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## Application of different isotherm models to the description of single-component and competitive adsorption data

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### Abstract

Previously reported competitive adsorption data of 2-phenylethanol and 3-phenylpropanol on ODS–silica with methanol–water mobile phase were fitted to the Langmuir isotherm, the generalized version of the Langmuir model suggested by statistical mechanics, and the Jovanovic competitive isotherm equations. The best results were obtained with the 11-parameter quadratic isotherm defined by the ratio of two second-degree polynomials, which takes into account all molecular interactions in both the solution and the sorbed monolayer. The Jovanovic model was used to derive a relationship widely applied to predict reversed-phase chromatography retention data as a function of aqueous binary mobile phases.

**Keywords:** Mobile-phase composition; Preparative chromatography; Adsorption isotherm; Retention model; 2-Phenylethanol; 3-Phenylpropanol

### 1. Introduction

Preparative liquid chromatography has become one of the most important purification techniques used by the pharmaceutical industry [1–5]. One of the major difficulties encountered in the development of new application methods, their scale up and their optimization, is the selection of the most suitable model of non-linear chromatography to account for the behavior of the individual band profiles and the acquisition of the experimental data required for the calculation of accurate solutions of this model

[2,3,5]. If the calculated profiles can be validated by their agreement with experimental profiles, a rapid optimization of the experimental conditions for maximum production rate, minimum production cost, or extreme of any other objective function can be achieved. This optimization is rapid, inexpensive compared to the conventional empirical approaches and avoids the wasting of chemicals.

Models based on continuity equations are powerful to describe the separation process [4] and are largely used with great success [5]. However, the effective use of these models requires that some important physical characteristics of the system used be modeled accurately. First among our needs is the appropriate modeling of the adsorption isotherms. Second is the modeling of the mass transfer kinetics. In most practical cases, however, the influence of the

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mass transfer kinetics on band profiles is small compared to that of thermodynamics. It can be treated as a correction and the equilibrium–dispersive model, which uses an apparent dispersion coefficient, has been quite successful. Thus, the first problem remains of paramount importance for all practical applications of non-linear chromatography. A number of isotherms models have been used to approximate the single-component and competitive adsorption data acquired in liquid chromatography. The Langmuir [6–17], bi-Langmuir [16–20], Fowler [6], Quadratic [6,7,13,15,16,21] and models derived from the IAS theory, like the LeVan–Vermeulen model [6,15,16,18] are the most useful. Some other important models have been almost ignored. For example, the Jovanovic model [22–24] has been used to account for single-component adsorption [25,26], but the competitive Jovanovic model remains ignored for the representation of the competitive adsorption data used in preparative HPLC.

The goal of this paper is the application of the single-component and the competitive adsorption isotherm models of Jovanovic to liquid chromatography. The use of this model permits the simple derivation of a conventional relationship, widely applied to predict the dependence of reversed-phase chromatography retention data as a function of the composition of aqueous binary mobile phases and the correct description of single-component and competitive adsorption data obtained by reversed-phase HPLC and data previously reported by us [6].

## 2. Theory

In this study, we compare the results obtained with six different models of competitive adsorption isotherms, the Langmuir model, two versions of the extended Langmuir model suggested by statistical thermodynamics, and three versions of the Jovanovic model. As in all studies of this type, we must acknowledge that the procedure used for the determination of the best values of the parameters of a model does not guarantee that the values obtained have the physical meaning given to them in the derivation of the equations of the model.

### 2.1. The competitive Langmuir isotherm

The competitive Langmuir model [27] is the simplest model used:

$$q_i = \frac{a_i C_i}{1 + \sum_{j=1}^n b_j C_j} \quad (1)$$

where  $q_i$  and  $C_i$  are the concentrations of the  $i$ th component at equilibrium in the stationary and the mobile phase, respectively,  $a_i$  and  $b_i$  are numerical coefficients, characteristic of the components and the chromatographic system. The ratio  $q_s = a_i/b_i$  is the monolayer capacity for the  $i$ th component. For this reason,  $a_i$  is often replaced by  $q_s b_i$  in Eq. 1. For the single components, Eq. 1 becomes [28]:

$$q_1 = \frac{q_{s,1} b_1 C_1}{1 + b_1 C_1} \quad (2a)$$

$$q_2 = \frac{q_{s,2} b_2 C_2}{1 + b_2 C_2} \quad (2b)$$

Thus, all the coefficients of the competitive isotherms, Eq. 1, can be derived from measurements made with single, pure compounds, which is very convenient from the experimental point of view. However, the basic assumptions of the competitive Langmuir isotherm model falter when  $q_{s,1} \neq q_{s,2}$ . A competitive isotherm derived from the coefficients of single-component Langmuir isotherms would not satisfy the Gibbs–Duhem relationship and would not be compatible with thermodynamics [31]. In practice, poor results are obtained in such cases.

### 2.2. The quadratic isotherm

We consider here two competitive forms of this isotherm, more often used as a single-component isotherm model. Statistical thermodynamics [7,21,32,33] shows that the general form of an isotherm equation should be the ratio of two polynomials of the same degree. For the first degree, we obtain the Langmuir isotherm, Eq. 1. For the second degree, which seems to be the most complex such model which can be used in practice, Ruthven and Goddard [33] have shown that:

$$\Theta_1 = \frac{q_1}{q_s}$$

$$= \frac{b_1 C_1 + b_{1,2} C_1 C_2 + 2b_{1,1} C_1^2}{1 + b_1 C_1 + b_2 C_2 + b_{1,2} C_1 C_2 + b_{1,1} C_1^2 + b_{2,2} C_2^2} \quad (3a)$$

$$\Theta_2 = \frac{q_2}{q_s}$$

$$= \frac{b_2 C_2 + b_{1,2} C_1 C_2 + 2b_{2,2} C_2^2}{1 + b_1 C_1 + b_2 C_2 + b_{1,2} C_1 C_2 + b_{1,1} C_1^2 + b_{2,2} C_2^2} \quad (3b)$$

where  $\Theta_i$  is the fractional coverage of a monolayer and the  $b_i$  and  $b_{i,j}$  are numerical coefficients. This model contains six parameters, including  $q_s$ , instead of three for the competitive Langmuir model (Eqs. 2a and 2b).

