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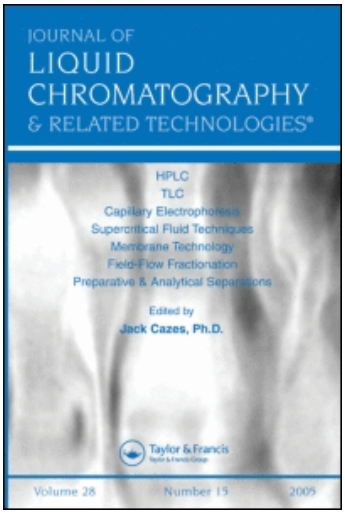

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
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Online publication date: 29 July 2004

To cite this Article Kaczmarski, K. , Sajewicz, M. , Pieniak, A. , Piętka, R. and Kowalska, T.(2005) 'Comparison of Lateral Interactions with Monocarboxylic and α,ω-Dicarboxylic Acids', Journal of Liquid Chromatography & Related Technologies, 27: 13, 1967 — 1980
To link to this Article: DOI: 10.1081/JLC-120039410
URL: http://dx.doi.org/10.1081/JLC-120039410

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JOURNAL OF LIQUID CHROMATOGRAPHY & RELATED TECHNOLOGIES®
Vol. 27, No. 13, pp. 1967–1980, 2004

Comparison of Lateral Interactions with Monocarboxylic and α,ω-Dicarboxylic Acids

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ABSTRACT

In this paper, we introduce part of a study originally devoted to investigating lateral interactions of monocarboxylic and α,ω-dicarboxylic acids analyzed on a low-activity stationary phase (cellulose powder) with low-polarity monocomponent mobile phases (decalin for monocarboxylic acids and 1,4-dioxane for α,ω-dicarboxylic acids). The presence, or absence, of lateral interactions for an analyte in a given chromatographic system can be judged from the shape of the respective concentration

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DOI: 10.1081/JLC-120039410 1082-6076 (Print); 1520-572X (Online)
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profile, so for this purpose, densitograms of the bands of interest must first be acquired.

Key Words: TLC; Lateral interactions; Higher fatty acids; Phenyl-substituted fatty acids; α,ω-Dicarboxylic acids; Retardation factor.

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INTRODUCTION

Chromatographic separations are used mainly for analytical purposes, a technique known as analytical chromatography. Chromatography is, however, gaining increasing importance as a tool enabling isolation of preparative amounts of substances. Such "preparative chromatography" is usually achieved with liquid chromatography (LC) and high performance liquid chromatography (HPLC), but occasionally with thin layer chromatography (TLC) also.

Each separation occurs because of the different interactions of each species with the stationary phase. To describe the partitioning process, a knowledge of the isotherm involved is needed. In analytical chromatography, the concentration of a species in an analyzed sample is very low, so that description of the retention process typically requires a knowledge of the slope of the isotherm when the concentration of the analyte is zero.

When chromatography is used in the preparative mode, the entire dependence of the equilibrium on the concentrations of adsorbed and nonadsorbed solute must be established. The equilibrium isotherm is usually nonlinear, and analysis of such isotherms is a necessary prerequisite for prediction of the retention mechanism.

Physicochemical description of retention processes in LC (planar chromatography included) is far from complete, and, for this reason, new studies are regularly undertaken, with the intention of improving existing retention models and/or introducing new ones. Established retention models in planar chromatography are oversimplifications, because, among other reasons, some of the intermolecular interactions in the chromatographic systems are disregarded. For example, none of the validated models focusing on prediction of solute retention takes into consideration so-called "lateral interactions," the term used to denote self-association of solute molecules.

The aim of this work was to gain insight into the role of lateral interactions in TLC band formation, by analyzing the band profiles of carboxylic acids chromatographed on cellulose powder with low-polarity monocomponent mobile phases.

THEORY

Study of the mechanism of adsorption in TLC is more difficult than in column LC. A nonlinear isotherm model in TLC can be elaborated only qualitatively, after assessment of chromatographic band shape and of the concentration distribution within this band. Phenomena characteristic of TLC band formation can have a major effect on the mechanism of retention.

