Nonlinear isotherm of benzene and its derivatives by frontal analysis

Xiaolong Wan, Ju Weon Lee, and Kyung Ho Row†

Center for Advanced Bioseparation Technology, Department of Chemical Engineering, Inha University,
253 Yonghyun-dong, Nam-gu, Incheon 402-751, Korea
(*Received 16 May 2008 • accepted 24 June 2008*)

Abstract−Adsorption behavior of a solute is one of the most important factors to consider when designing a batch and a continuous liquid chromatographic separation process. In liquid chromatography, this behavior is based on the adsorption equilibrium between the liquid mobile-phase and solid stationary-phase. However, most retention models have been developed under a linear adsorption isotherm: very few researchers have investigated the relationship between the adsorption parameters and the mobile phase composition, and some empirical models have been introduced. In this work, adsorption isotherms were obtained by a frontal analysis for three small molecular compounds (benzene, toluene, and chlorobenzene) on a commercial C_{18} bonded silica column. The absorption based on the Langmuir, Freundlich, and Langmuir-Freundlich models were investigated according to changes of the composition of methanol highly enriched eluent. The calculations and analysis of the coefficients obtained for the three models confirm that the adsorption data for solutes are best modeled with the Langmuir-Freundlich isotherm. In spite of the acceptable accuracy, Langmuir and Freundlich isotherm models couldn't satisfactorily describe the mechanism and provide objective information on the physical nature of the absorption.

Key words: Adsorption Isotherm Modeling, Frontal Analysis, Mobile Phase Composition

INTRODUCTION

The retention mechanisms that take place in reversed-phase liquid chromatographic (RP-LC) have been widely discussed [1-3]. Most of these studies were based on the use of linear chromatography data, i.e., on the measurement of the retention times of impulses and the determination of the retention factors of series of analytes. Research on the influence of different parameters on these retention factors, such as the nature and concentration of the organic modifier, the stationary-phase chemistry (e.g., monomeric or polymeric bonding, end-capping), and temperature has brought conclusions that are now classical.

In different reviews devoted to theoretical aspects of non-linear chromatography, it was concluded that an adequate simulation of a chromatographic separation process requires mainly reliable information on how the components of a mixture to be separated are distributed under equilibrium conditions between the mobile and stationary phases [4-6]. For a constant temperature, this information is represented by adsorption isotherms. In general, these functions can only be determined experimentally. Although several experimental methods are available, their application is still far from routine. In several papers, different experimental methods have been compared and evaluated [7-13]. In many works, only the single solute isotherms are determined experimentally, and the competitive isotherms are then predicted by using isotherm models. However, it has been shown that the available theoretical concepts offer only limited accuracy and the experimental determination of at least some multicomponent equilibrium data is recommended. Unfortunately, in this area, there are few reliable methods. Classical static methods have been frequently used [14] as well as perturbation methods [15,16].

Although a frontal analysis (FA) is considered a standard tool for measuring single solute isotherms and its potential to measure competitive isotherms is well known [6], this method is seldom applied to determine competitive isotherms.

These conclusions were based on the measurement of accurate adsorption isotherm data by the frontal analysis (FA) method. The adsorption isotherm was built step by step, concentration after concentration, and results from measurements performed on long series of injections of breakthrough curves. Clearly, the larger the concentration range investigated and the larger the number of data points acquired, the more accurate the determination of the best final isotherm model and of its isotherm parameters. The eventual limitations on precision and accuracy essentially originate from the accuracy and precision of the instrumentation itself (flow rate, flow mixer, thermostat) and from the overall reproducibility of the different unit functions of the apparatus. Experimentally, limits also arise from the amount of chemicals available (preparation, price) and the need to perform an entire whole series of data acquisitions within a reasonable lapse of time.

In this work, adsorption isotherms were obtained by a frontal analysis for three low-molecular compounds (benzene, toluene, and chlorobenzene) on a commercial C_{18} bonded column. The adsorption behaviors according to the changes of the mobile phase composition were investigated based on the adsorption Langmuir, Freundlich and Langmuir-Freundlich models. The isotherm model was derived from these experimental curves. In particular, the effect of the number of data points acquired on the determination of the best adsorption isotherm was studied. The distribution of these points in the concentration range is another important factor that was investigated.