Similar, but different, equations have been suggested for a quadratic model. For example, it has been suggested to write:

$$q_1 = \frac{a_1 C_1 + a_{1,2} C_1 C_2 + a_{1,1} C_1^2}{1 + b_1 C_1 + b_2 C_2 + b_{1,2} C_1 C_2 + b_{1,1} C_1^2 + b_{2,2} C_2^2} \quad (4a)$$

$$q_2 = \frac{a_2 C_2 + a_{2,1} C_1 C_2 + a_{2,2} C_2^2}{1 + b_1 C_1 + b_2 C_2 + b_{1,2} C_1 C_2 + b_{1,1} C_1^2 + b_{2,2} C_2^2} \quad (4b)$$

where  $a_{i,j}$  and  $b_{i,j}$  are numerical coefficients. The coefficients  $a_i$  and  $b_i$  can be determined from the single-component Langmuir models, Eqs. 2a and 2b, to which Eqs. 4a and 4b reduce in the case of single-component adsorption. The parameters  $a_{i,i}$  and  $b_{i,i}$  can be interpreted, with reference to the kinetic derivation of the Langmuir model, as accounting for the influence of the concentration of one component of the binary mixture on the rate of desorption of the other, thus becoming equal to zero for single-component adsorption. The simplified version of the models of Eqs. 4a and 4b is obtained neglecting this influence, as a first approximation. Then, the following expressions are obtained:

$$q_1 = \frac{a_1 C_1 + a_{1,2} C_1 C_2}{1 + b_1 C_1 + b_2 C_2 + b_{1,2} C_1 C_2} \quad (5a)$$

$$q_2 = \frac{a_2 C_2 + a_{2,1} C_1 C_2}{1 + b_1 C_1 + b_2 C_2 + b_{1,2} C_1 C_2} \quad (5b)$$

### 2.3. The Jovanovic isotherm

This isotherm model was derived for monolayer, non-localized adsorption, without lateral interactions on an homogeneous solid surface [22]. The derivation of the Jovanovic isotherm model is kinetic and considers the interactions between the mobile phase molecules and the adsorbed molecules. Later, the Jovanovic model was extended to mixtures of compounds having different distribution functions of the settling times of the adsorbed molecules on the surface [23,24].

#### 2.3.1. The original Jovanovic isotherm

In its original form, the competitive Jovanovic isotherm assumes that there is a zero dispersion of the settling times the distribution of which is given by the a function [23,24]:

$$q_1 = A_1 \frac{e^{a_{1,1} C_1 + a_{1,2} C_2} - e^{a_{1,2} C_2}}{1 + e^{a_{1,1} C_1 + a_{1,2} C_2} - e^{a_{1,2} C_2} + e^{a_{2,1} C_1 + a_{2,2} C_2} - e^{a_{2,1} C_1}} \quad (6a)$$

$$q_2 = A_2 \frac{e^{a_{2,1} C_1 + a_{2,2} C_2} - e^{a_{2,1} C_1}}{1 + e^{a_{1,1} C_1 + a_{1,2} C_2} - e^{a_{1,2} C_2} + e^{a_{2,1} C_1 + a_{2,2} C_2} - e^{a_{2,1} C_1}} \quad (6b)$$

These equations simplify in the case of a pure compound and we obtain:

$$q_i = A_i [1 - e^{-a_{i,i} C_i}] \quad (7)$$

#### 2.3.2. The Jovanovic isotherm with a random distribution of settling times

This competitive isotherm assumes, as the Langmuir model, that the distribution of settling times of the adsorbate molecules on the surface is completely random [24]. The isotherm is:

$$q_1 = A_1 \frac{b_{1,1} C_1 \frac{1 + b_{1,1} C_1 + b_{1,2} C_2}{1 + b_{1,1} C_1}}{1 + b_{1,1} C_1 \frac{1 + b_{1,1} C_1 + b_{1,2} C_2}{1 + b_{1,1} C_1} + b_{2,2} C_2 \frac{1 + b_{2,1} C_1 + b_{2,2} C_2}{1 + b_{2,2} C_2}} \quad (8a)$$

$$q_2 = A_2 \frac{b_{2,2}C_2 \frac{1+b_{2,1}C_1+b_{2,2}C_2}{1+b_{2,2}C_2}}{1+b_{1,1}C_1 \frac{1+b_{1,1}C_1+b_{1,2}C_2}{1+b_{1,1}C_1} + b_{2,2}C_2 \frac{1+b_{2,1}C_1+b_{2,2}C_2}{1+b_{2,2}C_2}} \quad (8b)$$

In the case of the adsorption of a pure compound ( $C_i = 0$ ,  $C_j \neq 0$ ), Eqs. 8a and 8b reduce to the equation of the Langmuir isotherm (Eq. 2), while for  $a_{i,j} = 0$ , they reduce to the competitive isotherm (Eq. 1).

