Extension of a Jovanovic–Freundlich isotherm model to multicomponent adsorption on heterogeneous surfaces

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Abstract

A recently proposed Jovanovic–Freundlich isotherm model for single component adsorption without lateral interactions on heterogeneous surfaces is extended to account for lateral interactions and for competitive adsorption. The model is tested using previously reported single component and competitive adsorption data of 2-phenylethanol and 3-phenylpropanol on ODS-silica with methanol–water as the mobile phase. A comparison is made regarding the ability of the Jovanovic–Freundlich and Langmuir–Freundlich models to predict competitive equilibria using the single component identified parameters. Fair predictions of the competitive data were obtained when using heterogeneous-surface models which do not take into account the possible interactions of phenylalcohols in the adsorbed phase via hydrogen bonding. Markedly improved predictions were obtained with models which account simultaneously for the two main sources of adsorbed phase nonideal behavior, i.e. adsorbate–adsorbate interactions and heterogeneity of the adsorbent surface. © 1998 Elsevier Science B.V.

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1. Introduction

Adsorption-based operations are important for large-scale industrial separations and are becoming more and more sophisticated. A case in point is the development of preparative chromatography in the pharmaceutical industry [1]. The optimization of these operations requires an accurate model of representation of the separation [2]. The calculation of elution band profiles using any of the chromatographic models available requires a knowledge of the multicomponent equilibria for the given separation [3]. For obvious economic reasons, preparative chromatography must be carried at high concentrations, in which case a nonlinear equilibrium takes place,

and the thermodynamic factors play an important role in the course of the separations. The accurate representation of multicomponent band profiles is possible only provided that an accurate representation of the competitive equilibria is available [3]. The rapid progress in the performance of computer software and hardware favors the use of more and more complete, hence complex models of chromatography. They are useless, however, unless good models of competitive equilibria are also available. The development of models for the prediction of multicomponent adsorption equilibria which would be useful in the domain of liquid chromatography has not reached the same degree of maturity as in other areas [4].

The prediction of multicomponent equilibria based on the information derived from the analysis of the

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single component adsorption data is an important issue [3]. While the number of reports regarding single component adsorption data measurements is large [5–32], there are few studies of multicomponent adsorption data because of the sheer volume of the experimental effort required. Most, if not all, studies on multicomponent adsorption refer to binary systems [10,14,23,26]. It seems that there are no reports on ternary systems [4]. There exist methods which allow reasonable estimates of the binary competitive adsorption equilibria employing the information derived from single component isotherms. These procedures allow a considerable reduction in the effort involved with the acquisition of multi-component adsorption data [33–35], provided that there exist satisfactory combining rules to relate the magnitude of the interactions between different molecules and the corresponding interactions be-tween molecules of the same kind [36]. For com-pounds of similar size and polarity, the classical geometric mean combining rule often gives a good approximation. However, for molecules of widely different size and polarity, as encountered frequently in chromatography, it seems that the proper inter-action parameters should be obtained from binary data. Once these values are known, the behavior of ternary or more complex mixtures could be predicted much more easily [36].

Different models have been used to correlate single component adsorption data and to predict multicomponent equilibria in the domain of liquid chromatography (LC). Some of them consider an ideal behavior of the system, without taking into account the possible sources of nonideal behavior, like the adsorbate–adsorbate interactions in the adsorbed phase, the heterogeneity of the adsorbent surface, the actual differences in the molecular size of the adsorbates, the loss of symmetry, clustering or dissociation of the adsorbates, the interactions among the components of the bulk liquid phase leading in some cases to the formation of associates, the limited solubility of the components in the bulk liquid phase, the irreversibility of the adsorption, or even the existence of synergistic effects [16,17,33–38]. Be-cause of the complexity of the systems under consid-eration, simplifications should be done in order to make the problem tractable. Among them we en-counter the application of simple models like the

Langmuir [6–9,11–15,18–20,22–24,27–29,40] and the Jovanovic model [6,7,39,40].

The Langmuir model considers that the adsorption process takes place on a surface composed of a fixed number of adsorption sites of equal energy, one molecule being adsorbed per adsorption site until monolayer coverage is achieved [41]. No other nonideal effects are included in this model. In addition, the multicomponent Langmuir model as-sumes equal adsorption capacities for all the com-ponents in the mixture, in order to satisfy the requirement of thermodynamic consistency [42]. The Langmuir model gives a good correlation of single component LC data in most situations [6–9,11–15,18–20,22–24,27–29,40]. This could possibly be a result of the mere fact that typical adsorption data in LC systems are linear over a rather wide concen-tration range [5,16,20,22,23,26] and that any two-parameter model can account for the initial curvature of the isotherm. The competitive Langmuir model has been often applied to LC systems [4,10,11,14,19,21–23,27,29,43–45]. In some cases, this model gives a good prediction of the binary data [10,14]. However, the predictions of multicomponent LC adsorption data or of multicomponent band profiles obtained with a competitive Langmuir model, using as parameters those of the single component isotherms, are often poor [11,19,21–23,27,29]. This fact suggests that the Langmuir model is only a convenient and empirical mean of single component data correlation and constitutes a crude representation of the real behavior of the system [4,8]. The Jovanovic model [46] keeps the same assumptions contained in the Langmuir model, only considering in addition the possibility of some mechanical contact between the adsorbing and de-sorbing molecules. Different extensions of the Jovanovic model for competitive adsorption [47,48] have been applied to LC data [39,40]. These exten-sions, however, require multicomponent data in order to identify the interactions parameters present in the model.

The ideal adsorbed solution theory (IAST) [49] was also applied to LC adsorption data [19,23,26,50], mainly via the IAST based LeVan–Vermeulen model [51]. The IAST model is thermo-dynamic in nature and allows the prediction of multicomponent behavior based on the analysis of

single component data. No assumptions are made regarding the nature of the single component data and any model could be used to correlate these data provided that a good fit is obtained, especially at low concentrations [49]. The LeVan–Vermeulen model relaxes the constraint contained in the competitive Langmuir model regarding the need of equal monolayer capacities for all the components of the mixture. Although in some cases the IAST model gives good predictions of the competitive data [26,28], the prediction of the multicomponent LC equilibria given by the IAST model is often poor and not better than the prediction given by the Langmuir model [19,23,40,50]. Moreover, it has been shown that the IAST theory usually fails for adsorbates exhibiting very different adsorbate sizes [52]. The original kinetic derivation of the Langmuir model has been modified and the models derived in such a fashion have been applied to LC data [53,54]. These models, however, usually require multicomponent data in order to extract the interaction parameters present, so their predictive capabilities are low. Other isotherm models try to account for one or several of the aforementioned nonideal effects. Models for homogeneous surfaces with lateral interactions like the Fowler [55], Ruthven [34], Moreau [56] and Kiselev [57,58] models were also applied to correlate and predict LC adsorption data [19,20,23,28,29,39,40,59]. Predictions of competitive equilibrium data obtained using these last models are improved with respect to those obtained using the Langmuir or the LeVan–Vermeulen models [23,59]. However, these predictions are still not in close agreement with experimental results. Furthermore, the values of the identified parameters may reflect, in some cases, a contradiction with the physical sense of the parameter initially introduced in the model [59]. It seems that taking into account the complexity of the phenomena under consideration and the relative simplicity of the models commonly applied, better models and experimental methods should be developed in order to take a closer look at the phenomena taking place at the molecular level.

Adsorbent surfaces are rarely homogeneous [35]. In the specific case of silica packings, there exists both experimental and theoretical evidence of the heterogeneity of these adsorbents [60–75]. Silica possesses an amorphous structure characterized by a wide distribution of pore sizes [65]. On these geometrically irregular surfaces, a greater concentration of active sites can be found in concave zones than in convex zones [65]. Silanization of bare silica is rarely complete, mainly because initially immobilized alkyl chains prevent the subsequent action of the silanizing agent on the unreacted silanols [73]. Thus, all reversed-phase silicas possess some unreacted silanols constituting high energy adsorption sites for polar molecules on these surfaces [60,64,65,68,73,74]. On the other hand, the bonded alkyl chains constitute low energy sites. So, qualitatively, there exist at least two main groups of sites. Additionally, the adsorbate–adsorbent interaction energy could vary within each group, thus originating a continuous bimodal energy distribution. For example, the silanols could be single, geminal or vicinal [64,74]. Other scenarios also take place. Depending on the size and geometry of the adsorbate and the length of the grafted alkyl chains, the active silanols could be more or less available to the given adsorbate [62], thus influencing the character of the adsorption energy distribution for the given component. Moreover, the geometry of the alkyl chains could be extended or collapsed depending on the polarity of the mobile phase [60,62]. The extended state usually prevails for organic-rich mobile phases, while the collapsed state appears to be valid for water-rich phases. Organic-rich phases also favor the intercalation of the organic modifier between the alkyl chains, thus increasing the possibility of the solute distribution in the grafted layer, provided that the partition mechanism is valid [62]. A controversial issue is the prevailing mechanism in reversed-phase separations. Some authors favor the adsorption mechanism [4] while others try to account also for the existence of a partitioning mechanism [76]. The distribution of alkyl chains on the surface is another controversial issue and both the random and patch models are believed to be valid for reversed-phase packings [61,70,77].

Several studies devoted to the determination of the energy distribution functions of silica packings have been published [65–71,73–75,78,79]. The majority of them deals with both bare and derivatized silicas in gas chromatography (GC). There are only a few analogous reports in the domain of liquid chromatography [67,69]. It seems that in solid–liquid systems,

the surface appears to be less heterogeneous [67,69]. For both GC and LC, the majority of the reported energy distribution functions are either left-hand side limited exponential distributions or quasi-Gaussian distributions skewed in the direction of high adsorption energies. In some cases, particularly in GC, multiple-peak distributions were also observed [65–71,73–75,78,79]. On the other hand, also for both GC and LC, derivatized silicas appear to be more homogeneous than bare silicas [68,69,71,72,74,78]. It seems that the silanization of the surface ''smooths'' the original multiple-peak energy distribution function of bare silica by blocking a considerable part of the high energy sites. Given the ill-posed nature of the problem of obtaining adsorption energy distributions only from adsorption equilibrium data [80–82], these results should be regarded with care. The aforementioned facts indicate the importance of accounting for the heterogeneity of the surface in order to achieve a better description of the adsorption equilibrium [8,11,18,50,52].