THEORY

1. Langmuir Model

†To whom correspondence should be addressed.
E-mail: rowkho@inha.ac.kr

The Langmuir model assumes that the adsorption process takes place on a surface composed of a fixed number of adsorption sites of equal energy, with one molecule adsorbed per adsorption site until monolayer coverage is obtained. The Langmuir model can be described by the equation

$$q=aC/(1+bC) \quad (1)$$

where C is the equilibrium concentration of the solute in the liquid-phase, q is the equilibrium concentration of the solute in the solid-phase, a/b is the maximum adsorption capacity, and b is the apparent dissociation constant, which represents the affinity between the solute and adsorbent. These parameters were estimated by the iterative Levenberg-Marquardt from the experimental data.

Some of the assumptions made in this model are not necessarily realistic, because of the large difference between macromolecules and small molecules in the adsorption mechanisms at the adsorption sites. The differences result mainly from (a) multiple-site binding for proteins, which often results in irreversible adsorption; (b) the heterogeneous nature of most solid surfaces; and (c) lateral and other interactions, referred to as cooperative interactions.

2. Freundlich Model

In the Freundlich model the adsorbed mass per mass of adsorbent is a power law function of the solute concentration:

$$q=KC^n \quad (2)$$

where K and n are the Freundlich equilibrium constant and the Freundlich isotherm power term, respectively. Unlike the Langmuir, the Freundlich equation does not become linear at low concentrations but remains convex; nor does not show it saturation or a limiting value. Although this model is usually applied in a strictly empirical sense, it can be of theoretical interest in terms of adsorption onto an energetically heterogeneous surface.

3. Langmuir-Freundlich Model

The single-component Langmuir-Freundlich model is described by the following equation:

$$q=eC^g/(1+fC^g) \quad (3)$$

where f is the apparent dissociation constant, which includes contributions from ligand binding to monomer, monomer-dimer, and more highly associated forms of proteins; e/f is the maximum adsorption capacity; and g is the Langmuir-Freundlich coefficient.

EXPEIMENTAL

1. Chemicals

The different mobile phases used in this work, whether for the determination of the adsorption isotherm data or for the elution of large-sized bands, were mixtures of distilled water and HPLC-grade acetonitrile, purchased from Duksan Pure Chemical Co. (Ansan, South Korea). The distilled water was filtered with a vacuum pump (Division of Millipore, Waters, U.S.A.) and a filter (HA-0.45, Division of Millipore, Waters, U.S.A.) prior to use. All the solutes, benzene, toluene, and chlorobenzene, were of analytical grade and were obtained from Oriental Chemical Industries (Incheon, South Korea). Each analyte was dissolved in a mixture of water and acetonitrile at different concentrations for each sample, ranging from 16% to 22%. These solutions were then sonicated for 30 min and

stored at 277 K. The working standards were re-prepared every two days to avoid potential errors from decomposition.

2. Apparatus

The chromatography system consisted of a Waters 600 s Multi solvent Delivery System and a Waters 616 liquid chromatography (Waters Associates, Milford, MA, U.S.A.), a Rheodyne injector (Cotati, CA, USA) valve with a 20 μl sample loop, and a variable wavelength 2487 UV dual channel detector. Millenium software (Ver. 3.2 Interface Eng., South Korea) on a PC was used as a data acquisition system. Experiments were performed with a commercially available Optimapak C_{18} (alkyl-) bonded phase column (4.6×150 mm i.d. 100 Å pore sizes, and 5 μm particles) purchased from Rs-Tech Co. (Daejeon, South Korea). Analyses were performed throughout at a temperature of 308 K at a flow rate of 1.0 mL/min in isocratic mode, and the elution profiles were monitored at λ of 280 nm. The mobile phases were composed of water with additional varying different concentrations of acetonitrile, an organic modifier. The retention times used in this study were the averages of at least three determinations. The results of the chromatographic experiments were evaluated by mathematical statistic techniques. The relative error of a single measurement did not exceed 5%.

3. Isotherm Measurements

The measurements were carried out at a constant temperature of 308 K. Ten concentration points, uniformly distributed within the investigated concentration range were acquired. The nonlinear calibration data were fitted to a third-degree polynomial.