### 2.3.3. The Jovanovic isotherm with a Heaviside distribution of settling times

In this case, the distribution of settling times is assumed to be accounted for by the Heaviside function [24]:

$$q_1 = A_1 \frac{Y_1}{1 + Y_1 + Y_2} \quad (9a)$$

$$q_2 = A_2 \frac{Y_2}{1 + Y_1 + Y_2} \quad (9b)$$

with:

$$Y_1 = (1 + b_{1,1}C_1 + b_{1,2}C_2) \left[ e^{a_{1,1}C_1 + a_{1,2}C_2} - \frac{e^{a_{1,2}C_2}}{1 + b_{1,1}C_1} \right] \quad (10a)$$

$$Y_2 = (1 + b_{2,1}C_1 + b_{2,2}C_2) \left[ e^{a_{2,1}C_1 + a_{2,2}C_2} - \frac{e^{a_{2,1}C_1}}{1 + b_{2,2}C_2} \right] \quad (10b)$$

In the case of the adsorption of a pure compound, Eqs. 9a and 9b become:

$$q_i = A_i \left[ 1 - \frac{e^{-a_{i,i}C_i}}{1 + b_{i,i}C_i} \right] \quad (11)$$

When  $a_{i,j} = 0$ , Eqs. 9 and 10 reduce to Eqs. 8 while

when  $b_{i,j} = 0$ , these same equations reduce to Eqs. 6. The higher degree of generality of the model expressed by Eqs. 9 compared to the previous models, expressed by Eqs. 1, 6, or 8 in terms of the settling times distribution function was previously reported by Vlad and Segal [24].

### 2.4. Relationship between retention factor and mobile phase composition in RPLC

In reversed-phase liquid chromatography, the dependence of the retention factor,  $k'_i$ , of the  $i$ th analyte on the composition of a binary aqueous mobile phase is usually approximated by the following relationship [29]:

$$\ln k'_i = \ln k'_{i,w} - S_i \phi_m \quad (12)$$

where  $k'_{i,w}$  is the retention factor of analyte  $i$  in pure water,  $\phi_m$  is the volume fraction of the organic modifier in the mobile phase, and  $S_i$  is a numerical coefficient characterizing the behavior of analyte  $i$ .

In a typical analytical separation by RPLC, two conditions are usually met: (1) the mobile phase concentrations of all the analytes are very low, significantly lower than the concentrations of the organic modifier(s) in the mobile phase ( $C_i < \phi_m$ ). As a consequence, the influence of any analyte on the adsorption of any other analyte is negligible; and (2) only the analytes and the organic modifier compete for the free sites which are available on the hydrophobic surface of the adsorbent.

These assumptions allow the use of a binary competitive isotherm to account for the influence of the concentration of the organic modifier on the adsorption behavior of the analyte. Starting from the original Jovanovic isotherm, Eqs. 6a and 6b, and assuming 1 to be the analyte and 2 the organic modifier, we can replace the exponential terms containing  $C_1$  by their series expansion since  $C_1$  is small. Eliminating the higher degree terms of the expansion, we obtain:

$$q_1 = A_1 \frac{a_{1,1}C_1 e^{a_{1,2}C_2}}{C_1 [a_{1,1}e^{a_{1,2}C_2} + a_{2,1}e^{a_{2,2}C_2} - a_{2,1}] + e^{a_{2,2}C_2}} \quad (13)$$

Because the concentration of the analyte is much smaller than that of the modifier ( $C_1 < C_2$ ), we can consider that<sup>1</sup>:

$$C_1 [a_{1,1} e^{a_{1,2} C_2} + a_{2,1} e^{a_{2,2} C_2} - a_{2,1}] < e^{a_{2,2} C_2} \quad (14)$$

and we obtain:

$$q_1 = A_1 \frac{a_{1,1} C_1 e^{a_{1,2} C_2}}{e^{a_{2,2} C_2}} \quad (15)$$

The retention factor is defined as  $k' = Fq_1/C_1$ , where  $F$  is the phase ratio. Combining this definition and Eq. 15 and taking the logarithm gives:

$$\ln k'_1 = \ln A_1 a_{1,1} F - (a_{2,2} - a_{1,2}) C_2 \quad (16)$$

Eqs. 12 and 16 are identical, with:

$$k'_{1,w} = A_1 a_{1,1} F \quad (17a)$$

$$S_1 = a_{2,2} - a_{1,2} \quad (17b)$$

The fact that the Jovanovic model predicts the correct dependence of the retention factor on the mobile phase composition in RPLC, which the Langmuir isotherm does not, suggests that it could be useful to account for the isotherm data obtained in this area.

### 3. Experimental

#### 3.1. Origin of experimental data

The experimental data used in this study have been previously reported [6]. They deal with the

<sup>1</sup> In pure water (i.e., hence  $C_2 = 0$ ), Eq. 13 gives the Langmuir isotherm, Eq. 2, hence  $k'_{1,w} = A_1 a_{1,1} F / (1 + a_{1,1} C_1)$ , which shows that the retention factor in pure water depends on the analyte concentration. The same conclusion follows from Eq. 13 for binary mobile phases. The first assumption made above, that the amount of any analyte adsorbed at equilibrium is independent of the presence of other components, is usually valid in analytical HPLC because of low concentrations. This requires that the relationship 14 be also valid, so that Henry's law holds for solutes in pure water or mixed mobile phases [34].

adsorption of 2-phenylethanol (PE) and 3-phenylpropanol (PP) on ODS-silica Vydac (Hesperia, CA, USA) with (50:50) methanol-water solution as the mobile phase. Frontal analysis was performed with a Gilson (Middleton, WI, USA) Model 302 pump, a 10-port Valco (Houston, TX, USA) valve, and a Spectroflow (Applied Biosystems, Ramsey, NJ, USA) 757 UV-detector. The composition at each intermediate plateau was determined using an on-line chromatograph assembled with a Beckman (Berkeley, CA, USA) Model 110B pump, a Valco 4-port valve, a YMC (Wilmington, NC, USA) cartridge column and another Spectroflow detector. Both UV analog signals were acquired with a Gilson Model 621 interface box and monitored with a computer.