Several models of this type were applied to liquid chromatography data. The model most often employed is the bi-Langmuir model [3], mostly for the description of the adsorption data of enantiomers on chiral stationary phases [8,19,26,30–32]. In these cases, the first term accounts for chiral-selective interactions and the second term for the nonselective molecular interactions between the enantiomers and the stationary phase [26,30,31]. For enantiomers, it seems that the bi-Langmuir model gives a good representation of both single-component and competitive adsorption data [26,30,31]. This is possibly a result of the fact that separations of this kind fulfil fairly well the assumptions underlying the Langmuir model, such as the achievement of saturation of the selective sites at low loadings and the identical behavior of both components on the nonselective sites at higher loads. The bi-Langmuir model was also applied to the correlation of protein adsorption equilibria on reversed phases [8,32]. In this case a crude model can be assumed, according to which two types of sites exist for the adsorption of the protein. The hydrophobic and hydrophillic patches or pockets of the protein adsorb on the alkyl chains and the silanols, respectively [8]. The identification of the actual nature of the interactions involved in this case

is of course beyond the simplification [32], but it is possible that the model captures one essential feature. Other isotherm data exhibiting inflection points were accounted by the sum of a Langmuir and a Quadratic term [25]. These data refer to the adsorption of phenyldodecane from acetonitrile onto porous carbon. In this case, the Langmuir term accounts for adsorption on one type of site at very low surface coverages and could be explained by selective adsorption of the alkyl chains on surface defects (micropores). On the other hand, the quadratic term accounts for adsorption on a second type of site (the flat 001 graphite planes) on which adsorbate–adsorbate interactions involving the alkyl groups take place at moderate degrees of surface coverage.

Other adsorption data on reversed-phase packings have been fitted using the sum of Henry and Langmuir terms. This model was justified in terms of the limited solubility of the adsorbates in the liquid phase and the possible association phenomena taking place in the adsorbed layer [16,17,27]. The majority of these multiterm isotherms assume the existence of a discrete number of different types of adsorption sites on the surface, each of them with a different value of the adsorbate–adsorbent interaction energy, thus assuming a discrete energy distribution [35]. Theoretically, as stated before, a continuous distribution of such adsorption energies is more probable. There exists a number of classical isotherm models for heterogeneous surfaces with continuous energy distributions: The Freundlich [83], Langmuir–Freundlich [84] and Toth [85] models are a few examples. Although models of this type were applied to the correlation and prediction of multisolute adsorption equilibria [35], they are yet almost unapplied in the domain of liquid chromatography. The Freundlich model was applied to the correlation of single component adsorption data of angiotensin II as an alternative to the correlation using the bi-Langmuir model [8]. In both cases, a fair correlation is obtained despite the fact that the Freundlich model uses two parameters instead of the four parameters contained in the bi-Langmuir model. The result can be explained by the fact that the Freundlich model is a generalization of the Langmuir model for a heterogeneous surface with a distribution function corresponding to an exponential decay [35]. It is

probable, of course, that the actual interaction of the peptide with the surface is much more complex than the simple picture provided by the Freundlich model. However, it seems that both models capture an essential feature of the process: the adsorbent heterogeneity. The above discussion indicates that it seems important to incorporate both the adsorbent heterogeneity and the lateral interactions in the isotherm models intended for the description of multicomponent, reversed-phase adsorption data. To achieve this aim, a recently reported Jovanovic–Freundlich isotherm model for single component adsorption on a heterogeneous surface is extended in this study to multicomponent adsorption. The model is modified in order to account for possible lateral interactions in the adsorbed phase and is applied to single component and multicomponent RP-HPLC adsorption data.

2. Theory

Adsorption isotherm models relate the equilibrium concentrations of the given component in the bulk phase, C, and in the adsorbed phase, q. When the model of monolayer adsorption is considered to be valid, the concentration of the component in the adsorbed phase is often expressed through the surface coverage, $\theta = q/q_s$, where q_s is the value of the monolayer capacity for the given component [34]. As stated previously, a heterogeneous surface is characterized by an energy distribution function. For sites with equal values of the adsorbate–adsorbent interaction energy, the so called homotattic sites, a model valid for an homogeneous surface is applied, known as the local isotherm. The global or overall surface coverage on the heterogeneous surface for the single component adsorption case, $\theta_t(C)$, is obtained from the integral equation [35]

$$\theta_t = \frac{q}{q_s} = \int_0^\infty \theta(C, \epsilon) F(\epsilon) \, d\epsilon \qquad (1)$$

where $\theta(C, \epsilon)$ is the local adsorption isotherm for homotattic sites with an adsorption energy ϵ, and $F(\epsilon)$ is the adsorption energy distribution. Eq. (1) is the fundamental equation in the theory of adsorption on heterogeneous surfaces [35]. For multicomponent

adsorption, an expression analogous to Eq. (1) is applied, where the single component overall and local isotherms are replaced by the competitive overall and local isotherm models, with corresponding integration regions for each component and multidimensional energy distribution function [35]. As local isotherms for heterogeneous adsorption, the Langmuir, Fowler–Guggenheim, or Jovanovic models may be employed. The former two local isotherms are those most applied in practice for systems without or with lateral interactions, respectively [35].

2.1. Simple models for heterogeneous surfaces

The models of this group share the same assumptions already contained in the simple models for homogeneous surfaces, such as the Langmuir and Jovanovic models. The only nonideal effect they try to account for is the heterogeneity of the adsorbent surface. A significant number of these overall isotherms for single component adsorption were originally proposed on empirical or semiempirical grounds, with the sole aim of describing accurately and simply the behavior of real systems. Many of them may be obtained with a local Langmuir behavior if an appropriate choice of the energy distribution function is done [35]. Thus, they often reduce to either the Langmuir or the Jovanovic model in the case of a homogeneous surface. No other nonideal effects are considered in these models.

2.1.1. The Jovanovic–Freundlich model
This semiempirical model for single component adsorption was recently derived from a differential relationship relating the surface coverage and the bulk concentration of the adsorbate [86]. The model reduces to the Jovanovic model when the surface is homogeneous. It reduces to the monolayer isotherm at high concentrations but it does not obey the Henry law at low concentrations. This model was applied successfully to the correlation of single-component gas adsorption data obtained for a series of chlorinated hydrocarbons on silica gel. The energy distribution corresponding to this model for Jovanovic local behavior is a quasi-Gaussian function skewed

in the direction of high adsorption energies [87]. The model is described by the equation

$$\theta_t = 1 - e^{-(aC)^\nu} \qquad (2)$$

where ν is the heterogeneity parameter (with $0 < \nu \leq 1$) and a is a constant, function of the sole temperature, which characterizes the magnitude of the adsorbate–adsorbent interaction energy [86]. An extension of this model to competitive binary adsorption can be derived following a procedure reported by Jaroniec et al. [35]. The method is rigorous if there is a linear correlation between the adsorption energies of the components of the mixture. In this case, the heterogeneity parameter for the mixture ($\bar{\nu}$) should be the same for both compounds. Thus, their energy distributions have identical shape, with a mere shift of their positions on the energy axis. The extension is derived in terms of a localized adsorption model which neglects lateral interactions in the surface phase and assumes the monolayer character of this phase. The extension is represented by the following set of equations

$$\theta_{t1} = \frac{a_1 C_1}{a_1 C_1 + a_2 C_2} \left[1 - e^{-(a_1 C_1 + a_2 C_2)^{\bar{\nu}}}\right] \qquad (3a)$$

$$\theta_{t2} = \frac{a_2 C_2}{a_1 C_1 + a_2 C_2} \left[1 - e^{-(a_1 C_1 + a_2 C_2)^{\bar{\nu}}}\right] \qquad (3b)$$

where subscript 1 and 2 stand for the first and second component, respectively. This model is purely predictive. A purely predictive model is a competitive isotherm model which uses only the coefficients of the single-component isotherms. It allows prediction of competitive isotherm behavior knowing only the single-component adsorption behavior. It is rigorous, as stated earlier, for equal values of the heterogeneity parameter of both components. It is clear that, in practice, this condition can be satisfied but for a few systems only. In the general case, different adsorption energy distributions should be expected for different compounds.

For components exhibiting different adsorption energy distributions, a numerical procedure was proposed to extend the adsorbed solution theory models to heterogeneous surfaces (HAST) [88,89]. The HAST method is based on the assumption of a perfect positive correlation between the adsorption energies of different components, which means that

the adsorption sites are supposed to be ranked from low energies to high energies in the same way for all the adsorbates. The procedure is not simple and is best suited for systems represented by a significant number of experimental data points, in order to permit the extraction of the different parameters of the distribution. The results of the calculations depend usually on the adsorption energy distribution selected to fit best the single component data [90]. Moreover, because the classical energy distribution functions usually contain temperature independent parameters [35], it is desirable that adsorption data measured at different temperatures be available. A simpler alternative to the HAST model was proposed for adsorbates having different energy distributions [91]. In this case, the heterogeneity parameter in Eqs. (3a) and (3b) ($\bar{\nu}$) can be estimated as the arithmetic mean of the heterogeneity parameters for the single components obtained by identification. Similar results were obtained with either the analytical model with mean values of the heterogeneity parameter or a numerical procedure corresponding to HAST [91]. The main gain of course, resides in the use of a simpler model requiring less computation. For a homogeneous surface, the model represented by Eqs. (3a) and (3b) reduces to the competitive Jovanovic model [92], given by these simpler equations

$$\theta_1 = \frac{K_1 C_1}{K_1 C_1 + K_2 C_2} \left[1 - e^{-(K_1 C_1 + K_2 C_2)}\right] \qquad (4a)$$

$$\theta_2 = \frac{K_2 C_2}{K_1 C_1 + K_2 C_2} \left[1 - e^{-(K_1 C_1 + K_2 C_2)}\right]. \qquad (4b)$$

Note that the Henry constant H is equal to the product $q_s K$.

2.1.2. The Langmuir–Freundlich model

This model was analyzed by Sips [84], who found that its energy distribution function corresponds to a symmetrical quasi-Gaussian function. The model reduces to the monolayer but does not obey the Henry law. At low concentrations, the model reduces to the Freundlich model. The Langmuir–Freundlich model reduces to the Langmuir model for the case of a homogeneous surface. The single component Langmuir–Freundlich model is

$$\theta_t = \frac{(aC)^{\nu}}{1 + (aC)^{\nu}} \tag{5}$$

The Jaroniec extension of the model is [35];

$$\theta_{t1} = \frac{a_1 C_1}{a_1 C_1 + a_2 C_2} \frac{(a_1 C_1 + a_2 C_2)^{\bar{\nu}}}{[1 + (a_1 C_1 + a_2 C_2)^{\bar{\nu}}]} \tag{6a}$$

$$\theta_{t2} = \frac{a_2 C_2}{a_1 C_1 + a_2 C_2} \frac{(a_1 C_1 + a_2 C_2)^{\bar{\nu}}}{[1 + (a_1 C_1 + a_2 C_2)^{\bar{\nu}}]}. \tag{6b}$$

Note that Eqs. (6a) and (6b) are also purely predictive. Another competitive extension of the Langmuir–Freundlich model is also commonly applied [34].

$$\theta_{t1} = \frac{(a_1 C_1)^{\nu_1}}{1 + (a_1 C_1)^{\nu_1} + (a_2 C_2)^{\nu_2}} \tag{7a}$$

$$\theta_{t2} = \frac{(a_2 C_2)^{\nu_2}}{1 + (a_1 C_1)^{\nu_1} + (a_2 C_2)^{\nu_2}} \tag{7b}$$

The model of Eqs. (7a) and (7b) is also purely predictive. Note that the extension represented by Eqs. (7a) and (7b) does not require the equality of the heterogeneity parameter (ν_1 and ν_2) for both components.