All isotherm data were obtained by a frontal analysis. One reservoir of the HPLC instrument delivered a stream of the mobile phase, while another reservoir delivered the sample solution. The desired concentration of the studied compound was obtained by selecting the concentration of the mother sample solution and the flow-rate fractions delivered by the two pumps. The breakthrough curves were recorded successively at a flow-rate of 1 ml/min, with a sufficiently long time delay between each breakthrough curve to allow sufficient time for re-equilibration of the column with the pure mobile phase. The injection time of the sample depends on the time required to
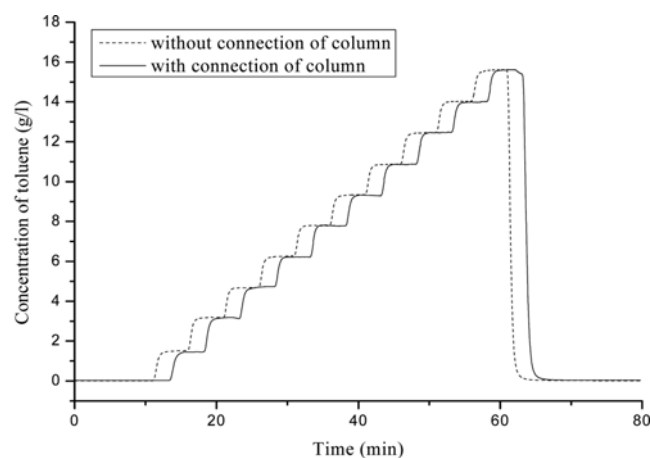

Fig. 1. The overlapped breakthrough curves of toluene with and without connection of column (Solid line is the breakthrough curve with the connection of the column and dash line is the breakthrough curve without the connection of the column.).

reach the plateau concentration at the outlet of the column. All the overloaded profiles needed for the validation of the fitted isotherms were recorded during the frontal analysis experiments.

In this study, three low-molecular hydrophobic solutes were used to measure the isotherm parameters on C₁₈ adsorbent, the representative adsorbent of RPLC. In this case, two different multi-step single-component frontal analyses were performed. The first case was done with the connection of the column, and the other case was without the connection. For the breakthrough curves without the connection of the column, the system volume including the dwell time was excluded from the breakthrough curve with the connection of the column by deducting the area of the breakthrough curve without connection from the area of the breakthrough curve with connection. Fig. 1 shows the overlapped breakthrough curves with and without connection of the column of toluene. The difference of area in each step represents the accumulated amount of solute in the column. Therefore, the adsorbed amount of solute is easily calculated by the volume fraction of the mobile phase and the stationary phase.

RESULTS AND DISCUSSION

An adsorption isotherm is a measure of the relationship between the concentration of bound and sample in a given system. By fitting the experimental adsorption isotherm to a mathematical model, it is possible to estimate the binding properties of the system by using the corresponding fitting coefficients. However, the selection of the guest molecule could directly influence the characterization of the system.

In this study, different concentrations of solutions of each sample, ranging from 16% to 22%, and different concentrations of organic mobile phase modifier, ranging from 85% to 94%, were evaluated. q was calculated according to the procedure described in the experimental section. Subsequently, the experimental adsorption isotherms were fitted to the Langmuir, Freundlich and Langmuir-Freundlich models. This was accomplished with the solver function in Origin-Pro 7.5 software by varying the fitting parameters to reach a value of 1 for the squared correlation coefficient (R^2).

Three similar-shaped hydrophobic molecules, benzene, toluene, and chlorobenzene, are applied in this study. The molecules are not homogeneous isomers. Benzene is more stable and might be expected for a system of six carbon-carbon single bonds and three carbon-carbon double bonds. The molecule is planar, the carbon atoms are at the corners of a regular hexagon, and delocalization of the electrons is complete. Toluene (methylbenzene) only has a methyl group attached to the benzene ring replacing one of the hydrogen atoms. It is a bigger molecule and hence the van der Waals dispersion forces will be bigger. Chlorobenzene is a chloro-substituted benzene.

The retention factors of the analytes were successfully correlated with their partition coefficients between water and n-octane (Log P), and have been shown to be proportional to the molecular size of the solute and directly affected by their solubility in the mobile phase. Some physicochemical properties for solutes are listed in Table 1 [17,18]. It is readily apparent that we tested two nonpolar solutes (benzene and toluene) and a low polarity solute (chlorobenzene). From a comparison of the aqueous solubility of benzene with reference to its structural influence by polarity, we can conclude

Table 1. The partition coefficients between water and *n*-octane (Log P), dipole moments (μ), and aqueous solubility of investigated solutes

Solute	Log P[a]	μ (D) [17]	Aqueous solubility (at 298 K)
Benzene	2.79	0.00	1750 mg/L [18]
Toluene	3.33	0.31	0.052%[b]
Chlorobenzene	3.66	1.54	0.49 mg/L [18]

[a]Data from the http://pubs.acs.org/subscribe
[b]Data from the http://macro.lsu.edu/howto/solvents.htm

that van der Waals dispersion forces between benzene molecules are quite strong. Toluene has a small permanent dipole, and thus there will be dipole-dipole attractions as well as dispersion forces. The dipole is due to the CH₃ group's tendency to "push" electrons away. This also affects the reactivity of methylbenzene. Chlorobenzene possesses a dipole moment that is oriented in the plane of its benzene ring. For these solutes, calculations indicate that the lowest energy configuration corresponds to a ring lying flat on the surface. In this orientation the dipole moment lies perpendicular to the radial electric field, which minimizes the polarization. Mobile phase components (water or acetonitrile) do not share this property; however, its response may be muted by competing adsorption on the adjacent hydrophobic C₁₈ surface and by intermolecular interaction that causes the modifier molecules.