#### 3.2. Non-linear least squares analysis

The fit of the experimental data points to the isotherm equations was accomplished using the software package Statgraphics v. 5.0. The fitting procedure requires prior identification of the common parameters in a system of non-linear equations. This task may be classified as a multi-variant, multi-objective, non-linear programming problem. Many methods are available to solve it. The procedure presented here is relatively simple and assures convergence in many cases, even for complex models containing a significant number of adjustable parameters. Thus, it can be used as a useful tool to solve practical problems.

The algorithm used is based on Marquardt's method [30]. The system of equations for the case of the Langmuir competitive isotherm model applied to a binary mixture is given in Eq. 1 or, for an  $n$ -component mixture by:

$$q_1 = \frac{a_1 C_1}{1 + \sum_{i=1}^n b_i C_i} \quad (18a)$$

$$q_2 = \frac{a_2 C_2}{1 + \sum_{i=1}^n b_i C_i} \quad (18b)$$

$$q_i = \frac{a_i C_i}{1 + \sum_{i=1}^n b_i C_i} \quad (18c)$$

$$q_n = \frac{a_n C_n}{1 + \sum_{i=1}^n b_i C_i} \quad (18d)$$

We need to identify the common parameters,  $b_1, b_2, \dots$  and the non-common parameters  $a_1, a_2, \dots$ . The non-linear regression procedure of Statgraphics permits the fit of the models of the type:

$$y = f(x_1, x_2, \dots, x_n) \quad (19)$$

where  $y$  is a dependent variable and  $x_1, x_2, \dots, x_n$  are independent variables. The system of Eqs. 18 is composed of several dependent ( $q_1, q_2, \dots, q_n$ ) and independent ( $c_1, c_2, \dots, c_n$ ) variables. Thus, it is impossible to process this system of equations directly with Statgraphics and we need to change it to an equivalent equation system having the form given in Eq. 19. The transformation is illustrated below for a binary mixture and four measurements of the equilibrium composition carried out on four different mixtures. For the  $i$ th measurement, the values of  $q_{1,i}, q_{2,i}, C_{1,i}$ , and  $C_{2,i}$  are determined. The experimental data vectors are:

$$q_{1,\text{exp}} = [q_{1,1}, q_{1,2}, q_{1,3}, q_{1,4}] \quad (20a)$$

$$q_{2,\text{exp}} = [q_{2,1}, q_{2,2}, q_{2,3}, q_{2,4}] \quad (20b)$$

$$C_{1,\text{exp}} = [C_{1,1}, C_{1,2}, C_{1,3}, C_{1,4}] \quad (20c)$$

$$C_{2,\text{exp}} = [C_{2,1}, C_{2,2}, C_{2,3}, C_{2,4}] \quad (20d)$$

The new variables are constructed as:

$$y_{\text{exp}} = [q_{1,1}, q_{1,2}, q_{1,3}, q_{1,4}, q_{2,1}, q_{2,2}, q_{2,3}, q_{2,4}] \quad (21a)$$

$$x_{1,\text{exp}} = [C_{1,1}, C_{1,2}, C_{1,3}, C_{1,4}, C_{1,1}, C_{1,2}, C_{1,3}, C_{1,4}] \quad (21b)$$

$$x_{2,\text{exp}} = [C_{2,1}, C_{2,2}, C_{2,3}, C_{2,4}, C_{2,1}, C_{2,2}, C_{2,3}, C_{2,4}] \quad (21c)$$

$$x_3 = [1, 1, 1, 1, 0, 0, 0, 0] \quad (21d)$$

$$x_4 = [0, 0, 0, 0, 1, 1, 1, 1] \quad (21e)$$

where  $x_3$  and  $x_4$  are logical, complementary variables. The new model is constructed as:

$$y_1 = \frac{A_1 b_1 x_{1,\text{exp}}}{1 + b_1 x_{1,\text{exp}} + b_2 x_{2,\text{exp}}} x_3 + \frac{A_2 b_2 x_{2,\text{exp}}}{1 + b_1 x_{1,\text{exp}} + b_2 x_{2,\text{exp}}} x_4 \quad (22)$$

The first term of the new model permits the fit of the experimental data to Eq. 18a for a binary mixture, while the second term permits the same fit to Eq. 18b. The method can be extended simply, first to as many experiments as desired for the two-component system, then to the system of Eqs. 18 for an  $n$ -component mixture and for  $m$  experiments. The values calculated for the isotherm parameters give the least residual sum of squares (RSS) for both components. The procedure minimizes the value of the following function

$$\text{RSS} = \sum_{i=1}^n (y_{\text{exp},i} - y_{t,i})^2 \quad (23)$$

where  $y_{\text{exp},i}$  is determined by the elements of the vectors such as the one in Eq. 20a and  $y_{t,i}$  is calculated using Eq. 22. The significance of the identified parameters and the selection of the most adequate model was performed using Fisher's test. The model selected was the one which exhibited the highest value for the Fisher parameter:

$$F_{\text{calc}} = \frac{(m-l) \sum_{i=1}^m (y_{\text{exp},i} - \overline{y_{\text{exp}}})^2}{(m-1) \sum_{i=1}^m (y_{\text{exp},i} - y_{t,i})^2} \quad (24)$$

where  $\overline{y_{\text{exp}}}$  is the mean value of the variable  $y_{\text{exp}}$  and  $l$  is the number of adjusted parameters of the model.

