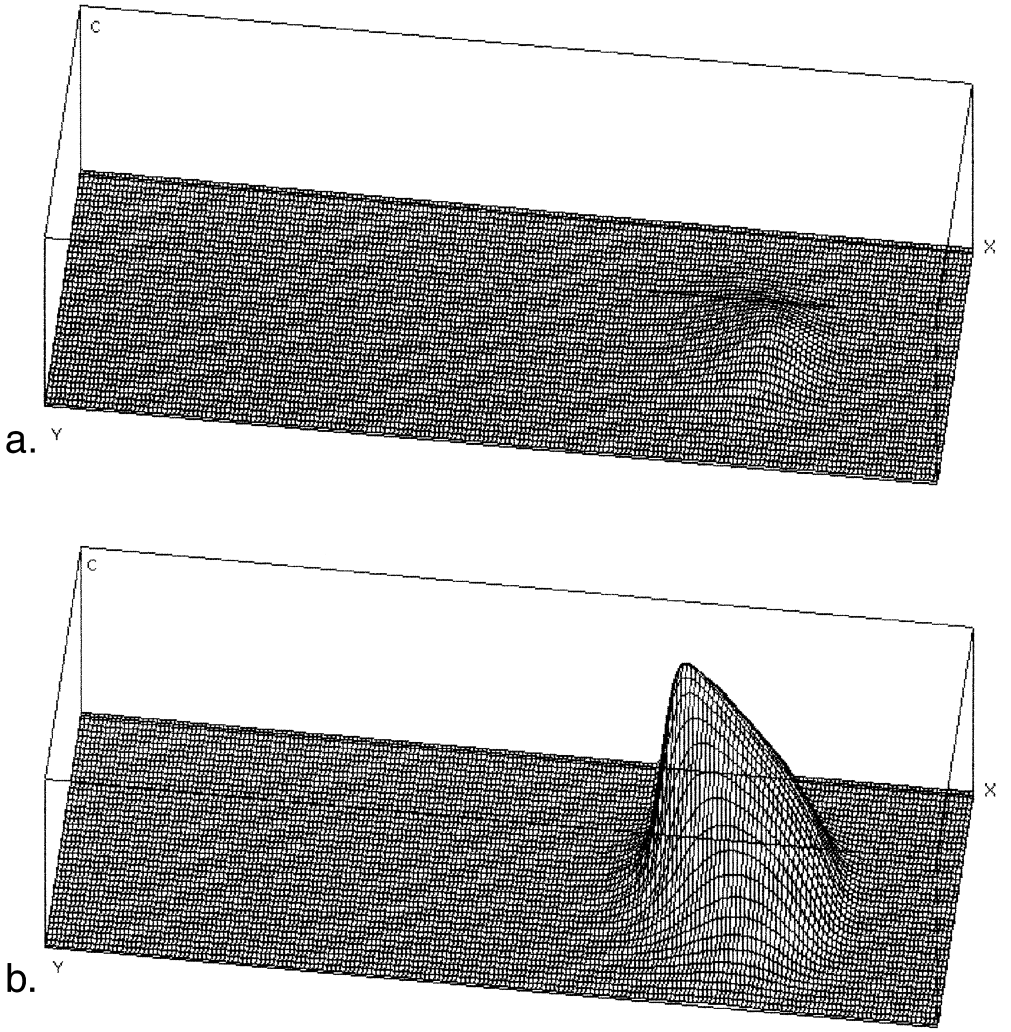

Figure 4. Simulated chromatogram for dodecanoic acid (C_{12}), a) concentration 0.010 mol L^{-1}, n = 1 and b) concentration 0.100 mol L^{-1}, n = 20.

K_1 = 165 [dm^3 mol^{-1}],
K = 8250 [dm^6 mol^{-2}].

Numerical values of n are given in the captions to the figures. With regard to the initial moment of development of the chromatograms, it was assumed that

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the analyte was spotted on to the adsorbent surface as a rectangular band of dimensions 3 mm × 2.5 mm.

The orthogonal collocation method on finite elements (OCFE) was used to solve the set of eqs (18). The OCFE method used in this study has been described elsewhere.[4-6] The set of ordinal differential equations obtained after OCFE discretization, was solved by means of the Adams–Moulton method implemented to the VODE procedure,[7] using relative and absolute error equal to 10^{-6}. The VODE procedure automatically chooses an appropriate time increment to fulfill the assumed error conditions. In each calculation, the number of internal collocation points in subdomains (elements) was equal to 3. The number of subdomains was chosen such that there were no visible oscillations in simulations of the band profiles; it was 50 in direction *X* and 10 in direction *Y*.

Positions of fronts and band maxima in Figs 4a and 4b are in good agreement with experimental results. Simulated band shapes also resemble real densitograms, although 'tailing' of the bands from the densitograms is somewhat more pronounced than that from simulations.

It should, perhaps, be added that if Model 1 is used to simulate the chromatograms, it is virtually impossible to obtain a simulated band cross-section resembling that on a densitogram obtained from 0.1 mol L^{-1} C_{12}.

CONCLUSIONS

Our observations justify the assumptions of theoretical Models 1 and 2 [and particularly the correctness of the relationship given by eq. (8)], introduced in this study. From the results obtained, it can be stated that with increasing concentrations (and, hence, with increasing molar quantities) of the analyte solutions spotted on to the chromatographic plates, these compounds form increasingly long associative multimers at the interface between the solid (adsorbent) and the mobile phase; this results in higher numerical values of *n* and quasi-automatic reduction of R_F values, as predicted in our theoretical considerations.

For the time being, we leave open the question of which approach is better for determination of the numerical values of analyte R_F coefficients, especially for analytes which tend to participate in lateral interactions.

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