The empirical adsorption-equilibrium isotherm models most frequently used in liquid-solid chromatography are the Langmuir and the Langmuirian-type (Freundlich, Langmuir-Freundlich, etc.) isotherm models [19]. The shape of the Langmuirian isotherms is always convex upward, indicating that there are no significant attractions between molecules of the adsorbate and that the adsorption capacity of the adsorbent is finite.

The experimental adsorption isotherms of benzene obtained at different conditions are shown in Fig. 2. The shape of the adsorption isotherm is concave upward on the C₁₈ surface, as demonstrated by
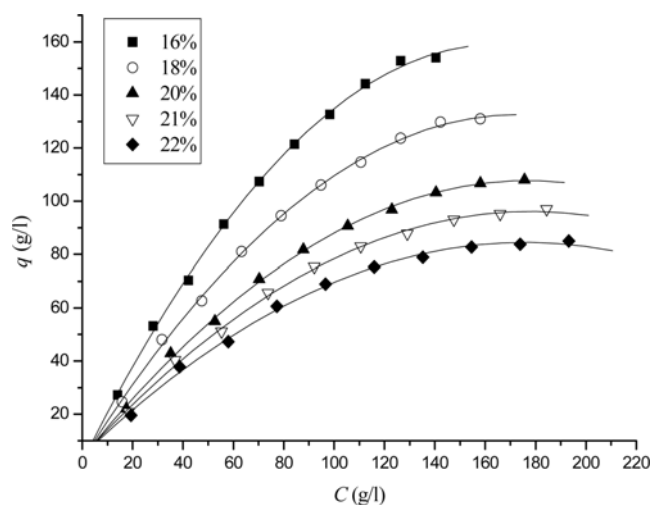

Fig. 2. Experimental isotherms of different concentrations of benzene on the C₁₈ column with different concentrations of acetonitrile in mobile phases.

the plot of q as a function of C, which increases constantly within the range of concentration accessible to measurement. For instance, if the mobile phase was acetonitrile 85% (v/v) and water 15% (v/v) - i.e., the chromatograms reported in Fig. 1 - the maximum concentration recorded at the column outlet and the maximum uploaded concentration were 10.93 and 65.19 g/*l*, respectively. The extrapolated value for q in these conditions is, accordingly, the most critical parameter. This is likely also the reason for the isotherm crossing observed in Fig. 2.

Analogous experimental isotherms were obtained for other investigated solutes (Figs. 3-4). It is evident that in the case of toluene, the intersection is most clearly expressed. It is apparent from Fig. 3 that the discrimination of q values becomes expressed with the relatively high C values. Comparing the toluene and benzene isotherms, it appears that the position of the methyl group on the benzene skel-

eton has a critical influence on the shape of the equilibrium isotherm. Nevertheless, the introduction of methyl groups in the benzene ring affects the q values positively. Similar tendencies are demonstrated for the experimental chlorobenzene isotherms shown in Fig. 4. It is worth nothing that the isotherms approach intersection in the region of low uploaded concentrations. Clearly, the polar chloride groups handle the absorption result in a positive growth q values. In these cases, the shapes of the adsorption isotherms are also unessential concave upward on the C_{18} surface.

It should also be emphasized that the benzene derivatives are sorbed in the following modifier concentration order - 94%<92%<90% <87%<85% - on the hydrophilic sorbent C_{18} (Figs. 2-4). Thus, as the concentration of acetonitrile in the mobile phase increases at the liquid-solid interface, the saturation capacity of the adsorbent for the solutes decreases.