The same procedure was applied to each of the isotherm models using the same set of experimental data [6] and following the same progressive approach as reported previously: (1) to determine the best values of the parameters for the single-component isotherm model and use them in the corresponding competitive model while fitting the remaining interaction parameters when needed; and (2) to empirically fit the whole set of parameters of the model.

#### 4. Results and discussion

The results of the regression analysis of the models evaluated are reported in Table 1. The first

column of this table gives the equation numbers of the isotherm models discussed in the text. The values of the RSS are listed separately for each component, in the cases of the single-component and the competitive isotherm data. The values between parentheses correspond to the competitive data. The global value of the RSS for the whole set of single and competitive data (RSS) is also given, as well as the value calculated for the Fisher parameter. For the sake of comparison with the results obtained in this study, Table 2 reports the results obtained previously [6].

#### 4.1. Langmuir isotherms

The fit of the Langmuir model (Eqs. 2a and 2b) to the single-component data gave values of the identified parameters which are statistically similar (in terms of the asymptotic 95% confidence interval) to those determined previously [6]. However, the values of the estimates are slightly different and the value of the RSS calculated using Eqs. 1 or 18a and 18b, and the competitive data is higher for PE and lower for PP compared to those reported [6]. The new global value of the RSS for both components is also lower. This justifies the recalculation of the parameters of the Langmuir model for the set of experimental data previously analyzed [6]. This ensures homogeneity in the analysis of the suitability of the several models used in this study because the use of these models, which were not tested previously, requires the calculation of the Langmuir single-component identified parameters.

The empirical fit of the competitive Langmuir model (Eqs. 1) gives a value of RSS which is lower than the one previously reported [6]. The parameters  $A_1$  and  $b_1$  are statistically different from those reported previously, while  $A_2$  and  $b_2$  are similar. All the parameters are significantly different from those determined for single-component adsorption. The RSS of PP is lower than the one reported [6], whereas it is higher for PE. The best fit of the model to the whole set of experimental data causes compromises in the estimates of the data for both components. In the previous analysis [6], the compromise was mainly on the estimate of the PP data (see Table 2) and the fit of the PE data remained as good as the one obtained when using only the single-

component parameters in the competitive model. These differences are probably a result of the use of a different software package and of the application of different objective functions in the least-squares minimization procedures in the present work and in the previous study [6,21].

#### 4.2. Simplified quadratic isotherm

The fit of the 7-coefficient quadratic models (Eqs. 5a and 5b), which uses the four parameters determined by regression of the single-component data, gives a value of the RSS which is lower than the one previously reported [6] for the same test. The value of the RSS for PE is slightly higher while the one for PP is significantly lower. The value of  $a_{2,1}$  remains similar. The values of the coefficients  $a_{1,2}$  and  $b_{1,2}$  are different, especially the latter which, although small, is significantly different from zero. The negative value of  $a_{2,1}$  shows that an increase in the mobile phase concentration of PE produces a greater decrease of the stationary phase concentration of PP than predicted by the Langmuir model (Eq. 1). The positive value of  $a_{1,2}$  reflects an influence of the mobile phase concentration of PP on the stationary phase concentration of PE at equilibrium which is opposite to the influence of PE on PP. The influence of  $a_{2,1}$  may be explained in terms of the kinetic equations from which Eqs. 5a and 5b are derived from [21]. The positive value of  $b_{1,2}$  results in an increase in the value of the denominator in Eqs. 5a and 5b and in an additional decrease in the stationary phase concentration of both components at equilibrium, compared to that predicted by the Langmuir model.

The empirical fit of the experimental data to the model results in statistically similar values for all the identified parameters in this work as well as in our previous study [6], with the exception of  $b_{1,2}/b_{2,1}$ . The value obtained for  $b_{1,2}/b_{2,1}$ , although small is statistically significant. The value of the global RSS is lower than previously reported [6]. As in the case of the empirical fit of the Langmuir model, the RSS of PP is lower than that reported previously [6], whereas that of PE is higher.

The best fit of the model to the whole set of experimental data is achieved by sacrificing some of the accuracy of the estimation of the data for both