2.1.3. Other models

There exists a great variety of adsorption isotherm models for heterogeneous surfaces without lateral interactions. Other important classical models are the Freundlich [83], Toth [85], Redlich–Peterson [93], UNILAN [94], Temkin–Pyzhev [95], Dubinin–Radushkevich [96], Dubinin–Astakhov [97], Generalized Freundlich [98] and Marckzewsky–Jaroniec [99] models. Among these models, the Langmuir–Freundlich model has been used extensively for the description of single component and competitive experimental data on heterogeneous surfaces [35]. For this reason, we included the Langmuir–Freundlich model in the present study in order to compare its results with the results provided by the Jovanovic–Freundlich model regarding the prediction of the experimental data analyzed here.

An alternative to the classical models employed in this study is the use of models based on the numerical solution of the integral Eq. (1), for any given combination of an adsorption energy distribu-

tion and a local isotherm model [89]. This last approach is not covered in this paper.

2.2. Combined models for heterogeneous surfaces

These models attempt to account for additional nonideal effects, such as possible lateral interactions in the adsorbed layer. The importance of taking into account in adsorption studies possible adsorbate–adsorbate interactions in the monolayer has often been stressed [22,23,27,59]. Several models of this type have been reported. The Temkin model for heterogeneous surfaces has been extended to take into account lateral interactions in the case of protein adsorption [100]. Several models which consider a uniform distribution of the adsorption energy were also extended to account for adsorbate–adsorbate interactions in the monolayer [101,102]. It is worth noting that some of these models can also be derived using the procedure proposed by Jaroniec et al. [103], intended for the extension of heterogeneous-surface models without lateral interactions to the situation when lateral interactions could take place. Several derivations employing a statistical thermodynamics approach show that the adsorption of a binary mixture on a homogeneous surface can be represented by the following adsorption isotherm model [38,104,105]

$$K_1 C_1 = \frac{\theta_1}{(1 - \theta_1 - \theta_2)^{r_1}} e^{-r_1(\chi_1 \theta_1 + \chi_{12} \theta_2)} \tag{8a}$$

$$K_2 C_2 = \frac{\theta_2}{(1 - \theta_1 - \theta_2)^{r_2}} e^{-r_2(\chi_{21} \theta_1 + \chi_2 \theta_2)} \tag{8b}$$

In these equations, the fractional coverage of the i-component is $\theta_i = r_i q_i / q_{sl}$, where r_i is the number of lattice sites occupied by one molecule of the i-component and q_{sl} is the total number of lattice sites. So, r_i is a measure of the adsorbate size in the monolayer and the model given by Eqs. (8a) and (8b) makes it possible to account for the differences in the monolayer capacities of the adsorbates, which is important in adsorption studies [8,22]. Monolayer capacities in LC systems are usually interpreted in terms of the Langmuir model [4,8,9,16,18,27]. However, since the Langmuir model is a crude approximation, especially at high coverages, the identified

parameters are likely to be in error. The parameters χ_1 and χ_2 in Eqs. (8a) and (8b) account for the energy of interaction between molecules of the first and the second component, respectively. The parameters χ_{12} and χ_{21} (which have, in principle, the same value) account for the cross-interactions between molecules of component 1 and of component 2. If there are no great differences in size or polarity between the molecules of the two components undergoing interactions, the value of the cross parameter can be estimated using the geometric mean of the single component parameters [36], i.e.

$$\chi_{12} = \chi_{21} = (\chi_1 \chi_2)^{1/2} \qquad (9)$$

For single component adsorption, the model is represented by the expression

$$KC = \frac{\theta}{(1-\theta)^r} \, e^{-r\chi\theta} \qquad (10)$$

In the particular case in which the molecules of each component occupy only one adsorption site in the lattice, $r_1 = r_2 = 1$, this model reduces to the multicomponent Fowler–Guggenheim (FG) model, when derived using the Bragg–Williams approximation [105].

$$K_1 C_1 = \frac{\theta_1}{1-\theta_1-\theta_2} \, e^{-(\chi_1\theta_1 + \chi_{12}\theta_2)} \qquad (11a)$$

$$K_2 C_2 = \frac{\theta_2}{1-\theta_1-\theta_2} \, e^{-(\chi_{21}\theta_1 + \chi_2\theta_2)} \qquad (11b)$$

For single component adsorption, the Fowler model is [55]

$$KC = \frac{\theta}{1-\theta} \, e^{-\chi\theta} \qquad (12)$$

The model represented by Eq. (10) can be used as local isotherm model in Eq. (1) to describe the adsorption on a heterogeneous surface of components of different sizes undergoing lateral interactions in the adsorbed layer. The parameter q_{sl} should be maintained constant for all components when analyzing single-component data because this parameter is a property of the lattice. The solution of this problem is numerical and involves the identification of a significant number of adjustable parameters. Thus, the use of this model is best suited when an

abundant set of single-component data is analyzed for the identification of all the parameters. The following simplifications are needed in order to render the problem tractable: (i) for adsorbates of similar size the FG model can be used as local isotherm model; (ii) the exponential terms in Eqs. (11a) and (11b) reflect the nonideal behavior of the adsorbed phase; their definition assumes a random distribution of sites on the heterogeneous surface; therefore, we assume that the nonideal behavior of the adsorbed phase is a function of the total coverage and, within this assumption, that the local values of the adsorbed phase concentration found in the exponential terms mentioned above can be replaced by the overall concentrations on the whole heterogeneous surface; and (iii) the extension of any single component heterogeneous isotherm model without lateral interactions to the case of heterogeneous multicomponent equilibria with lateral interactions is possible assuming the existence of a linear correlation between the adsorption energies of the components of the mixture. As stated before, the components of the mixture should have equal values of the heterogeneity parameter in order to fulfil the condition of identical shape of the energy distribution functions which are merely located in different positions along the energy axis.

Adopting the aforementioned simplifications, analytical models for multicomponent adsorption with lateral interactions on heterogeneous surfaces can be obtained. This procedure was proposed and discussed by Jaroniec and coworkers using a statistical thermodynamics approach [35]. The resulting models, however, have not been verified extensively with experimental data, especially with data for multisolute adsorption liquid–solid equilibrium [35].

2.2.1. The Fowler–Guggenheim/Langmuir–Freundlich (FG/LF) model

Keeping in mind the aforementioned assumptions, a single component FG/LF model was proposed [35], represented by the equation

$$\theta_t = \frac{(aC \, e^{\chi\theta_t})^\nu}{1 + (aC \, e^{\chi\theta_t})^\nu} \qquad (13)$$

To simplify the writing of the multicomponent

isotherm equations, let us define the following functions,

$$\Phi_1 = \frac{a_1 C_1 e^{\chi_1 \theta_{t1} + \chi_{12}\theta_{t2}}}{[a_1 C_1 e^{\chi_1 \theta_{t1} + \chi_{12}\theta_{t2}} + a_2 C_2 e^{\chi_{21}\theta_{t1} + \chi_2 \theta_{t2}}]} \qquad (14a)$$

$$\Phi_2 = \frac{a_2 C_2 e^{\chi_{21}\theta_{t1} + \chi_2 \theta_{t2}}}{[a_1 C_1 e^{\chi_1 \theta_{t1} + \chi_{12}\theta_{t2}} + a_2 C_2 e^{\chi_{21}\theta_{t1} + \chi_2 \theta_{t2}}]} \qquad (14b)$$

The multicomponent FG/LF is represented by the following set of equations [35]

$$\theta_{t1} = \Phi_1 \frac{[a_1 C_1 e^{\chi_1 \theta_{t1} + \chi_{12}\theta_{t2}} + a_2 C_2 e^{\chi_{21}\theta_{t1} + \chi_2 \theta_{t2}}]^{\bar{\nu}}}{\{1 + [a_1 C_1 e^{\chi_1 \theta_{t1} + \chi_{12}\theta_{t2}} + a_2 C_2 e^{\chi_{21}\theta_{t1} + \chi_2 \theta_{t2}}]^{\bar{\nu}}\}} \qquad (15a)$$

$$\theta_{t2} = \Phi_2 \frac{[a_1 C_1 e^{\chi_1 \theta_{t1} + \chi_{12}\theta_{t2}} + a_2 C_2 e^{\chi_{21}\theta_{t1} + \chi_2 \theta_{t2}}]^{\bar{\nu}}}{\{1 + [a_1 C_1 e^{\chi_1 \theta_{t1} + \chi_{12}\theta_{t2}} + a_2 C_2 e^{\chi_{21}\theta_{t1} + \chi_2 \theta_{t2}}]^{\bar{\nu}}\}} \qquad (15b)$$

Although the previous set of equations includes complex nonlinear functions of the adsorbed phase concentrations, the model is purely predictive, based solely on single component parameters. Note that for $\nu = 1$, Eqs. (15a) and (15b) reduce to the competitive FG model represented by Eqs. (11a) and (11b).