The most characteristic feature of chromatographic bands is that the longer the development time and the greater the distance from the origin, the greater become their surface areas. This phenomenon is not restricted to planar chromatography only, but it occurs in all chromatographic techniques. Band broadening arises as a result of eddy and molecular diffusion, the effects of mass transfer, and the mechanism of solute retention. The first three phenomena cause symmetric spreading of the chromatographic band in relation to its geometrical center.

The mechanism of solute retention is also responsible for band broadening when the concentration of an analyte is so high that equilibrium between the surface and mobile-phase concentrations is on the nonlinear part of the isotherm. Use of densitometric detection has, however, provided an insight into the concentration profiles of chromatographic bands, thus enabling estimation of the role of solute retention in the peak broadening and prediction of the retention mechanism. Figure 1 shows three examples of band-concentration profiles in the absence of the mass overload. The peak in

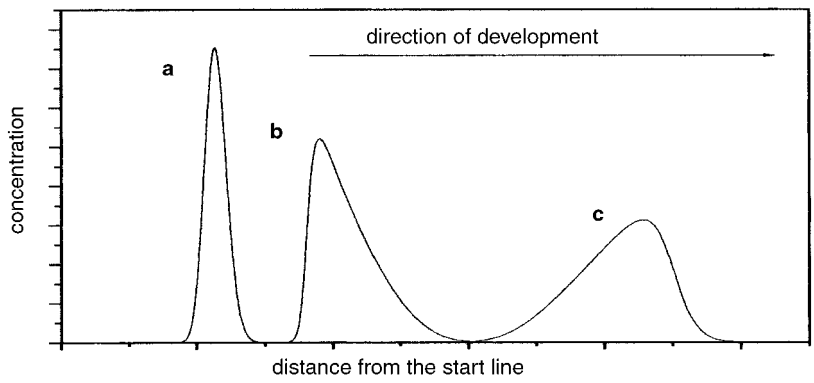

Figure 1. Three examples of concentration profiles along the chromatographic stationary phase bed: (a) symmetrical without tailing; (b) skewed with tailing toward the mobile-phase front; and (c) skewed with tailing towards the origin of the chromatogram.

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Fig. 1 denoted (a) is obtained for the linear isotherm, peak (c) is obtained for the Langmuir-type isotherm, and peak (b) is valid for the anti-Langmuir-type isotherm.

The Langmuir and the anti-Langmuir isotherms can be represented by the equation

$$q = \frac{a * C}{1 \pm b * C} \tag{1}$$

where q is the surface concentration, C is the concentration in the mobile phase, and a and b are the isotherm parameters; "+" and "−" serve for the Langmuir and anti-Langmuir isotherms, respectively. The anti-Langmuir isotherm should be regarded as an empirical equation, because it cannot be derived from a physicochemical background. Peaks very similar to peak (b) in Fig. 1 can, however, be obtained when the adsorbed molecules tend to interact with each other, or form multilayer structures.[1,2]

Dicarboxylic acids can form linear associative multimers (Fig. 2) held together by hydrogen bonding (a maximum of four hydrogen bonds can be formed by each molecule of such an acid). This is because of the presence of the two negatively polarized oxygen atoms of the carbonyl groups and the two positively polarized hydrogen atoms of the hydroxyl groups.

Monocarboxylic acids can form cyclic dimers (Fig. 3). It seems that as a result of direct contact of higher fatty acids with an adsorbent, the rings of the prevalent cyclic dimers are forcibly opened (e.g., because of the inevitable intermolecular interactions that result from hydrogen bonding with the hydroxyl groups of the cellulose), thus, considerably shifting the self-association equilibrium toward the linear-associative multimers.

For both types of acid (i.e., monocarboxylic and dicarboxylic), conditions necessary to form multilayer structures (or other interactions) among the adsorbed molecules are fulfilled. If so, anti-Langmuir-type concentration profiles should be observed for lengthwise cross-sections of the chromatographic bands.

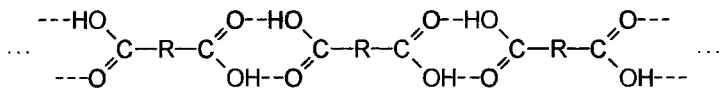

Figure 2. Schematic representation of the self-association of dicarboxylic acids as a result of intermolecular hydrogen bonding.