In general, any adsorption isotherm models will relate the analyte concentration in the bulk mobile phase to the apparent solid phase concentration. It is assumed that the solution contains only two components, the solute and the solvent, and thus they are really single-component isotherms. However, in our experimental case, the mobile phase is comprised of an organic modifier (acetonitrile) dissolved in water. Thus, the adsorption system becomes a ternary system. Theoretically, binary isotherms should be used, accounting for the competition between the solute and the organic modifier for adsorption. However, in this case, the simplification of replacing the binary isotherm with single-component isotherm, the coefficients of which depend on the concentration of the modifier, is valid. This is because the adsorption of the organic modifier is weak compared to that of the analyte, and the competition for adsorption between the analyte and acetonitrile is negligible. The variation of the concentration of the organic modifier essentially affects the Gibbs free energy of the analyte in the bulk mobile phase. However, the situation becomes more complex if the content of the organic modifier in the eluent is high. In this case, the modifier the molecules of which tend to aggregate at interface with the bonded layer, causing the formation of microenvironments (in most cases a monolayer is formed) in which the mobile phase properties are different from those in the bulk.

Although there is a risk of oversimplification, the only possible choices for studying the FA profile were the simple Langmuir, Freundlich and Langmuir-Freundlich isotherms. As partial support of this, it is noted that in some isolations (for example, in the case of preparative scale chromatography or simulated moving bed (SMB)), adsorption isotherms are sometimes considered as "working-curves" to describe the separation process under well-specified conditions and for the optimization of the experimental variables, without large concern for their physical meaning. The experimental adsorption data acquired were fitted to the equations of the Langmuir, Freundlich, and Langmuir-Freundlich models. The parameters are shown in Tables 2-4.

Analyzing the data obtained with the Langmuir model, shown in Table 2 and Fig. 5, two aspects can be exploited: (1) the notable agreement among the q estimates at the different mobile phase compositions; (2) the a/b dependence being inversely proportional to the monolayer capacity. The Langmuir isotherm (Eq. (1)) represents a case where the binding of the analyte can be described by a finite number of identical surface sites. It is often assumed that if data
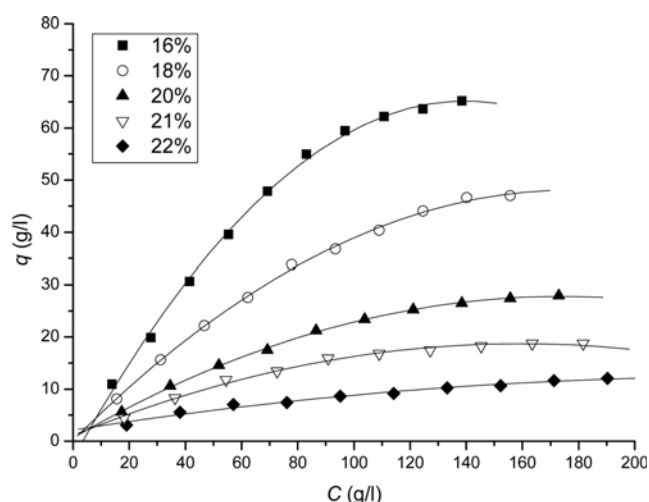

Fig. 3. Experimental isotherms of different concentrations of toluene on the C_{18} column with different concentrations of acetonitrile in mobile phases.
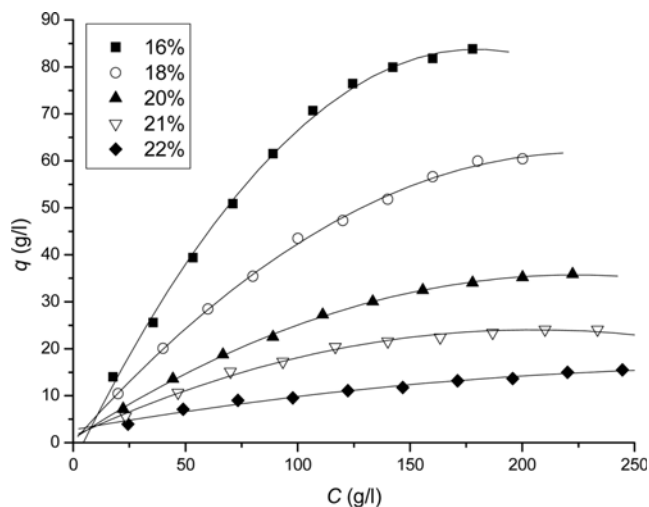

Fig. 4. Experimental isotherms of different concentrations chlorobenzene on the C_{18} column with different concentrations of acetonitrile in mobile phases.