Table 1  
Summary of the non-linear regression analysis

Model	Parameters	RSS		$\Sigma$ RSS	$F_{\text{calc}}$
		PE	PP		
Eqs. 1 and 2 SCD <sup>a</sup>	$q_{s,1} = 154 \pm 7$ $a_1 = 2.30 \pm 0.01$ $b_1 = 0.015 \pm 0.001$ $q_{s,2} = 134 \pm 12$ $a_2 = 4.7 \pm 0.2$ $b_2 = 0.035 \pm 0.005$	0.002 (3.08)	0.444 (249.61)	253.14	22.99
Eqs. 1 best fit	$q_{s,1} = 49 \pm 8$ $a_1 = 2.8 \pm 0.2$ $b_1 = 0.06 \pm 0.01$ $q_{s,2} = 230 \pm 60$ $a_2 = 3.9 \pm 0.2$ $b_2 = 0.02 \pm 0.01$	2.24 (6.59)	12.39 (13.11)	34.33	169.5
Eqs. 5 and 2 SCD	$a_1 = 2.3 \pm 0.01$ $a_{12} = 0.08 \pm 0.04$ $a_2 = 4.7 \pm 0.2$ $a_{21} = -0.17 \pm 0.06$ $b_1 = 0.0150 \pm 0.0009$ $b_2 = 0.035 \pm 0.005$ $b_{12} = 0.006 \pm 0.004$ $b_{21} = 0.006 \pm 0.004$	0.002 (1.74)	0.444 (42.29)	44.48	132.61
Eqs. 5 best fit	$a_1 = 2.3 \pm 0.2$ $a_{12} = 0.03 \pm 0.04$ $a_2 = 4.0 \pm 0.2$ $a_{21} = -0.07 \pm 0.06$ $b_1 = 0.02 \pm 0.02$ $b_2 = 0.017 \pm 0.004$ $b_{12} = 0.005 \pm 0.002$ $b_{21} = 0.005 \pm 0.002$	0.03 (1.40)	10.00 (12.67)	24.10	231.64
Eqs. 4 and 2 SCD	$a_1 = 2.3 \pm 0.01$ $a_{12} = 0.04 \pm 0.04$ $a_{11} = -0.06 \pm 0.04$ $a_2 = 4.7 \pm 0.2$ $a_{21} = -0.23 \pm 0.06$ $a_{22} = 0.05 \pm 0.04$ $b_1 = 0.0150 \pm 0.0009$ $b_2 = 0.035 \pm 0.005$ $b_{11} = -0.004 \pm 0.002$ $b_{22} = -0.001 \pm 0.001$ $b_{12} = 0.003 \pm 0.004$ $b_{21} = 0.003 \pm 0.004$	0.002 (2.74)	0.444 (27.65)	30.84	181.05
Eqs. 4 best fit	$a_1 = (10 \pm 16) 10^9$ $a_{12} = (14 \pm 12) 10^8$ $a_{11} = (15 \pm 10) 10^9$ $a_2 = (6 \pm 8) 10^8$ $a_{21} = (22 \pm 16) 10^9$ $a_{22} = (3 \pm 2) 10^9$ $b_1 = (7 \pm 6) 10^9$ $b_2 = (6 \pm 4) 10^8$ $b_{11} = (14 \pm 10) 10^7$ $b_{22} = (9 \pm 10) 10^7$ $b_{12} = (16 \pm 14) 10^6$ $b_{21} = (16 \pm 14) 10^6$	0.14 (1.37)	0.02 (2.45)	3.98	1320.5



Table 1 (continued)

Model	Parameters	RSS		$\Sigma$ RSS	$F_{\text{calc}}$
		PE	PP		
Eqs. 6 and 7 SCD	$A_1 = A_2 = 79 \pm 4$ $a_{11} = 0.029 \pm 0.002$ $a_{22} = 0.057 \pm 0.004$ $a_{12} = 0.02 \pm 0.01$ $a_{21} = -0.06 \pm 0.01$	0.002	0.7	51.46	116.14
Eqs. 6 best fit	$A_1 = 43 \pm 6$ $a_{11} = 0.06 \pm 0.01$ $a_{12} = 0.020 \pm 0.02$ $A_2 = 117 \pm 26$ $a_{22} = 0.034 \pm 0.008$ $a_{21} = 0$	(4.04)	(46.72)	30.25	189.82
Eqs. 8 and 2 SCD	$A_1 = 154 \pm 7$ $b_1 = 0.015 \pm 0.001$ $b_{12} = 0$ $A_2 = 134 \pm 12$ $b_2 = 0.035 \pm 0.005$ $b_{21} = -0.065 \pm 0.008$	0.002	0.444	69.88	86.66
Eqs. 8 best fit	$A_1 = 65 \pm 22$ $b_{11} = 0.04 \pm 0.02$ $b_{12} = 0$ $A_2 = 201 \pm 46$ $b_{22} = 0.020 \pm 0.006$ $b_{21} = -0.02 \pm 0.02$	(2.59)	(18.40)	31.21	183.94
Eqs. 9, 10 and 11 SCD	$A_1 = A_2 = 134 \pm 7$ $a_{11} = 0.031 \pm 0.01$ $b_{11} = -0.01 \pm 0.01$ $b_{22} = 0.035 \pm 0.003$ $a_{21} = -0.073 \pm 0.01$ $b_{12} = a_{22} = 0$ $b_{21} = a_{12} = 0$	0.001	0.44	46.69	129.68
Eqs. 9 and 10 best fit	$A_1 = 89 \pm 42$ $b_{11} = 0.027 \pm 0.02$ $A_2 = 206 \pm 46$ $b_{22} = 0.020 \pm 0.005$ $a_{21} = -0.04 \pm 0.02$ $b_{12} = a_{22} = 0$ $b_{21} = a_{12} = a_{11} = 0$	(1.37)	(18.04)	28.59	200.79

<sup>a</sup> Competitive model which uses single-component identified parameters.

components. In the previous study [6], the main loss was experienced on the estimate of the PP data, as seen in Table 2. It is worth noting the statistical similarity between the following sets of parameters:  $a_1$  from the best fit of Eqs. 5 and from the single-component data (Eqs. 2);  $a_{1,2}$  from the best fit of Eqs. 5 and from the fit of the data to Eqs. 5 when using the single-component parameters for the  $a_i$ s and  $b_i$ s;  $a_2$  from the best fit of Eqs. 5 and from the

best fit of the single-component data to Eqs. 1;  $b_1$  from the best fit of Eqs. 5 and from the fit of the single-component data to Eqs. 2;  $b_2$  from the best fit of Eqs. 5 and from the best fit of Eqs. 1;  $b_{1,2}$  from the best fit of Eqs. 5 and from the fit of Eqs. 5 when using the single-component identified parameters. These similarities are the obviously the result of the relationship between the Langmuir and the 7-parameter quadratic model.