2.2.2. The Fowler–Guggenheim/Jovanovic–Freundlich (FG/JF) model

Like for the extension of the Langmuir–Freundlich model described in Section 2.2.1, other single-component heterogeneous-surface models without lateral interactions can be extended to take into account the possible adsorbate–adsorbate interactions in the monolayer. We extended the Jovanovic–Freundlich model [86] using the same procedure [35] leading to the FG/LF model presented above. The single-component isotherm obtained is represented by the following equation

$$\theta_t = 1 - e^{-(aC e^{\chi \theta_t})^{\bar{\nu}}} \qquad (16)$$

The corresponding competitive model, is represented by the following set of equations

$$\theta_{t1} = \Phi_1 \{1 - e^{-[a_1 C_1 e^{\chi_1 \theta_{t1} + \chi_{12}\theta_{t2}} + a_2 C_2 e^{\chi_{21}\theta_{t1} + \chi_2 \theta_{t2}}]^{\bar{\nu}}}\} \qquad (17a)$$

$$\theta_{t2} = \Phi_2 \{1 - e^{-[a_1 C_1 e^{\chi_1 \theta_{t1} + \chi_{12}\theta_{t2}} + a_2 C_2 e^{\chi_{21}\theta_{t1} + \chi_2 \theta_{t2}}]^{\bar{\nu}}}\} \qquad (17b)$$

In the special case of a homogeneous surface, the single component model represented by Eq. (16) reduces to

$$\theta = 1 - e^{-(KC e^{\chi \theta})} \qquad (18)$$

In turn, Eq. (18) reduces to the Jovanovic model [46] if the lateral interactions are neglected (i.e. if $\chi = 0$). Accordingly, the multicomponent model represented by Eqs. (17a) and (17b) reduces to the model described by the following equations in the case of a homogenous surface

$$\theta_1 = \Psi_1 \{1 - e^{-[K_1 C_1 e^{\chi_1 \theta_1 + \chi_{12}\theta_2} + K_2 C_2 e^{\chi_{21}\theta_1 + \chi_2 \theta_2}]}\} \qquad (19a)$$

$$\theta_2 = \Psi_2 \{1 - e^{-[K_1 C_1 e^{\chi_1 \theta_1 + \chi_{12}\theta_2} + K_2 C_2 e^{\chi_{21}\theta_1 + \chi_2 \theta_2}]}\} \qquad (19b)$$

where

$$\Psi_1 = \frac{K_1 C_1 e^{\chi_1 \theta_1 + \chi_{12}\theta_2}}{[K_1 C_1 e^{\chi_1 \theta_1 + \chi_{12}\theta_2} + K_2 C_2 e^{\chi_{21}\theta_1 + \chi_2 \theta_2}]} \qquad (20a)$$

$$\Psi_2 = \frac{K_2 C_2 e^{\chi_{21}\theta_1 + \chi_2 \theta_2}}{[K_1 C_1 e^{\chi_1 \theta_1 + \chi_{12}\theta_2} + K_2 C_2 e^{\chi_{21}\theta_1 + \chi_2 \theta_2}]} \qquad (20b)$$

In turn, Eqs. (19a) and (19b) reduce to the competitive Jovanovic model [106] given by Eqs. (4a) and (4b) if the lateral interactions are neglected (i.e. if $\chi_1 = \chi_2 = \chi_{21} = \chi_{12} = 0$).

3. Experimental

3.1. Origin of experimental data

The experimental data analyzed in this study were previously reported [23]. They describe the single-component and competitive adsorption behavior of 2-phenylethanol (PE) and 3-phenylpropanol (PP) on a chemically bonded, C_{18} silica (Vydac, Hesperia, CA, USA) from a (50:50, v/v) solution of methanol and water used as the mobile phase. These data were obtained via frontal analysis, through the retention time of breakthrough curves. Competitive data were acquired following the procedure described by Frenz et al. [10], which involves also the determination of

the composition of the eluent during elution of the intermediate plateau in a binary breakthrough curve.

The experimental setup included a Gilson (Middleton, WI, USA) Model 302 pump, a ten-port Valco (Houston, TX, USA) valve, and a Spectroflow (Applied Biosystems, Ramsey, NJ, USA) 757 UV detector. The concentration of the adsorbates in the mobile phase at each intermediate plateau was determined using an on-line HPLC system assembled with a Beckman Berkeley, CA, USA) Model 110B pump, a Valco four-port valve, a YMC (Wilmington, NC, USA) cartridge column and an additional Spectroflow detector. Both UV signals were acquired with a Gilson Model 621 interface box and monitored with a microcomputer.

3.2. Nonlinear least squares analysis

Regressions of the experimental data to the adsorption isotherm models were performed using a corrected Gauss–Newton algorithm. For models which are implicit with respect to the solid phase concentration, such as the heterogeneous-surface models with lateral interactions, the numerical inversion of the models with respect to the surface coverage was accomplished using a modification of the Powell hybrid method for the solution of nonlinear equations. These algorithms are implemented in the NAG Library [106]. The calculations were performed on the mainframe computers of the University of Tennessee Computer Center. In this study we are concerned with the search for models allowing the prediction of competitive equilibria using only the single-component identified parameters.

When fitting the single component data, the response surface of the optimization problem often exhibits several minima (global and/or local), especially when the model exhibits a significant degree of nonlinear behavior, for example, in the case of heterogeneous-surface models with lateral interactions. To avoid being trapped in local minima, we carried out the identification process several times, using a different initial guess vector each time. This is a convenient empirical way to determine if the solution converges toward the global minima. However, the parameters already identified for simpler models like the Langmuir model, previously reported [39], were always used for one of the initial guess

vectors. The procedure calculates the values of the isotherm parameters which minimize the residual sum of squares (RSS) for both components

$$\text{RSS} = \sum_{i=1}^{n} (q_{\text{ex},i} - q_{\text{t},i})^2 \tag{21}$$

where $q_{\text{ex},i}$ are the elements of the vector q_{ex} containing the given experimental adsorbed phase concentrations (n data points of the single component data or the whole set of both single component and competitive data) of phenylalcohols and $q_{\text{t},i}$ are the corresponding theoretical values calculated by the model being studied.

The selection of the most adequate model was performed using the Fisher's test. The model selected was the one which exhibited the highest value of the following Fisher parameter [107]:

$$F_{\text{calc}} = \frac{(n-l) \sum_{i=1}^{n} (q_{\text{ex},i} - \overline{q_{\text{ex}}})^2}{(n-1) \sum_{i=1}^{n} (q_{\text{ex},i} - q_{\text{t},i})^2} \tag{22}$$

where $\overline{q_{\text{ex}}}$ is the mean value of the vector q_{ex} and l is the number of adjusted parameters of the model. Note that Eq. (22) does not represent the conventional use of the Fisher distribution because there is only one adsorbed phase data point for each mobile phase concentration data point. The second factor in the RHS of Eq. (22) contains the sum of residuals given by Eq. (21) in the denominator. So, the higher F_{calc}, the better the model correlates the data. The first term in the numerator of the RHS of Eq. (22) decreases with increasing the number of parameters in the model. So, Eq. (22) shows to which extent the introduction of a new parameter in the model can actually decrease in a significant way the RSS. Thus, Eq. (22) allows the comparison of models having a different number of parameters [107].

4. Results and discussion

The results of the regression analysis of the models evaluated are reported in Tables 1–3. Table 4 compares the results obtained with different models in this and in previous studies [23,39,59]. The corresponding values of the RSS are listed separately

Table 1
Summary of the nonlinear regression analysis

No.	Model	Parameters	RSS		Σ RSS	F_{calc}
			PE	PP		
1	Eqs. (4a) and (4b)	$q_{s1}=q_{s2}=79$ $K_1=0.029$ $K_2=0.057$	0.002 (1.972)	0.6962 (231.4)	234.1	25.19
2	Langmuir	$q_{s1}=154$ $K_1=0.015$ $q_{s2}=134$ $K_2=0.035$	0.002 (3.08)	0.444 (249.61)	253.14	22.99
3	Eqs. (11a) and (11b)	$q_{s1}=75$ $K_1=0.03047$ $\chi_1=0.6434$ $q_{s2}=316$ $K_2=0.0153$ $\chi_2=-2.037$	0.001 (1.608)	0.225 (79.98)	81.82	69.2
4	Eqs. (11a) and (11b)	$q_{s1}=75$ $K_1=0.03047$ $\chi_1=0.6434$ $q_{s2}=316$ $K_2=0.0153$ $\chi_2=-2.037$	0.001 (9.3)	0.225 (370.3)	379.8	14.91
5	Eqs. (11a) and (11b)	$q_{s1}=154$ $K_1=0.015$ $\chi_1=0.0$ $q_{s2}=316$ $K_2=0.0153$ $\chi_2=-2.037$	0.002 (3.459)	0.225 (143.0)	146.7	38.6
6	Eqs. (11a) and (11b)	$q_{s1}=75$ $K_1=0.03047$ $\chi_1=0.6434$ $q_{s2}=134$ $K_2=0.035$ $\chi_2=0.0$	0.001 (1.561)	0.444 (240)	241.6	23.44
7	Eqs. (11a) and (11b)	$q_{s1}=q_{s2}=273$ $K_1=0.008444$ $\chi_1=-0.8631$ $K_2=0.01774$ $\chi_2=-1.6203$	0.0031 (2.365)	0.2433 (255.9)	258.5	22.21
8	Eqs. (19a) and (19b)	$q_{s1}=51$ $K_1=0.04479$ $\chi_1=0.2525$ $q_{s2}=169$ $K_2=0.02855$ $\chi_2=-1.0862$	0.001 (1.35)	0.243 (123.3)	124.9	45.33

Table 1
Summary of the nonlinear regression analysis

No.	Model	Parameters	RSS		Σ RSS	F_{calc}
			PE	PP		
9	Eqs. (19a) and (19b)	$q_{s1}=51$	0.001	0.243	348.1	16.27
		$K_1=0.04479$				
		$\chi_1=0.2525$	(7.71)	(340.1)		
		$q_{s2}=169$				
		$K_2=0.02855$				
		$\chi_2=-1.0862$				
10	Eqs. (19a) and (19b)	$q_{s1}=79$	0.002	0.243	141.2	40.1
		$K_1=0.029$				
		$\chi_1=0.0$	(3.37)	(137.6)		
		$q_{s2}=169$				
		$K_2=0.02855$				
		$\chi_2=-1.0862$				
11	Eqs. (19a) and (19b)	$q_{s1}=51$	0.001	0.7	226.6	24.99
		$K_1=0.04479$				
		$\chi_1=0.2525$	(1.23)	(224.7)		
		$q_{s2}=79$				
		$K_2=0.057$				
		$\chi_2=0.0$				
12	Eqs. (19a) and (19b)	$q_{s1}=q_{s2}=180$	0.0032	0.2463	251.3	22.84
		$K_1=0.01282$				
		$\chi_1=-0.7284$	(2.403)	(255.6)		
		$K_2=0.02693$				
		$\chi_2=-1.2267$				

Homogeneous models.

Table 2
Summary of the nonlinear regression analysis

No.	Model	Parameters	RSS		Σ RSS	F_{calc}
			PE	PP		
1	Eqs. (6a), (6b), (7a), (7b)	$q_{s1}=154$	0.002	0.0272	63.25[a]	89.52[a]
		$a_1=0.015$				
		$\nu_1=1.0$	(28.04)[a]	(35.18)[a]	270.3[b]	20.95[b]
		$q_{s2}=216$				
		$a_2=0.01566$	(1.31)[b]	(274)[b]		
		$\nu_2=0.8986$				
2	Eqs. (3a) and (3b)	$q_{s1}=74$	0.002	0.0221	66.20	85.53
		$a_1=0.029$				
		$\nu_2=1.0$	(18.61)	(47.57)		
		$q_{s2}=126$				
		$a_2=0.02781$				
		$\nu_2=0.891$				

Heterogeneous models without lateral interactions.
[a] Eqs. (3a) and (3b).
[b] Eqs. (7a) and (7b).