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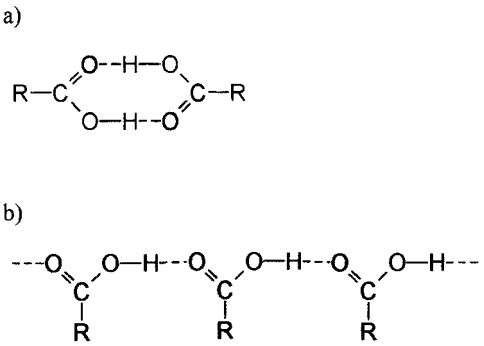

Figure 3. Schematic representation of self-associative structures involving intermolecular interaction of higher fatty acids by hydrogen bonding: (a) cyclic associative dimer and (b) linear associative multimer.

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EXPERIMENTAL

Experiments were performed with monocarboxylic acids (i.e., higher fatty acids and phenyl-substituted fatty acids) and α,ω-dicarboxylic acids from the three groups listed in Tables 1–3.

In all experiments, the stationary phase was microcrystalline cellulose (TLC plates precoated with cellulose powder; Merck KGaA, Darmstadt, Germany, cat. #1.05730). Decalin was used as the mobile phase for monocarboxylic acids and 1,4-dioxane for α,ω-dicarboxylic acids. Development was performed in the ascending mode in a Stahl-type chromatographic chamber.

Chromatograms were visualized by treatment with an ethanolic solution of bromocresol green.[3] The respective densitograms were then obtained by use of a Shimadzu (Kyoto, Japan) model CS9301 PC scanning densitometer,

Table 1. The applied test solutes (higher fatty acids) from group 1.

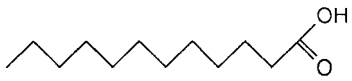
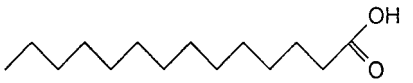
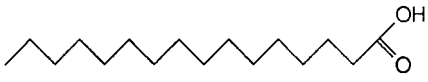
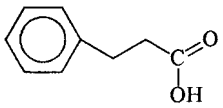
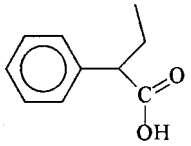
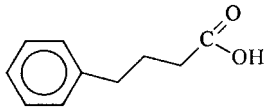
Higher fatty acid	Schematic structure
Dodecanoic (lauric) acid	
Tetradecanoic (myristic) acid	
Hexadecanoic (palmitic) acid	

Table 2. The applied test solutes (phenyl-substituted fatty acids) from group 2.

Phenyl-substituted fatty acid	Schematic structure
3-Phenylpropionic acid	
2-Phenylbutyric acid	
4-Phenylbutyric acid	

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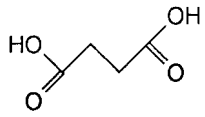
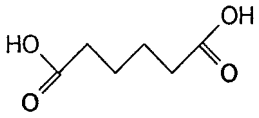
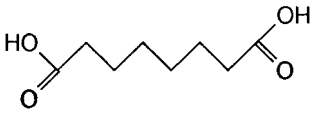
using a rectangular-cross-section light beam; the wavelength was 625 nm and the rectangular dimensions were 0.05 mm × 0.5 mm. The detector used in this densitometer is sensitive only to analytes active in the visible or ultraviolet regions of the spectrum, in the sense that the ability of the analyte to absorb light or to fluoresce is quantified. In this work, the analytes were optically inactive, and it was, therefore, necessary to visualize them. The visualizing procedure reduces the quality of the densitogram, however, because of

Table 3. The applied test solutes (α,ω-dicarboxylic acids) from group 3.

α,ω-Dicarboxylic acid	Schematic structure
Succinic acid	
Adipic acid	
Suberic acid	

noise originating from uneven distribution of the visualizing reagent (i.e., the bromocresol green dye) on the surface of the stationary phase. Interpretation of the densitograms obtained was, therefore, possible only after preliminary denoising, which was conducted by approximation using the smoothing spline fit.[4]

A different method of detection was used for the analytes from group 2, presented in Table 2. For these, the densitograms were obtained by use of a Desaga (Heidelberg, Germany) CD 60 densitometer equipped with the Windows-compatible ProQuant program package. The concentration profiles were recorded in ultraviolet (UV) light (in the reflectance mode) at a wavelength of 260 nm; the dimensions of the rectangular light beam were 0.02 mm × 0.4 mm. The densitograms obtained were relatively smooth and, therefore, needed no extra smoothing.