Table 2  
Summary of previously reported [5] results

Model	Parameters	RSS	
		PE	PP
Eqs. 1 and 2 SCD	$A_1=153$ $a_1=2.3$ $b_1=0.015$ $A_2=124$ $a_2=4.82$ $b_2=0.039$	(2.4)	(287)
Eqs. 1 best fit	$A_1=109$ $a_1=2.4$ $b_1=0.022$ $A_2=200$ $a_2=3.83$ $b_2=0.01913$	0.20 (1.78)	30.6 (16.4)
Eqs. 5 and 2 SCD	$a_1=2.30$ $a_{12}=0.030$ $a_2=4.82$ $a_{21}=-0.20$ $b_1=0.015$ $b_2=0.039$ $b_{12}=b_{21}=0$	(1.26)	(75.8)
Eqs. 5 best fit	$a_1=2.30$ $a_{12}=0.02$ $a_2=3.85$ $a_{21}=-0.075$ $b_1=0.021$ $b_2=0.022$ $b_{12}=b_{21}=0$	0.22 (0.93)	48.6 (8.3)

#### 4.3. Complete quadratic isotherm

The fit of the complete, 11-coefficient quadratic model (Eqs. 4) using the values of the parameters  $a_i$  and  $b_i$  determined by regression of the single-component data to the Langmuir model (Eqs. 1) affords a value of the RSS which is lower than the one obtained with the best fit of the data to the Langmuir model and to the 7-parameter quadratic equation (Eqs. 5). The assumptions on which the equations (Eqs. 4) of this model are based make it possible to take into account the molecular interactions between adsorbate molecules in both the solution and the sorbed monolayer. The derivation of the model considers that the rates of adsorption and desorption of each component are linear functions of the concentrations of both components in both phases. The four parameters  $a_{1,1}$ ,  $a_{2,2}$ ,  $b_{1,1}$  and  $b_{2,2}$  account

for the influence of the concentration of one component of the binary mixture on the rate of desorption of the other, while this influence is not considered in the Eqs. 5. This should improve the accuracy of the former model (Eqs. 4). The parameters  $a_{1,2}$ ,  $a_{2,1}$ ,  $b_{1,2}$  and  $b_{2,1}$  are statistically similar to those determined in a similar manner for the 7-parameter quadratic model using single-component derived parameters.

The empirical fit of the experimental data to the Eqs. 4 resulted in a low value of the RSS (see Table 1), as expected, since model errors decrease with increasing number of the adjustable coefficients. The RSS value is lower than the one obtained for any other model studied here or previously [6]. It is even better than the one obtained with the Fowler model [6]. However, the values of the estimates obtained are very different from those determined with any of these models. The adjustment errors are higher, due to the significant numbers of parameters involved in the fitting procedure. The numerical values of the estimates are physically unrealistic, for example, the monolayer capacity. This situation occurs often when experimental data are fitted to complex models with many parameters. The equation tends to become empirical and its parameters to lose their physical meaning.

Eqs. 4 are explicit with respect to the mobile phase concentrations of the components. Accordingly, they can be implemented directly in programs for the calculation of band profiles in non-linear chromatography. They do not suffer from the serious practical drawback of the Fowler isotherm model which requires the implementation of its numerical inversion in each loop of the program, causing a considerable increase of the CPU time required.

#### 4.4. The original Jovanovic isotherm

The single-component Jovanovic model (Eq. 7a for one component, with  $a_{2,1} = C_2 = 0$ ) accounts fairly well for the experimental data. The RSS for PE has the same value as the one obtained with the Langmuir model while the one obtained for PP is higher, as seen in Table 1. The difference between the values of the monolayer capacity obtained for PE and PP by the separate regression analysis of each

single-component data was not significant in statistical terms and a unified value was estimated for the whole set of single-component data. The fit of the competitive model (Eqs. 6a and 6b) with these values of the single-component parameters ( $a_{1,1}$  and  $a_{2,2}$ ) permitted the obtention of a RSS value which was less than the one obtained with the competitive Langmuir model (Eqs. 1). The parameters  $a_{1,2}$  and  $a_{2,1}$  account for the interactions between the two components. The coefficient  $a_{2,1}$ , which characterizes the influence of the mobile phase concentration of PE on the amount of PP adsorbed on the stationary phase has a higher absolute value, is negative, and was determined with less error than the converse cross-coefficient,  $a_{1,2}$ .

These facts show that the non-ideal influence of the concentration of PE over the amount of PP adsorbed is stronger than the converse. They confirm the results previously established with the two versions of the quadratic model. It seems that the influence of PP over PE is almost ideal, and can be accounted for quite well by the majority of the models previously tested, even by the competitive Langmuir model which uses the single-component identified parameters and takes no account of any adsorbate–adsorbate interactions. The negative value obtained for  $a_{2,1}$  implies, in terms of the Jovanovic model [23], that the increase of the mobile phase concentration of PE causes an increase of the number of the PP molecules desorbed during the settling time, for a given equilibrium number of adsorbed PP molecules. In other words, this means that the PE present in the mobile phase ‘extracts’ the adsorbed PP. This is an interesting result because, in the derivation of the isotherm equations of the Jovanovic model [22–24], there is no explicit reference to the possibility of finding negative values for the interaction parameters  $a_{i,j}$ . Accordingly, the physical meaning of the parameters obtained is questionable.

The fitting of the experimental data to Eqs. 6a and 6b gave a value of RSS lower than the one obtained with the fitting of the same data to the competitive Langmuir model (Eqs. 1). The similarity between the values obtained for the monolayer capacity ( $A_1$ ) and the non-linear parameters ( $b_1$  and  $a_{1,1}$ ) for both models is remarkable. This result may be related to the fact that the Langmuir model can be derived from the Jovanovic model by expanding the ex-

ponentials in power series and neglecting the non-linear terms. During this operation, the parameters depending on two different subscripts, which are those accounting for the interactions between different components, vanish [23]. This does not mean, however, that the competitive Langmuir model can be considered as a particular case of the Jovanovic model (Eqs. 6) [24]. A similar situation is observed between the values  $A_2$ ,  $a_{2,2}$  from the best fit of the Jovanovic model and the terms  $a_2$  and  $b_2$  obtained from the best fit of the Langmuir model (Eqs. 2) using single-component data.