Table 3
Summary of the nonlinear regression analysis

No.	Model	Parameters	RSS		Σ RSS	F_{calc}
			PE	PP		
1	Eqs. (15a) and (15b)	$q_{s1} = 59$	0.0009	0.0035	39.53	139.26
		$a_1 = 0.03698$				
		$\chi_1 = 0.9126$	(31.12)	(8.405)		
		$\nu_1 = 0.9865$				
		$q_{s2} = 112$				
		$a_2 = 0.02424$				
		$\chi_2 = 1.4174$				
		$\nu_2 = 0.8251$				
2	Eqs. (17a) and (17b)	$q_{s1} = 42$	0.0009	0.0036	40.88	
		$a_1 = 0.05292$				134.66
		$\chi_1 = 0.4122$	(19.6)	(21.27)		
		$\nu_1 = 0.988$				
		$q_{s2} = 83$				
		$a_2 = 0.03591$				
		$\chi_2 = 0.6672$				
		$\nu_2 = 0.832$				

Heterogeneous models with lateral interactions.

for each component in each case. The values be-
tween parentheses correspond to the competitive
data. The global value of the RSS for the whole set
of single and competitive data (Σ RSS) is also given,
as well as the value calculated for the Fisher
parameter. Figs. 1 and 2 illustrate the correlation of
the single component data (SCD) and the prediction
of binary data employing the FG/LF model, for PE
and PP, respectively. Figs. 3 and 4 illustrate the
results of a similar analysis employing the FG/JF
model.

4.1. Models for homogeneous surfaces

In order to establish further comparisons with the
models for heterogeneous surfaces tested in this
study, it is useful to comment on the results obtained
with several models for homogeneous surfaces.

4.1.1. The Jovanovic model
In a previous study we analyzed the data of both
phenylalcohols in terms of the Jovanovic model [39].
We also used several extensions of the Jovanovic
model for competitive adsorption [47,48]. These
extended models contain cross-interaction parameters
whose values must be identified from the binary
data. So, the prediction of binary equilibria employ-

ing only the information derived from the analysis of
the single component data is not possible with these
models. However, the extension of the Jovanovic
model to competitive adsorption which is represented
by Eqs. (4a) and (4b) permits the calculation of
multicomponent equilibria using only the parameters
of the single-component isotherm model, identified
from single component experimental data, as previ-
ously reported [39]. The result of the calculation is
reported in Table 1, entry 1. For the sake of
comparison, the results obtained with the Langmuir
model and previously reported [39] are also given in
Table 1, entry 2. Note that the prediction of the
competitive data for both PE and PP given by the
Jovanovic model is better than the prediction given
by the competitive Langmuir model but that the
improvement is not great.

4.1.2. The Fowler model
Initially, it is useful to assess if the differences in
size between the adsorbates would be a significant
source of nonideality in the system under considera-
tion. The Van der Waals areas (A_{wi}) and volumes
(V_{wi}) of both PE and PP, calculated according to the
Bondi method [108], are given in Table 5, together
with the areas of adsorbate–adsorbent contact A_{si},
calculated following Snyder [109]. Note that the

Table 4
Summary of the nonlinear regression analysis

No.	Model	RSS		Σ RSS	F_{calc}	Ref.
		PE	PP			
1	Langmuir and LeVan–Vermeulen	0.002 (3.08)	0.444 (249.61)	253.14	22.99	[23]
2	Eqs. (4a) and (4b)	0.002 (1.972)	0.6962 (231.4)	231.4	25.19	T.S.
3	Eqs. (11a) and (11b)	0.001 (1.608)	0.225 (79.98)	81.82	69.20	T.S
4	Eqs. (19a) and (19b)	0.001 (1.35)	0.243 (123.3)	124.9	45.33	T.S.
5	Ruthven	0.0018 (30.25)	0.0051 (360.1)	390.36	14.51	[59]
6	Moreau et al.	0.001 (2.49)	0.32 (121.7)	124.51	45.48	[59]
7	Kiselev	0.0017 (2.42)	0.20 (114.46)	117.08	48.36	[59]
8	Eqs. (6a) and (6b)	0.002 (28.04)	0.0272 (35.18)	63.25	89.52	T.S.
9	Eqs. (3a) and (3b)	0.002 (18.61)	0.0221 (47.57)	66.20	85.53	T.S.
10	Eqs. (15a) and (15b)	0.0009 (31.12)	0.0035 (8.405)	39.53	139.26	T.S.
12	Eqs. (17a) and (17b)	0.0009 (19.6)	0.0036 (21.27)	40.88	134.66	T.S.

T.S. – This study.

values of A_{si} are approximately half those of A_{wi}, according to Snyder's assumption that the molecules lie flat on the adsorbent surface [109]. Recalling that according to the results of the solvophobic theory of reversed-phase LC [110] the contact area adsorbate–adsorbent at infinite dilution is about 20% of A_{wi} and taking into account the values in Table 5, it is clear that the area of contact of PP should be slightly larger (ca. 10%) than the area of contact of PE. If we assume as a first approximation that the area of contact is independent of the surface coverage, the value of the parameter r_2 in equations should be slightly higher than the value of the corresponding parameter r_1. Taking into account that the individual monolayer capacities are defined as $q_{si} = q_{sl}/r_i$, it follows that the monolayer capacity should be slightly higher for PE than for PP. This approximation may be crude because it is possible that the area of

adsorbate–adsorbent contact in a compact monolayer be different from the value at infinite dilution, due to the adsorbate–adsorbate interactions. Note that because of the direct proportionality established between r_i and A_{wi} within the framework of the solvophobic theory, it follows that

$$\frac{q_{s1}}{q_{s2}} = \frac{A_{w2}}{A_{wi}} \tag{23}$$

Assuming as a first, crude approximation, that the Langmuir model is valid for the system under consideration, the LHS of Eq. (23) can be calculated using the values of the monolayer capacities previously reported [39]. The result is equal to 1.149. On the other hand, the RHS of Eq. (23) can be computed using the values from Table 5, giving a value equal to 1.144. The match is satisfactory and shows that the values obtained are close to 1. It seems that the
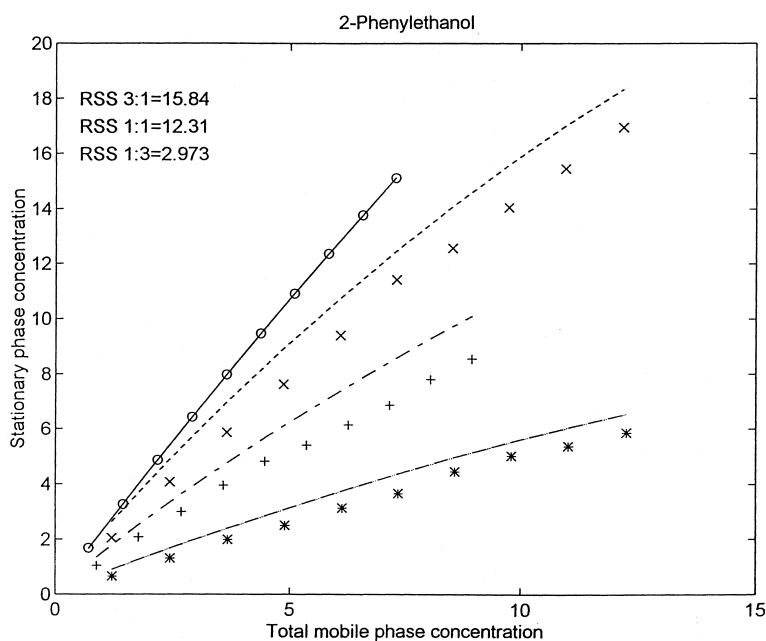
Fig. 1. Comparison between experimental adsorption data of 2-phenylethanol and values calculated using the competitive FG/LF model [Eq. (22)] and single component parameters. For mixtures, the mobile phase concentration is expressed via the relative composition of PE and PP. All concentrations in mg/ml. Symbols: data for single component, ○; data for 3:1 mixtures (three parts of PE and one part of PP), ×; data for 1:1 mixtures (equal parts of both components), +; and data for 1:3 mixtures (one part of PE and three parts of PP), *. On the graph is also indicated the RSS calculated for each set of experiments performed with a constant relation of the mobile phase concentrations of the phenylalcohols.

monolayer capacities derived from the Langmuir model are consistent with the results derived from the solvophobic theory for dilute solutions of the adsorbates [110].

The previous calculation shows that as a first approximation, the areas of contact adsorbate–adsorbent are similar. Then, the Fowler model represented by Eq. (12) can be used to analyze the data in terms of an homogenous model with lateral interactions. Note that this version of the Fowler model is different from the version employed in some of our previous studies, in which the adsorbate–adsorbent equilibrium constant (K_i) had the same value for both components [23,59]. The model represented by Eqs. (11a) and (11b) releases this restriction. The results of the regression analysis are given in Table 1, entries 3–7. The fit of the Fowler model to the single component data (SCD), see Table 1, entries 3–4; gives a higher value of the monolayer capacity for PP while on the other hand it gives a higher value of the low concentration equilibrium constant

(LCEC) for PE. These values are related by the Henry constant which is higher for PP. The fact that q_{s1} is not equal to q_{s2} within the framework of these models is an inconsistency possibly due to the application of a relatively simple model to a rather complex experimental system.