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RESULTS AND DISCUSSION

Experimental Lengthwise Concentration Profiles

The densitograms obtained are presented in Figs. 4–9. The lengthwise concentration profiles obtained for the higher fatty acids generally resembled

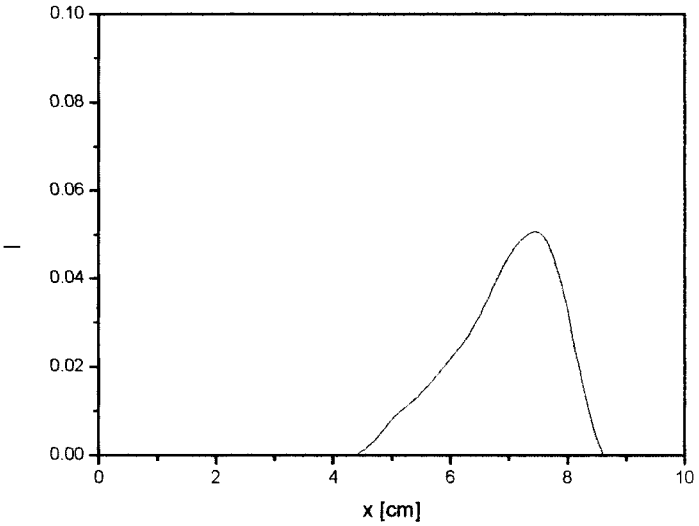

Figure 4. Densitograms obtained from hexadecanoic acid for sample concentration $C = 0.025\,\text{mol}\,\text{L}^{-1}$.

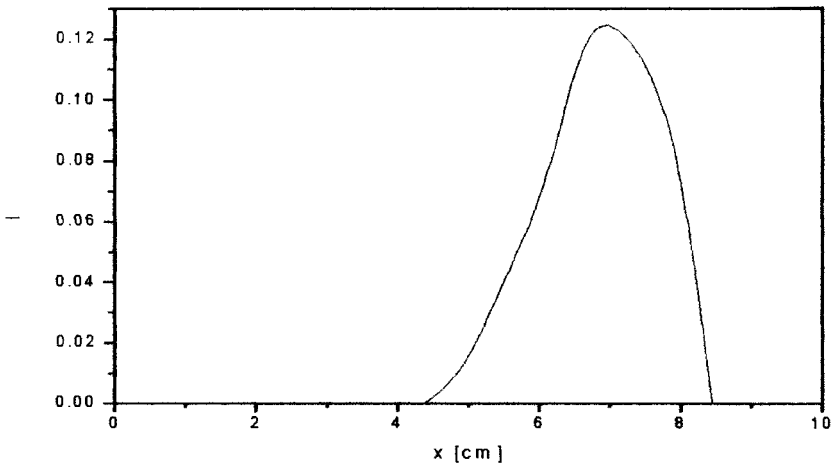

Figure 5. Densitograms obtained from dodecanoic acid for sample concentration $C = 0.1\,\mathrm{mol\,L^{-1}}$.

peaks generated with the aid of the Langmuir-type isotherm (Fig. 4). Peak profiles like those presented in Fig. 5, suggesting the possibility of lateral interactions,[5] were obtained only for the highest concentrations and for the shortest aliphatic chain lengths.

For α,ω-dicarboxylic acids, anti-Langmuir concentration profiles were most pronounced for compounds with the longest aliphatic chains, as is apparent from Fig. 6. From the densitograms obtained, it is apparent that α,ω-dicarboxylic acids are more prone than monocarboxylic acids to form anti-Langmuir peak profiles. This suggests lateral interactions are stronger for dicarboxylic acids than for monocarboxylic compounds, which seems a natural consequence of the possibility of their forming two hydrogen bonds at each end of the dicarboxylic acid molecule (Fig. 1).