Table 2. Parameters of Langmuir isotherm obtained with different acetonitrile content in the mobile phase

Sample	Concentration	Mobile phase (% ACN/water, V/V)	a	b	R^2
Benzene	16%	85/15	2.2785	0.0072	0.9966
	18%	87/13	1.8939	0.0067	0.9962
	20%	90/10	1.6030	0.0087	0.9947
	21%	92/8	1.3042	0.0083	0.9934
	22%	94/6	1.2283	0.0094	0.9893
Toluene	16%	85/15	1.0178	0.0076	0.9846
	18%	87/13	0.6311	0.0066	0.9959
	20%	90/10	0.4103	0.0084	0.9940
	21%	92/8	0.2764	0.0095	0.9906
	22%	94/6	0.1892	0.0109	0.9844
Chlorobenzene	16%	85/15	1.0186	0.0059	0.9846
	18%	87/13	0.6308	0.0051	0.9959
	20%	90/10	0.4105	0.0066	0.9940
	21%	92/8	0.3564	0.0099	0.9864
	22%	94/6	0.1892	0.0085	0.9844

Table 3. Parameters of Freundlich isotherm obtained with different acetonitrile content in the mobile phase

Sample	Concentration	Mobile phase (% ACN/water, V/V)	K	n	R^2
Benzene	16%	85/15	5.9656	0.6699	0.9858
	18%	87/13	5.9048	0.6342	0.9819
	20%	90/10	5.5458	0.5876	0.9742
	21%	92/8	5.1950	0.5600	0.9683
	22%	94/6	5.4324	0.5239	0.9556
Toluene	16%	85/15	2.6216	0.6682	0.9831
	18%	87/13	1.7061	0.6693	0.9871
	20%	90/10	1.3801	0.5966	0.9699
	21%	92/8	1.5659	0.5168	0.9656
	22%	94/6	0.8025	0.4989	0.9895
Chlorobenzene	16%	85/15	2.8495	0.6682	0.9637
	18%	87/13	1.8538	0.6693	0.9834
	20%	90/10	1.5273	0.5966	0.9732
	21%	92/8	1.7017	0.5007	0.9444
	22%	94/6	0.9689	0.4993	0.9883

follows the Langmuir isotherm, it is indicative of a specific interaction between the compound and a surface. The Langmuir isotherm can be used to determine the maximum adsorption capacity of this specific site and also includes a constant related to the saturation capacity.
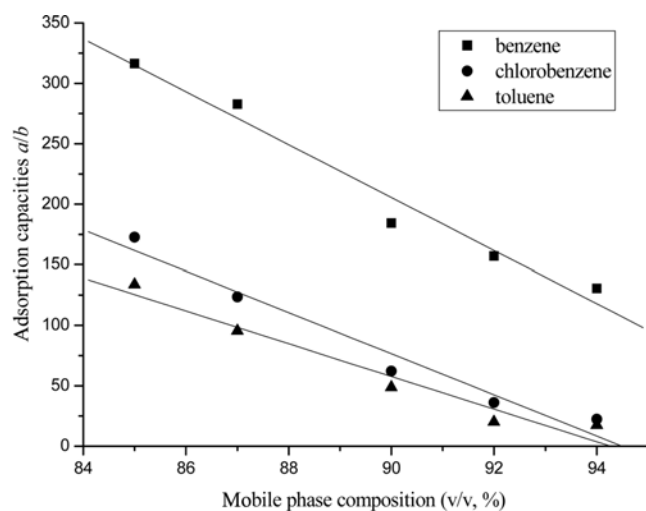
A frequently empirical isotherm is the Freundlich relationship (Eq. (2)), which allows for a heterogeneous surface that is more often seen in natural systems. The Freundlich isotherm is a non-linear model that includes the distribution coefficient K and a factor n. By including the factor n, which describes the deviation from linearity, it is in reality a modification of the linear model. When n=1, the Freundlich model becomes equal to the linear model. When n>1, the sorption constant increases with increasing solution concentration, perhaps reflecting an increase in the hydrophobic character of the surface after a monolayer. When n<1, K decreases with the solution concentration as the low energy sites are occupied. n slightly greater than 1 is often found for organic solutes. Unfortu-

nately, the Freundlich isotherm is, in contrast to the Langmuir isotherm, purely empiric and does not give any estimate of the adsorption maximum. The Freundlich isotherm parameters are reported in Table 3.