The value of the adsorbate–adsorbate interaction parameter is positive for PE and negative for PP. The absolute value is higher for PP. The fact that $\chi_1 > 0$ and $\chi_2 < 0$ renders the exponents in Eq. (12) negative and positive, respectively. Although, in principle, these values may be positive or negative [55], it is clear that positive values of the exponent imply that repulsion forces between molecules predominate in the adsorbed layer. Conversely, negative values of the exponent imply that attraction forces between molecules predominate. Taking into account the hydrogen-bonding nature of both phenylalcohols it is difficult to imagine that repulsive interactions could exist between their molecules in the monolayer at low or intermediate surface coverages. When the
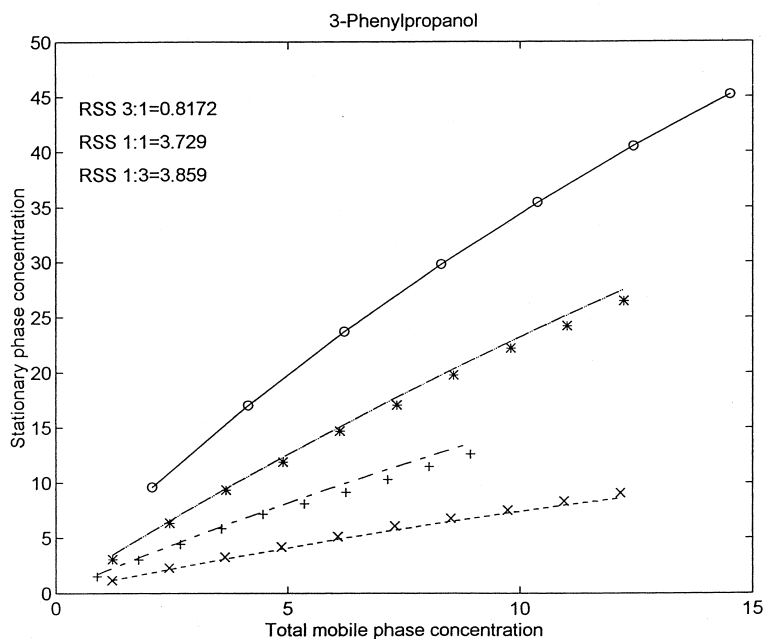
Fig. 2. Same as Fig. 1 but for data for 3-phenylpropanol.

layer is not heavily packed it is reasonable to expect that the molecules are not located close to each other and then the attraction forces should predominate. Moreover, it is difficult to accept that the interactions between molecules of PE be qualitatively different from the interactions between PP molecules. The contradiction between the physical meaning of the values of the adsorbate–adsorbate interaction parameter for the two components has been pointed out previously in the study of the extension of the Fowler model which considers equal values of the LCEC for both components [59]. This result and the fact that the identified values of the monolayer capacities are different, renders the model thermodynamically inconsistent for the data under consideration [34].

To calculate the competitive data based on the parameters identified with the SCD, we can use the geometric mean combining rule for the determination of the cross-interaction parameter, χ_{12}. However, a difficulty arises because of the different signs of the two individual values of χ. We decided to use the absolute values under the square root and later to assign either a positive or a negative value to the calculated χ_{12} parameter. The result obtained when

the negative sign is assigned to the calculated value of χ_{12} is given in Table 1, entry 3. In this case, it is implicitly assumed that the behavior of PP dominates the behavior of the binary monolayer. Conversely, the result obtained when using the positive sign, hence assuming that the behavior of the mixed monolayer is similar to the behavior of the pure PE monolayer, is reported in Table 1, entry 4. In the former case, repulsive interactions are assumed in the monolayer, in the later case it is attractive interactions which are assumed. The assumption of repulsive interactions gives clearly a better prediction of the competitive data, which is contradictory with physical intuition. This situation is probably related to the fact that the absolute value of the parameter χ_2 is about three times larger than that of χ_1. The Fowler model assuming attractive interactions gives a result which is even worse than the Langmuir model. Finally, it does not make much sense that an improvement in the fit of the PP SCD requires the assumption of repulsive forces between PP molecules in the monolayer.

Let us now make the more reasonable assumption that only one type of interaction (repulsive, attractive, or none at all) predominates in the monolayer.
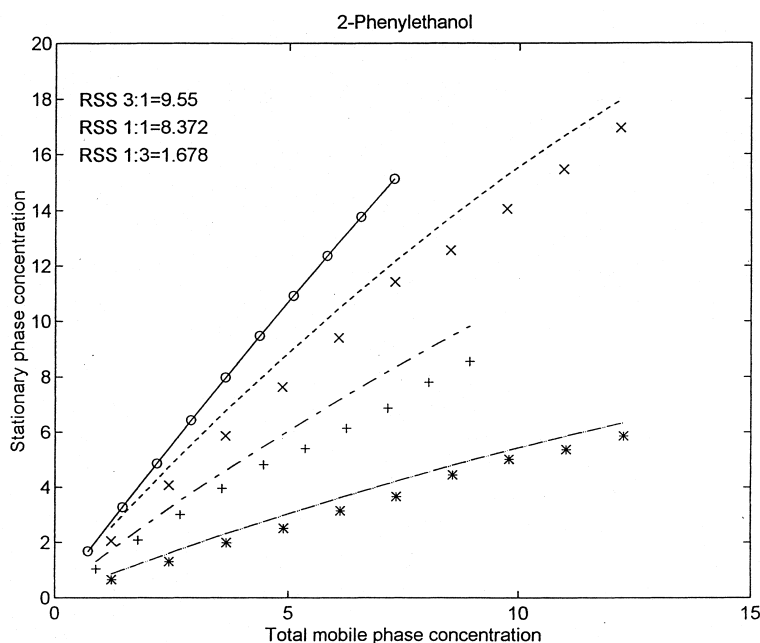
Fig. 3. Comparison between experimental adsorption data of 2-phenylethanol and values calculated using the competitive FG/JF model [Eq. (23)] and single component parameters. For mixtures, the mobile phase concentration is expressed via the relative composition of PE and PP. All concentrations in mg/ml. Symbols: data for single component, ○; data for 3:1 mixtures (three parts of PE and one part of PP), ×; data for 1:1 mixtures (equal parts of both components), +; and data for 1:3 mixtures (one part of PE and three parts of PP), *. On the graph is also indicated the RSS calculated for each set of experiments performed with a constant relation of the mobile phase concentrations of the phenylalcohols.

The results obtained when one assumes only repulsive or no interactions, i.e. that $\chi_i \leq 0$, are given in Table 1, entry 5. They are similar to those previously reported [59]. Note that the values of the LCEC for both components are almost equal. This fact explains why a very good fit of the combined two sets of SCD data was obtained previously with the assumption of equal values of the K_i parameters for the two components [59]. In this case, the best fit of the PE SCD is still given by the Langmuir model ($\chi_1 = 0$) and χ_{12} is set equal to χ_2, thus assuming again that the adsorbate–adsorbate interactions in the monolayer are dominated by PP. Note that the prediction of the multicomponent data set obtained with the condition $\chi_i \leq 0$ is worse than the prediction obtained when considering both attractive and repulsive interactions in the adsorbed layer (Table 1, entry 3). Still, the prediction is better than the one given by the competitive Langmuir model, which assumes no adsorbate–adsorbate interactions at all in the monolayer.

On the other hand, if one assumes that there cannot be repulsive interactions (i.e. $\chi_i \geq 0$), we obtain the converse result: the PE data are best described by the Fowler model while the PP data are best described by the Langmuir model (Table 1, entry 6). Note that in this case also, the two values of the LCEC are similar. In this case, χ_{12} is set equal to χ_1 and the competitive data calculated. The result obtained is worse than in the previous case (repulsive interactions in the monolayer). Although the prediction is slightly better than the one given by the Langmuir model (Table 1, entry 2), it is worse than the one given by the Jovanovic model (Table 1, entry 1), a model which does not consider any adsorbate–adsorbate interactions in the monolayer. Finally, the requirement for thermodynamic consistency states that the monolayer capacities should be the same for both components. Taking this restriction into account, the whole set of SCD was fitted to the Fowler model. The results are given in Table 1, entry 7. In this case the LCEC is higher for PP, a direct
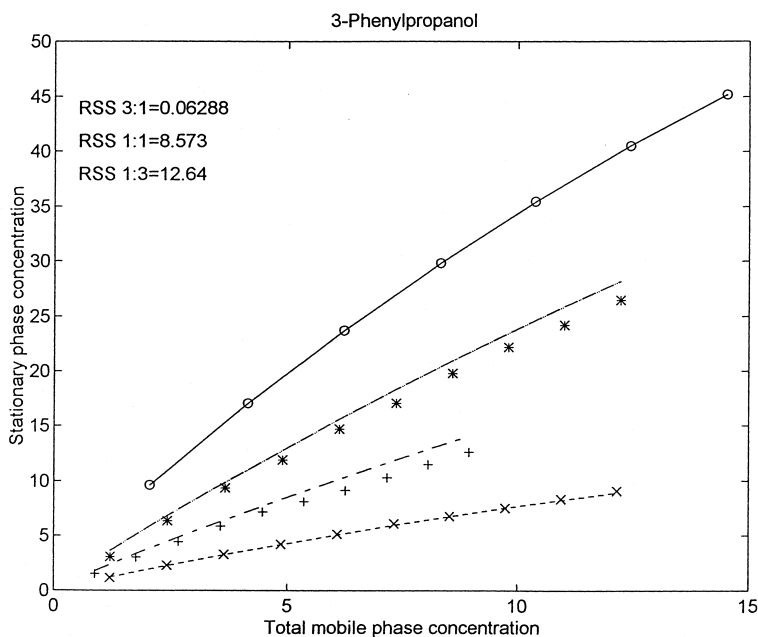
Fig. 4. Same as Fig. 3 but for data for 3-phenylpropanol.

consequence of the larger Henry constant of this compound. Both values χ_i obtained are negative, suggesting repulsive interactions in the monolayer. The prediction of the competitive data is worse than the one given by either the Langmuir or the Jovanovic models (See Table 1, entries 1–2), models which assume no interactions. Note that the Jovanovic model also assumes equal values of the monolayer capacities for both components. So, the introduction of the requirement for thermodynamic consistency in the fitting of the data by the Fowler model does not improve the prediction of the multicomponent data with respect to the one given by a simpler, thermodynamically consistent homogeneous-surface model like the Jovanovic or Langmuir model.

To summarize, the Fowler model can correlate the SCD better and predict multicomponent data of both

phenylalcohols better than the homogeneous-surface models which assume no lateral interactions, i.e. the Langmuir and the Jovanovic models. However, these results are possible only by assuming different monolayer capacities for both components and by considering repulsive interactions in the monolayer. The former assumption makes the model thermodynamically inconsistent; the latter seems to be physically unrealistic. These results render suspicious the validity of the Fowler model for the system of components under consideration.

4.1.3. The Jovanovic model with lateral interactions

The results obtained with this model [Eqs. (18), (19a), (19b)] are given in Table 1, entries 8–12. Note that the results provided by this model are very similar to the ones given by the Fowler model discussed previously, as expected. Both models are equivalent, i.e. for homogeneous surfaces with lateral interactions. These results are given mainly for the sake of comparison. The extensions so far reported for the Jovanovic model assume that there are no lateral interactions in the adsorbed layer [47,48]. It seems that the model represented by Eqs. (19a) and

Table 5
Geometrical characteristics of the adsorbates

Adsorbate	V_{wi} (cm^3/mol)	A_{wi} (cm^2/mol)	A_{si} (Å^2)
PE	73.54	9.37×10^9	72.68
PP	83.77	10.72×10^9	80.33

(19b) could be one of the possible extensions of the Jovanovic model to the case when lateral interactions on the surface are to be taken into account.