The most pronounced anti-Langmuir behavior was observed for the phenyl-substituted monocarboxylic acids, especially 2-phenylbutyric acid (Fig. 7).

It seems that lateral interactions are strongest for the phenyl-substituted monocarboxylic acids investigated in this study, because of at least two factors—(i) the relatively short aliphatic moiety and (ii) substitution of the aliphatic chains with the phenyl group. Obviously, the longer the aliphatic chain moiety in a given molecular structure, the greater is the steric hindrance and the more shielded are the respective functional groups. Consequently, the probability of their participating in hydrogen-bond formation (i.e., in lateral interactions) is lower. This becomes particularly evident when the higher fatty acids (test solutes from group 1) and their respective concentration

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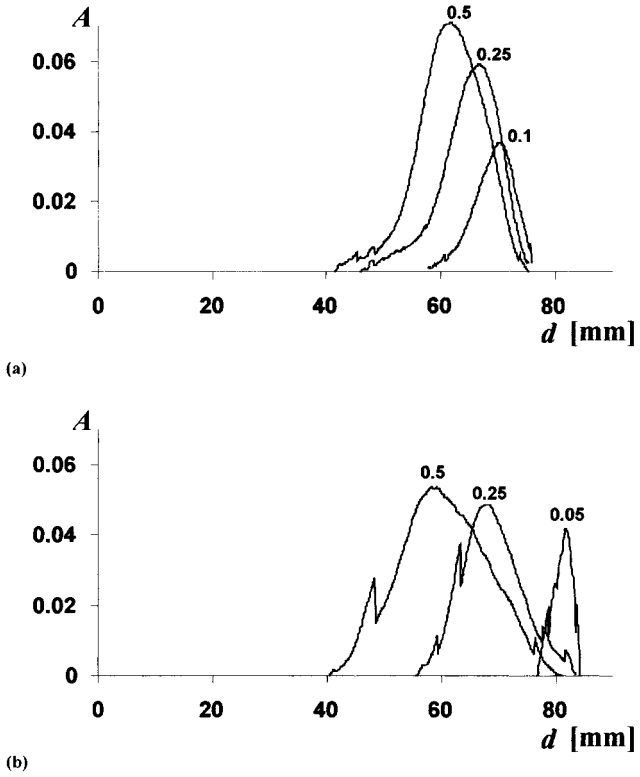

Figure 6. Densitograms obtained from 3-phenylpropionic acid. Sample concentrations were: (1) 0.2, (2) 0.3, (3) 0.4, and (4) 0.5 mol L^{-1}.

profiles, indicative of Langmuir-type adsorption isotherms, are compared with the phenyl-substituted fatty acids (test solutes from group 2) and their substantially different concentration profiles, indicative of anti-Langmuir-type adsorption isotherms. The important structural difference between the phenyl-substituted fatty acids and the other two groups of the test solutes is their mixed aryl aliphatic structure. The presence of the flat phenyl group in the structure of these solutes results in far less acute steric hindrance than the aliphatic chain and, therefore, it is less effective at preventing the carboxyl functional group from self-associating. The flat phenyl group is, moreover, negatively charged because of its delocalized π-electrons, and, therefore, also prone to participate in hydrogen bonding as an electron donor. Summing up, the molecules of phenyl-substituted fatty acids can participate in two different kinds of intermolecular hydrogen bonds—those involving the

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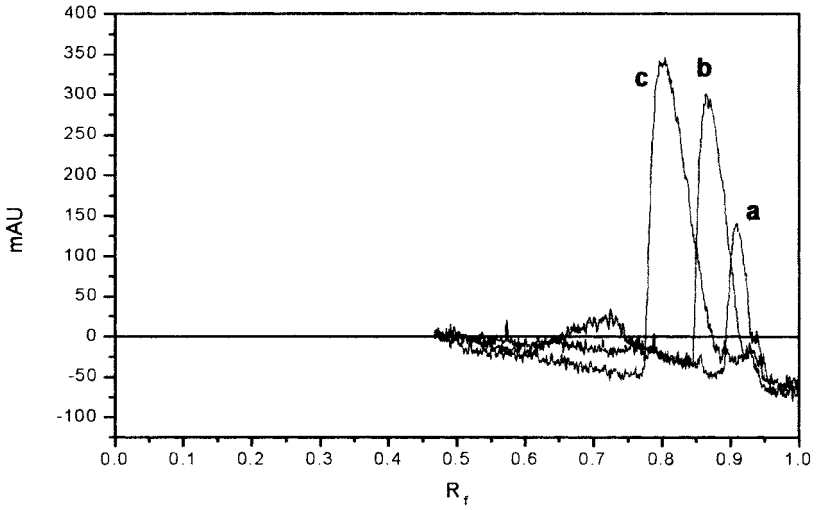