The Langmuir-Freundlich model (Eq. (3)) was analyzed by Sips, who found that the energy distribution function corresponds to a symmetrical quasi-Gaussian function. At low concentrations, the model reduces to the Freundlich model, and in the case of a homogeneous surface, it reduces to the Langmuir model [6]. For purely independent noninteracting sites, the value of g is 1. For positive cooperativity of the protein binding sites, g is greater than 1, while when 0<g<1, there is negative cooperativity in the binding process. The value of g can thus be employed as an empirical coefficient, representing the type and the extent of cooperativity present in the binding interaction. Since the Langmuir-Freundlich model has more than two adjustable parameters, it is not easily fitted to the experimental data by linear regression or graphical means. In this

Table 4. Parameters of Langmuir-Freundlich isotherm obtained with different acetonitrile content in the mobile phase

Sample	Concentration	Mobile phase (% ACN/water, V/V)	e	f	g	R^2
Benzene	16%	85/15	1.3866	0.0054	1.1516	0.9978
	18%	87/13	1.0241	0.0045	1.1758	0.9977
	20%	90/10	0.7407	0.0049	1.2241	0.9973
	21%	92/8	0.5162	0.0040	1.2574	0.9969
	22%	94/6	0.3732	0.0035	1.3277	0.9953
Toluene	16%	85/15	0.1784	0.0021	1.5166	0.9951
	18%	87/13	0.3318	0.0045	1.2082	0.9978
	20%	90/10	0.1711	0.0045	1.2536	0.9973
	21%	92/8	0.0799	0.0036	1.4357	0.9969
	22%	94/6	0.0208	0.0015	1.2689	0.9965
Chlorobenzene	16%	85/15	0.1565	0.0014	1.5166	0.9951
	18%	87/13	0.2963	0.0031	1.2082	0.9978
	20%	90/10	0.1606	0.0033	1.2536	0.9972
	21%	92/8	0.0715	0.0025	1.4357	0.9969
	22%	94/6	0.0231	0.0013	1.0696	0.9912

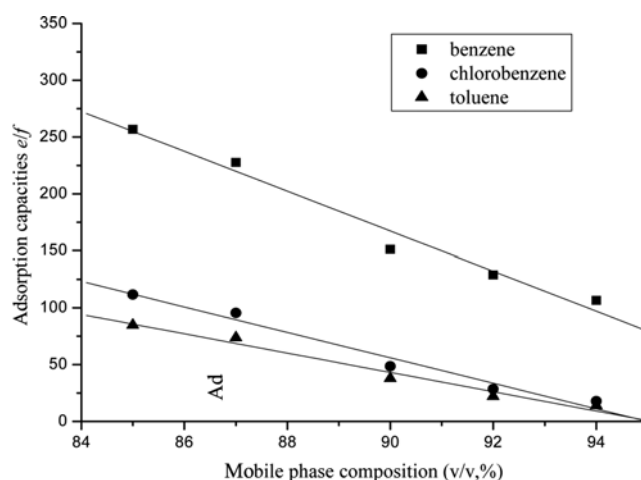**Fig. 5. Adsorption capacities of different analytes in Langmuir models with different concentrations of acetonitrile in mobile phases.**

Fig. 6. Adsorption capacities of different analytes in Langmuir-Freundlich models with different concentrations of acetonitrile in mobile phases.

case, it is necessary to apply a nonlinear least-squares analysis. The Langmuir-Freundlich isotherm parameters are reported in Table 4.

Table 2 reports the parameters of Langmuir isotherm when the Eq. (1) was applied.

From Fig. 5, the adsorption capacities a/b of Langmuir isotherm for benzene are significantly different. The biggest coefficient values were found for the benzene (130.6702<a/b<316.4583). The values of the specific saturation capacity of the adsorbent were quite close for toluene and chlorobenzene. This is consistent with the similarity of the three compounds in terms of structure and binding sites onto the stationary phase. For chlorobenzene, the coefficient value, the a/b, decreases from 22.2588 to 172.6441 showing decreased polarity that is supported by comparing values of Log P and μ from Table 1. For the same reasons, the values for toluene and chlorobenzene should less than that for the benzene.

Table 3 reports the parameters of the Freundlich isotherm when

Eq. (2) was applied.

As expected for the investigated organic solutes, the values of n were less than 1 in all cases. An analysis of the values of K (Table 3) revealed that their variation in accordance with the composition of the mobile phase did not have a systematic character. The smallest values of the distribution coefficients K were found for the toluene (0.8025) and chlorobenzene (0.9689) with 94% (v/v), and for benzene (5.1950) with 92% of acetonitrile concentration in the mobile phase. Higher K values were established with 85% (v/v) of acetonitrile concentration for benzene (5.9656), for toluene (2.6216) and for chlorobenzene (2.8495).