4.2. Models for heterogeneous surfaces with no lateral interactions

4.2.1. The Langmuir–Freundlich and the Jovanovic–Freundlich models

4.2.1.1. Correlation of single-component data (SCD) by the single component isotherm model

The fit of the single component PP data to either of these two models gives a fit which is much better than the fit given by the majority of the isotherm models for homogeneous surfaces applied to the data (see Tables 2 and 5 for the sake of comparison). Note that the comparison is more meaningful when analyzing only three-parameter models, i.e. the Fowler, Moreau, Kiselev, Langmuir–Freundlich and Jovanovic–Freundlich models. This result is unexpected because neither the Langmuir–Freundlich model nor the Jovanovic–Freundlich model reduces to the Henry Law at low concentrations. On the other hand, all the homogeneous-surface models reduce to the linear isotherm at low concentration. It is often claimed that an important feature of any adsorption isotherm model is its capability to reduce to Henry law at low concentrations [111]. Although this claim is important and generally considered as valid, there exists theoretical results justifying the existence of Freundlich-type behavior at low concentrations [112]. Moreover, there are specific cases such as in this study, in which isotherms which do not reduce to Henry law (Langmuir–Freundlich or Jovanovic–Freundlich) and produce better results than models that do (e.g., Fowler, Moreau or Kiselev models). As a matter of fact, there are even models which reduce to the Henry law but cannot correlate the data at all, as is the case of the UNILAN [94] model (see later). Both the Jovanovic–Freundlich and the Langmuir–Freundlich models are able to give a good correlation of the experimental data analyzed here, which are fairly linear over most of the concentration range studied [23]. The observation of rather linear isotherms is valid for the majority of experimental isotherms obtained in reversed-phase liquid chromatography systems [5,16,20,22,26]. This picture is very different from the situation usually encountered for gas–solid systems, where strong nonlinearities are usually observed [33].

In the present case, the good correlation obtained with models which do not reduce to Henry Law may be related to the fact that the experimental data analyzed were acquired in an intermediate range of concentrations. These data do not cover either the region of saturation of the adsorbent (monolayer range) or the low concentration range of the Henry zone. So, serious deviations from the Freundlich model have only minor consequences for the quality of the fit. The fact that the two models give almost the same correlation is a convenient situation from the point of view of the model robustness. Thus, if data are available which cover the intermediate range of concentrations, it should be possible to successfully use any one of these two models. This intermediate concentration range is very important for the process or preparative applications of chromatography. In practice, nearly all preparative separations are performed in this range. The Henry zone is much less important in preparative separations; it is important only for analytical applications. In this region, solutes adsorb independently, without competing with other adsorbates. The distribution of the mobile phase components in the system determines the distribution of the solutes and the influence of solute adsorption on the adsorption of any solvent component is truly negligible. It is more difficult to understand the behavior of the system near saturation. If there are any adsorption sites with adsorbate–adsorbent interaction energies less than that of the average alkyl chain-solute interaction, the energy distribution will have a low energy branch. It is doubtful that this can be spread over a wide energy range. The high energy decay seems to be sufficient to characterize the energy distribution of the system.

The value of the monolayer coverage obtained is higher for PP than for PE (Table 2, entries 1 and 2). The fact that q_{s1} is not equal to q_{s2} is an inconsistency expected from the application of a simplified model to real phenomena. The Jovanovic–Freundlich and Langmuir–Freundlich models consider as local isotherms the competitive Jovanovic and Langmuir models for a homogeneous surface, respectively [35]. These multicomponent homogeneous-surface models are thermodynamically consistent only under the

assumption of equal adsorption capacities for all the components present in the mixture [34]. If equal adsorption capacities are assumed for all the components on each patch of the surface, integration over all patches should give equal adsorption capacities of the two components on the overall heterogeneous surface. As stated above, the two phenylalcohols studied have a similar size, as derived from the values shown on Table 5. However, their geometry is not simple and they may have different areas of contact with the solid surface in the region of monolayer coverage. It remains difficult to describe the position of the molecules of adsorbates actually in contact with the surface of reversed-phase packing materials and the structure of the adsorbed monolayer [4,8]. The solid phase concentrations corresponding to monolayer capacity which have been measured in the case of LC systems were usually found to be larger than the maximum capacities calculated from the surface area of the adsorbent and the area of contact adsorbate–adsorbent corresponding to a flat configuration [8,16]. Since the available data do not approach the saturation region close enough, it is impossible to obtain an unbiased estimate of the saturation capacities for both components. This is often the case in LC-based adsorption data. Concentrations are low and do not approach the saturation region [5,6,8–10,12–26], often as a result of the limited solubility of the compounds studied in the mobile phase [9,16,17,27], as it is in the present case. This is unfortunate because unbiased estimates are important to decide whether the saturation capacities for any model should be considered similar or different. Once the saturation capacities are identified it is also possible to derive from the values of the Henry constant the degree of adsorbate–adsorbent interaction for the different adsorbates. Note that the values of the parameters characterizing the adsorbate–adsorbent interaction energy in these heterogenous-surface models (a_i) are very close for both components. Also, the surface behaves as if it were nearly homogeneous for both PE and PP (with $\nu_2 \simeq 0.9$ for both phenylalcohols). That the surface is almost homogenous for both components seems to be quite a realistic assumption according to published values of the isosteric heats of adsorption on RP phases [15].

4.2.1.2. Prediction of competitive adsorption data using the parameters of the single component isotherm in a competitive isotherm model

The prediction of the competitive adsorption data was carried out considering the arithmetic mean value for the mixed heterogeneity parameter present in Eqs. (3a), (3b), (6a) and Eq. (6b), following Yang et al. [91].

The prediction of the competitive isotherm data for PP obtained with the Langmuir–Freundlich or the Jovanovic–Freundlich model ranks among the best achieved in this or in previous studies (Table 2, entries 1 and 2) [23,39,60]. On the other hand, the prediction of the same data for PE ranks among the worst ones (see Table 5). This could be the result of the use of a rather crude combining rule for the mixed heterogeneity parameter, as stated earlier. The deviations observed in the prediction of the PE data are close with both models and for both sets of competitive data. From Table 5 it is clear that all homogeneous-surface models tested, in this or earlier work [23,39,59] produce deviations in the prediction of competitive data which are much larger for PP than for PE. As a result the overall prediction of the competitive data given by either the Langmuir–Freundlich or the Jovanovic–Freundlich model is better than that given by any homogeneous-surface model tested before [23,39,59]. The prediction of the LRC extension of the Langmuir–Freundlich model is poor (Table 2, entry 1), worse than the prediction of the Langmuir model.

Introducing the conditions for thermodynamic consistency (i.e. $q_{s1} = q_{s2}$ and $\nu_1 = \nu_2$ [92]) in the fitting process leads to results qualitatively similar to the results presented earlier for the Fowler model. Namely, a worse fit of the SCD and a worse prediction of the binary data.

4.2.2. Other isotherm models

We tried unsuccessfully to fit the experimental data under consideration to the UNILAN [94] and the Dubinin–Radushkevich [96] adsorption isotherm models. We were not able to obtain stable convergence of the minimization algorithm for these models toward the global minimum. The program remained trapped continuously in local minima. Furthermore, the values of the identified parameters varied dramatically from one local minima to another

one. In the case of the UNILAN model this failure could be attributed to the fact that this model is based on a uniform distribution of adsorption sites, an unlikely distribution for silica-based reversed-phase materials. As stated above, the energy distribution functions which are reasonably expected for these materials are either low adsorption-energy limited exponential distributions or quasi-Gaussian distributions skewed in the direction of high adsorption energies. For the particular reversed-phase packing material employed in this study (Vydac) it has been found by different methods that the micropore size distribution is a Gaussian-like distribution covering a range from ca. 30 to 200 Å, with a maximum around 65–80 Å [113]. It has been shown also that there exists a relationship between the adsorption energy distribution of an adsorbent and the corresponding micropore size distribution [90]. So, the energy distributions and the pore size distributions experimentally found for silica adsorbents do not support the model of a uniform distribution of the adsorption energy.

On the other hand, following the IUPAC classification of pore size [35], the adsorbent employed in this study may be classified as a mesoporous adsorbent, for which the pore size ranges from 20 to 500 Å. From the experimental pore size distribution of the Vydac material used here, it can be derived that the cross-sectional area of the pores ranges from ca. 700 to 30 000 $Å^2$, with a maximum between ca. 3000 and 5000 $Å^2$. Taking into account that the maximum contact areas of PE and PP (Table 5) are 72.68 and 80.33 $Å^2$, respectively; it is clear that the average cross-sectional area of the pores is about 50-times larger than that of PP. Under such conditions it seems difficult that any pore filling mechanism could take place, hence the assumptions underlying the Dubinin–Radushkevich model cannot be met [96]. This last model is more suitable for microporous adsorbents, with pore sizes under 20 Å for which the dimensions of the pores and of the adsorbates are close and pore volume is nearly completely filled with the adsorbate. The Dubinin–Radushkevich model has been very successful in the description of adsorption processes of gases and vapors on activated carbons, zeolites and other microporous adsorbents but not on silica [35]. We also fitted the data under consideration to the Freun-

dlich [83], Toth [85] and Redlich–Peterson models [93]. However, both the correlation of the single component data and the prediction of the multi-component data obtained for all these models were worse than the ones provided by the Jovanovic–Freundlich and Langmuir–Freundlich models. These results are not provided for the sake of brevity.

4.3. Heterogeneous-surface models with lateral interactions

In principle, both phenylalcohols can undergo adsorbate–adsorbate interactions on the surface via hydrogen bonding. It seems interesting to account for this effect in an attempt to improve the characterization of the particular system under consideration. The separation of solutes having hydroxyl groups or other moieties able to generate strong adsorbate–adsorbate interactions is common in reversed-phase chromatography. Additionally, the organic modifiers commonly employed in such systems are also polar molecules which may contribute to the interactions in the adsorbed phase. So, it seems that models which account for lateral interactions in the monolayer may represent an improved picture of the possible phenomena taking place in reversed-phase separations.

4.3.1.1. Correlation of single-component data (SCD) by the single component isotherm models

The fit of the SCD by the FG/LF and FG/JF models is very good (Table 3, entries 1 and 2 respectively), especially for PP. The fit of the SCD data given by these models is the best one achieved by any model employed in this study or in previous studies (Table 4) [23,39,59]. These models are also the first ones to correlate the SCD of both phenylalcohols with the same degree of accuracy. This is an important feature of these models. As is clear from Table 3, entries 1 and 2, the values of the RSS for both components have the same order of magnitude. By contrast, the models previously analyzed correlate the SCD with a value of the RSS which is several orders of magnitude larger for PP than for PE (cf. Table 4). The values of the saturation capacities obtained with the FG/LF and FG/JF models for both components are different. The monolayer capacity value is higher for PP than for PE. The considera-

tions exposed above regarding this result (cf. discussion of the heterogeneous-surface models with no lateral interactions) hold here as well. On the other hand, the value of the adsorbate–adsorbent interaction constant (a_i) obtained is greater for PE than for PP; although both values have the same order of magnitude in both models. These results agree with the fact that both adsorbates are homologs which should undergo the same interactions. Furthermore, for both models, the interactions in the adsorbed layer are attractive and the values of χ_2 are always greater than the values of χ_1. In conclusion, these models behave better than the corresponding homogeneous-surface models with lateral interaction, for which differences in the order of magnitude and the sign of the adsorbate–adsorbate interaction parameters were obtained (cf. Table 1, entries 3 and 4).