Figure 7. Densitograms obtained from 4-phenylbutyric acid. Sample concentrations were: (1) 0.1, (2) 0.2, (3) 0.3, (4) 0.4, (5) 0.5, and (6) 1.0 mol L^{-1}.

carboxyl functional group (which result in two hydrogen bonds per acid molecule) and those that involve the aromatic rings (and result in a single hydrogen bond per acid molecule). This dual type of intermolecular interaction is shown schematically in Fig. 8. One outcome of this study is, therefore, unequivocal evidence that of the three test solutes examined the phenyl-substituted monocarboxylic acids participate most effectively in lateral interactions. This conclusion is briefly summarized in Table 4.

Retardation Factor

The numerical values of the R_F coefficients of the analytes were determined from the maximum values of the concentration profiles of the bands; examples of the R_F values obtained are presented in Table 5. The relationship

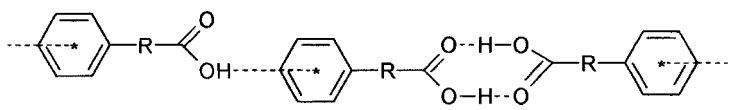

Figure 8. Mixed linear-cyclic dimers of fatty acids with phenyl substituents (which involve carboxyl groups and the aromatic π-electrons).

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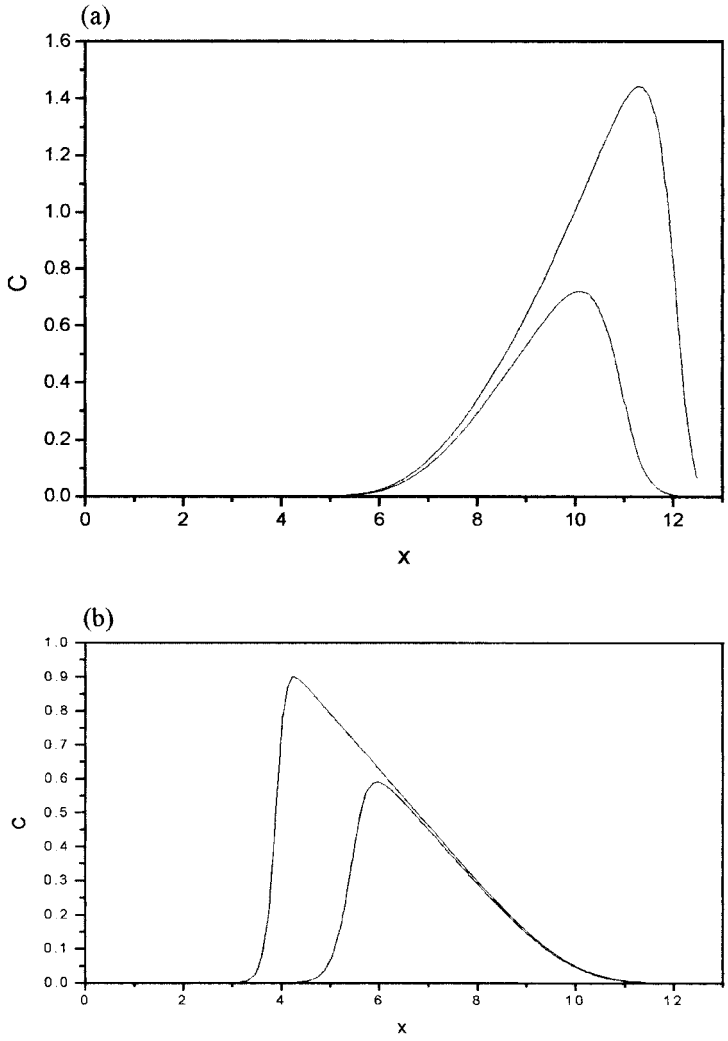