Table 4 reports the parameters of the Langmuir-Freundlich isotherm when Eq. (3) was applied. In this case, the Langmuir-Freundlich equation provides the highest value of the correlation coefficient (R^2), and thus is the model to which the experimental data fit best. As expected, for the investigated organic solutes, the values of g were more than 1 in most cases. Fig. 6 shows that the adsorption

capacities e/f of the Langmuir-Freundlich isotherm for benzene are the biggest (106.6286<e/f<256.7778), and the values of the specific saturation capacity of the adsorbent are quite close for toluene and chlorobenzene. For all investigated sorbates, the values of coefficients increase with the decrease of the amount of acetonitrile in the mobile phase. With the lowest modifier content (85%, v/v), this order becomes: benzene>chlorobenzene>toluene. As the aqueous solubility of a hydrophobic compound decreases (Table 1), the specific saturation capacity of the adsorbent increases, likely from entropy-driven interaction with the surface. In our experiment, the modifier is a water-soluble organic solvent. An organic modifier can decrease q by increasing the apparent solubility. The presence of a dissolved organic modifier commonly reduces the adsorption of a given chemical. This may be due to the increased solubility of the chemical in such a solution, or to competitive adsorption.

The adsorption capacity is the amount of adsorbate at complete monolayer coverage. It gives the maximum sorption capacity of sorbent and e/f is the Langmuir-Freundlich isotherm parameter that relates to the energy of adsorption.

CONCLUSION

1. The adsorption isotherms of benzene, toluene, and chlorobenzene were acquired by frontal analysis on commercial C_{18} bonded column with five different mobile phases, aqueous solutions of acetonitrile (85, 87, 90, 92 and 94%, v/v). The adsorption isotherms are always strictly convex upward in acetonitrile/water solutions.

2. Langmuir, Freundlich, and Langmuir-Freundlich adsorption isotherm models were fitted to the plot of the experimental adsorption isotherm. The calculations and analysis of the coefficients obtained for three models confirm that the adsorption data for solutes are best modeled with the Langmuir-Freundlich isotherm. We supposed that at the high concentrations of organic modifier (85-94% v/v), the Langmuir and Freundlich isotherm models could not satisfactorily describe the mechanism and provide objective information about the physical nature of the absorption despite its acceptable accuracy. Thus, the Langmuir-Freundlich adsorption isotherm model is more appropriate to describe absorption of hydrophobic solutes on the C_{18} surface using the data obtained by FA.

ACKNOWLEDGMENTS

REFERENCES

1. C. Horváth, W. R. Melander and I. Molnar, *J. Chromatogr. A*, **125**, 129 (1976).
2. J. G. Dorsey and K. A. Dill, *Chemical Reviews*, **89**, 331 (1989).
3. F. Gritti and G. Guiochon, *J. Chromatogr. A*, **1097**, 98 (2005).
4. L. R. Snyder, *Principles of adsorption chromatography,* Marcel Dekker, New York (1968).
5. H. Poppe, *J. Chromatogr. A*, **656**, 19 (1993).
6. G. Guiochon, S. Golshan-Shirazi and A. Katti., *Fundamentals of preparative and nonlinear chromatography*, Academic Press, New York (1994).
7. R. M. Nicoud and A. Seidel-Morgenstern, *Isolation Purif.*, **2**, 165 (1996).
8. J. F. K. Huber and R. G. Gerritse, *J. Chromatogr. A*, **58**, 137 (1971).
9. A. W. J. De Jong, J. C. Kraak, H. Poppe and F. Nooitgedacht, *J. Chromatogr. A*, **193**, 181 (1980).
10. J. M. Jacobson, J. Frenz and C. Horváth, *Ind. Eng. Chem. Res.*, **26**, 43 (1987).
11. J. M. Jacobson and J. Frenz, *J. Chromatogr. A*, **499**, 5 (1990).
12. S. Golshan-Shirazi, S. Godbane and G. Guiochon, *Anal. Chem.*, **60**, 2630 (1988).
13. O. Liseca, P. Hugob and A. Seidel-Morgenstern, *J. Chromatogr. A*, **908**, 19 (2001).
14. A. Seidel, E. Tscheutschler, K. H. Radeke and D. Gelbin, *Chem. Eng. Sci.*, **40**, 215 (1985).
15. C. B. Ching, K. H. Chu and D. M. Ruthven, *AIChE J.*, **36**, 275 (1990).
16. C. Blümel, P. Hugo and A. Seidel-Morgenstern, *J. Chromatogr. A*, **865**, 51 (1999).
17. K. Chan, N. S. Jensen, P. M. Silber and P. J. O'Brien, *Chemico-Biological Interactions*, **165**, 165 (2007).
18. D. R. Lide, *CRC handbook of chemistry and physics*, 75th ed., Boca Raton, Florida (1994).
19. A. Cavazzini, G. Bardin, K. Kaczmarski, P. Szabelski, M. Al-Bokari and G. Guiochon, *J. Chromatogr. A*, **957**, 111 (2002).