The similarity between the values of the heterogeneity parameter obtained from the correlation of the FG/LF and FG/JF models is worth noting. The value for PE is very close to one, suggesting an almost homogeneous surface for this component. This result is similar to the one obtained previously with the Langmuir–Freundlich and Jovanovic–Freundlich models. On the other hand, the correlation of the PP data by the two models gives a value of $\nu_2 \simeq 0.8$, instead of 0.9 obtained with the Langmuir–Freundlich or the Jovanovic–Freundlich models (Table 2, entries 1 and 2). So, the heterogeneous-surface models with lateral interactions predict a greater degree of surface heterogeneity for PP and almost the same degree of heterogeneity for PE than the heterogeneous-surface models with no lateral interactions.

4.3.1.2. Prediction of competitive adsorption data using the parameters of the single component isotherm in a competitive isotherm model

The FG/LF model predicts an RSS of the PP competitive data (Table 3, entry 1) which is about four times less than that predicted by the Langmuir–Freundlich model (Table 2, entry 1). Thus, the inclusion of lateral interactions in the heterogeneous-surface model significantly improves the prediction of the competitive data for PP. A similar comparison of the predictions of the FG/JF and the Jovanovic–Freundlich models shows a twofold reduction of the RSS of the competitive data for PP. The same degree of improvement is not achieved with the PE competi-

tive data, for which the RSS values previously obtained are nearly unchanged (a slight increase compared to the results of the Langmuir–Freundlich or the Jovanovic–Freundlich models is observed). The predictions of the whole set of the competitive data given by both the FG/LF and FG/JF models are the best ones obtained here or in previous studies [23,39,59], giving the lowest values of Σ RSS. The prediction of the PE data is better accomplished by the FG/JF model while the prediction of the PP data is better done by the FG/LF model. Both models, however, give close values of Σ RSS. The JF/FG model predicts the same degree of deviations of the competitive data for both phenylalcohols.

Note that the use of homogeneous-surface models with lateral interactions (Table 4, entries 3–7) produced a nearly twofold decrease in the value of Σ RSS compared to the result obtained with the corresponding homogeneous-surface model with no lateral interactions (Table 4, entries 1–2). Instead, the use of heterogeneous-surface models with no lateral interactions (Table 4, entries 8–9) produced an almost fourfold decrease in the value of Σ RSS compared to the result of homogeneous-surface models with no lateral interactions (Table 4, entries 1–2). Finally, the use of heterogeneous-surface models with lateral interactions (Table 4, entries 10–12) produced a sixfold decrease in the value of Σ RSS compared to the result given by homogeneous-surface models with no lateral interactions (Table 4, entries 1–2). It seems from these results that the consideration of the surface heterogeneity is of major importance. Also it is clear that the successive inclusion of nonideal effects in the single component model improves the pure prediction of competitive data based solely on the single component parameters.

Figs. 1 and 3 show that the deviations for the PE competitive data increase with increasing PE concentration in the mixture. Similarly, Figs. 2 and 4 show also that the deviations for the PP competitive data increase with increasing PP concentration in the binary mixture. The deviations observed in the prediction of the competitive data for both components increase also as we approach the single component data. As stated above, the combining rule used for the combined heterogeneity parameter necessary for the calculation of the multicomponent data causes a decrease in the accuracy of the

predicted data as we move toward the single component data. Obviously, taking the simple arithmetic mean of the individual values for the combined value of the heterogeneity parameter does not allow this parameter to tend toward the proper individual value when the relative concentration of the other component in the mixture vanishes. A more refined combining rule such as the one proposed by the HAST model [88,89] could be more accurate for the system under consideration, although it is much more complex. Furthermore, the number of data points in the set of competitive adsorption data and SCD available is too limited to justify the introduction of another degree of freedom.

Taking into account the importance of the experimental errors made and the simplifying assumptions underlying the FG/LF and the FG/JF models, the predictions obtained are in reasonable agreement with the experimental data [23]. Unfortunately, the heterogeneous-surface models with lateral interactions suffer from the important drawback that they cannot be inverted analytically with respect to the mobile phase concentrations of the components. This considerably complicates their implementation in the use of process chromatography models, when multiple evaluations of the multicomponent equilibria are required in the calculation of the propagation of large concentration bands along chromatographic columns.

Introducing in the fitting process of the SCD the same conditions of thermodynamic consistency as stated above for the FG/LF and the FG/JF models, i.e. $q_{s1} = q_{s2}$ and $\nu_1 = \nu_2$ [92], we obtain results qualitatively similar to the ones obtained for the Fowler model where no improvement in the prediction of the competitive data is observed with respect to the results given by the Langmuir model. Thus, satisfaction of the requirements of thermodynamic consistency for the heterogeneous-surface models with lateral interactions also does not permit a significant improvement of the prediction of the competitive data already achieved with thermodynamically consistent homogeneous-surface models.

5. Conclusions

In this paper, the prediction of competitive isotherm data was attempted using models which assume the surface to be heterogeneous and considering possible lateral interactions in the adsorbed phase. The multicomponent isotherm models which consider both lateral interactions and surface heterogeneity were found to account better for competitive data in a purely predictive way. This result is illustrated by the comparison between the results obtained with these models and with other models tested here and in previous studies [23,39,59]. These models, however, exhibit the same drawback as other models for homogeneous surfaces with lateral interactions like the Fowler and Kiselev models. It is impossible to invert them analytically, as required for the calculation of adsorbed phase concentrations with the algorithms used to model nonlinear chromatography [3], and their numerical inversion prohibitively increases the run time of the programs. One solution to this situation could be first to predict the competitive equilibria using the more accurate time-consuming model and later to correlate the data generated employing an explicit, correlative model like the quadratic model. The quadratic model usually provides an accurate representation of the multicomponent data [39]. In this way, the numerical inversion of the more complex models can be avoided. The prediction of reversed-phase competitive adsorption data based on the values of the identified parameters of single component isotherms derived from experimental SCD is a complex task, as shown by the results presented in this and in previous studies [23,39,59]. This approach, although highly desirable from an experimental point of view, is complicated by our poor understanding of the phenomenon of adsorption from the liquid phase. The results reported in this paper give an idea of the difficulties involved, although they are restricted to the specific, relatively simple case of two immediate homologs. Note that for compounds similar to those analyzed in this study, simple combining rules can be successful in accounting for the adsorbate–adsorbate cross-interaction parameters based on the single component parameters. However, the problem will become much more complicated for adsorbates differing greatly in size and/or polarity [36]. The results of this study show that the use of homogeneous-surface models with lateral interactions permit a better prediction of competitive equilibria based on the SCD identified parameters than that given by homogeneous-surface models with no lateral interactions. However, the contradictory

values obtained for the adsorbate–adsorbate inter-
action parameters render suspicious the ability of
these models to capture at least the essential features
of the actual phenomena involved. On the other
hand, the heterogenous-surface models with no later-
al interactions tested in this study also gave a fair
prediction of the competitive data based on the
parameters identified from the SCD analysis. Thus it
seems that the surface heterogeneity plays an im-
portant role in the overall behavior of the system.

In another context, the heterogeneous-surface
models with lateral interactions considered here
exhibit several common features, (i) higher values of
the adsorbate–adsorbent interaction parameter for PE
than for PP; (ii) a very good and similar fit of the
SCD for both components, especially for PP, these
correlations being the best ones achieved by any
model tested; (iii) similar values of the adsorbate–
adsorbate interactions in the adsorbed phase, as
expected for similar compounds. These models pro-
duced the best prediction of the competitive data
based on single component parameters among all the
models tested. This result can be explained by the
fact that these models account for the two main
contributions to adsorbed phase nonideal behavior,
namely the adsorbent surface heterogeneity and the
adsorbate–adsorbate lateral interactions. The predic-
tions obtained are in reasonable agreement with the
experimental data if one considers the unavoidable
experimental errors and the use of a rather simple
rule to mix different adsorption energy distributions.
These models, however, possess thermodynamic
inconsistencies arising from the fact that the iden-
tified monolayer capacities for both components are
different, while equal monolayer capacities are as-
sumed in their derivation. On the other hand, when
the requirements for thermodynamic consistency of
any nonideal model are introduced in the regression
analysis of the data, no improvement is achieved in
the prediction of competitive data over the prediction
given by the simplest ideal models for homogeneous
surfaces with no lateral interactions. It is possible
that a more refined model based on the use of Eqs.
(8a) and (8b) in the integral equation (Eq. (1)) with a
subsequent application of the HAST procedure
[88,89] to predict the behavior of adsorbates with
different energy distributions will give more accurate
predictions in a more thermodynamically sound way.

However, this type of model will require the use of a
wider set of experimental data, which we are in the
process of obtaining.

Other sources of nonideal behavior which have not
been considered in the models used in this study are:
(i) The possible solute–solute interactions in the
bulk liquid phase, e.g., via hydrogen bonding among
the solutes and the mobile phase components, which
would cause departure from an ideal solution be-
havior [8,22,23,27,114]. However, taking into ac-
count the relatively low range of concentration of the
phenylalcohols in the mobile phase which was
investigated, it is reasonable to expect that their
activity coefficients does not vary in this range. (ii)
The fact that, in the general case, all the components
of the mobile phase are adsorbed, to some extent.
However it has been shown that when the adsorption
of the solute is much stronger than the adsorption of
the solvent, neglecting the solvent competition is
usually a good approximation [13]. Moreover, pub-
lished experimental data indicate the weak adsorp-
tion of methanol on reversed-phase packing materials
[13,114–118]. For mobile phases containing equal
volume fractions of methanol and water, the surface
excess of methanol is close to zero, giving equal
compositions of the adsorbed layer and the bulk
phases [117].

Finally, this study provides useful models of
prediction of multicomponent equilibria in RP-HPLC
based on the use of single component identified
parameters. Although it is likely that these models do
not represent exactly the actual phenomena taking
place in the systems under consideration, it is also
possible that some of the models analyzed here
capture the two essential features determining the
behavior of the system: the heterogeneity of the
adsorbent surface and the lateral interactions between
molecules in the adsorbed layer. The degree of
inconsistency still present in them arises from the
simplifcations included in their derivation.

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