Figure 9. Lengthwise concentration profiles for the (a) Langmuir and (b) anti-Langmuir isotherm for initial band concentrations of 1 and 2 mol L^{-1}.

between R_F and the amount of sample spotted (as demonstrated in Table 5) is typical of all our experiments with carboxylic acids. The retardation factor always decreases as the amount of sample is increased, irrespective of the type of solute considered. Such a relationship is characteristic of the anti-Langmuir isotherm, but not of the Langmuir isotherm.

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Table 4. The maximum number and types of hydrogen bonds per molecule of acid as a principal cause of self-association of the three groups of organic acids considered.

Group of acids	The associative system involved	Maximum number of H-bonds per acid molecule
Higher fatty acids	Cyclic through the carboxyl group; Linear through the carboxyl group	2
α,ω-Dicarboxylic acids	Cyclic through the carboxyl group;	4
Fatty acids with phenyl substituent	Cyclic through the carboxyl group; Linear through the aromatic π-electrons	3

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The lengthwise concentration profiles calculated for the Langmuir and the anti-Langmuir isotherms are presented in Fig. 9. The amount of compound in the band was calculated by use of a model discussed elsewhere.[1] The model of the isotherms was

$$q = \frac{2 * C}{1 \pm 0.5 * C}$$

where " + " and " − " apply to the Langmuir and anti-Langmuir isotherms, respectively.

Table 5. Numerical values of the R_F coefficient for chromatographic bands of 4-phenylbutyric acid developed with decalin on cellulose plates.

Concentration of spotted sample (mol L^{-1})	R_F
0.1	0.92
0.2	0.90
0.3	0.87
0.4	0.85
0.5	0.82
1.0	0.68

As is apparent from Fig. 9, for the Langmuir isotherm, the maximum value of the higher peak is shifted toward the mobile-phase front, whereas for the anti-Langmuir isotherm, it is shifted toward the origin. Thus, for the Langmuir isotherm, the R_F value should increase with increasing amount of analyte, whereas for the anti-Langmuir isotherm, it should decrease. It is, however, commonly observed that experimental R_F values always decrease with increasing amount of analyte spotted. In our opinion, it is impossible to decide which kind of isotherm is responsible for an outcome observed by study of the retardation factor alone.

Shift of the highest peaks toward the origin is most probably inherent in the very technique of TLC. In this technique, the investigated analyte is dissolved in an appropriate solvent and then spotted on the chromatographic plate. The plate is first dried and then the chromatogram is developed. The analyte (in our experiment all the samples investigated were solids) dissolves in the mobile phase and then starts migrating along the chromatographic plate. It must be kept in mind that the dissolution time is proportional to the amount of analyte and to the mass-transfer resistance to dissolution. The larger the amount of the analyte, the longer is the dissolution time and the longer is the chromatographic band also. It seems that the retarded migration of chromatographic bands for larger amounts of analyte is mainly connected with slow dissolution of an analyte, and that this is the predominant reason for the decreasing R_F values, irrespective of the real isotherm. Even for the anti-Langmuir isotherm, for which a decreasing R_F value is a generic phenomenon, with larger amounts of analyte the band profiles are more shifted in the direction of the origin (see, for example, Fig. 7). On the other hand, theoretical simulations predict that the shift occurs to the 'shock' part of the anti-Langmuir bands only, whereas, the position of the peak beginning does not depend on the concentration. This discrepancy between theory and practice seems to confirm the important contribution of non-instantaneous dissolution of an analyte to the measured value of the retardation factor.

The phenomena discussed above make prediction of the process of surface adsorption rather difficult, although the concentration profiles of solutes, such as 2-phenylbutyric and 3-phenylpropionic acid, seem to give strong evidence in support of the occurrence of lateral interactions among adsorbed molecules of the acids.

ACKNOWLEDGMENT

The authors wish to thank the firm Merck KGaA (Darmstadt, Germany) for supplying the test compounds and precoated cellulose plates used in this study.

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Received September 29, 2003
Accepted November 10, 2003
Manuscript 6346F

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