#### 4.5. The Jovanovic isotherm with random distribution of settling times

The fit of the experimental data to this second Jovanovic model (Eqs. 8), a model which uses the single-component parameters identified from the Langmuir model confirms the previous result, regarding the different influences of the mobile phase concentrations of the two adsorbates on the amount of the other one adsorbed at equilibrium. The value of  $b_{1,2}$  is near 0, which confirms the weak influence of the mobile phase concentration of PP on the amount of PE adsorbed. Because this model (Eqs. 8) reduces to the Langmuir model (Eqs. 1), for values of the  $b_{i,j}$  parameters equal to 0, it is obvious that the influence of PP over PE is almost ideal and may well be accounted by the Langmuir model, as stated previously. It is worth noting the similarity between: (1) the absolute value, error and sign found for  $a_{2,1}$  from the best fit of Eqs. 6 using single-component data; and (2) those found for  $b_{2,1}$  from the similar fit of Eqs. 8 because these two coefficients have a similar physical meaning. The value obtained for the RSS with this model is larger, however, than that obtained for the model of Eqs. 6. So, this second Jovanovic model, which considers a completely random distribution of the settling times, is less adequate to account for the adsorption data in the chromatographic system studied.

The empirical fit of the whole set of experimental data to Eqs. 7 gives a value of RSS slightly higher than the one derived from the empirical fit of same data to the previous model (Eqs. 6). Noteworthy is the statistical similarity between the parameters  $A_1$ ,

$b_{1,1}$ ,  $A_2$  and  $b_{2,2}$  derived from the empirical fit of the data to Eqs. 7 and the parameters  $A_1$ ,  $b_1$ ,  $A_2$  and  $b_2$  derived from the empirical fit of the same data to Eqs. 1.

#### 4.6. The Jovanovic isotherm with Heaviside distribution of settling times

The fit of the experimental data for the pure components to the non-competitive form of this last model (Eq. 11) gave values for the monolayer capacity of both components which were not statistically different, so a unique value was estimated from a fit of the whole set of single-component data to the two Eqs. 11. When  $a_{i,j} = 0$ , Eqs. 9 and 10 reduce to Eqs. 8 while when  $b_{i,j} = 0$  these same Eqs. reduce to Eqs. 6. The higher degree of generality of the model expressed by Eqs. 9 compared to the models corresponding to Eqs. 1, 6 or 8 in terms of the settling times distribution functions was reported elsewhere [24]. It is noteworthy that the values obtained for the parameter  $a_{1,1}$  from the fit of the data to Eq. 11 and to Eq. 7 are statistically the same. An identical situation is encountered for the values of  $b_{2,2}$  derived from Eqs. 11 or 2. The value derived for the parameter  $A$  from Eq. 11 is similar to the one obtained for PP by regression of the data to the Langmuir model (Eq. 2). This is in compliance with these parameters having a similar physical significance in all models. However, there are significant differences on the one hand between the values of  $b_{1,1}$  obtained from the fit of the data to Eq. 11 and of  $b_1$  obtained from their fit to Eq. 2 and on the other hand between the values obtained for  $a_{2,2}$  from the fit of the data to Eqs. 11 and 6. The value of the RSS for the fit of the data to Eqs. 11 is the lowest obtained for the single-component models evaluated. There is no simple physical explanation to the negative value of  $b_{1,1}$ . The zero value obtained for  $a_{2,2}$  implies that the adsorption of PP pure is better accounted for by the Langmuir model, as stated previously. Because the experimental data fit well to the equations of the model is no guarantee that the values obtained for the parameters have the physical meaning afforded to them in the derivation of the equations of this model.

The similarity between the values of the monolayer capacity estimated for each compound in terms of two single-component adsorption isotherm models

should be underlined. This comment applies whether the model used is expressed by Eqs. 7 or 11. These compounds make a pair of monofunctional homologs without any great difference between their chain lengths. It is possible that their structural differences have only little influence on the value of the surface area of contact between the adsorbates and the surface, as a result of the preferential spatial orientation of the adsorbates with respect to the surface. This facts also explain why the LeVan–Vermeulen model [31], previously tested [6], did not significantly improve the quality of the fit obtained with the Langmuir model. The values of the monolayer capacity obtained from a fit of the data to the single-component Langmuir model, although statistically different (20%), are very close, thus also giving support to this hypothesis.

The fit of the experimental data to Eqs. 9 and 10 using the values of the parameters identified in the single-component study above confirmed the assumption made previously regarding the weak influence of PP on the adsorption of PE due to adsorbate–adsorbate interactions ( $a_{1,2} = b_{1,2} = 0$ ). The  $a_{2,1}$  value is similar to that obtained in the similar fit of the data to Eq. 6, whereas the value obtained for  $b_{2,1}$  is 0, at variance from the result derived from the fit of the data to Eq. 8. The value obtained for RSS is the lowest one obtained within any of the Jovanovic models, but only slightly. Accordingly, it is not possible to conclude whether the higher degree of generality of the model [24] makes it a better predictor of experimental data in the specific case studied.

In spite of the complexity of this model, the empirical fit of the experimental data to the competitive model (Eqs. 9, 10) did not significantly improve the value of the RSS compared to the values obtained with the other models tested. For this reason, it is not worth using this model to account empirically for the whole set of experimental data. The values of the parameters obtained do not deserve special comment.

## 5. Conclusions

The present study confirms the need of continuing the search for adsorption isotherm models which

could correctly predict the competitive behavior of the components of a binary mixture using parameters identified from single-component adsorption behavior. None of the models tested previously [6] or evaluated in this study gave results which are completely satisfactory, although all of them predict the competitive behavior of the two components studied better than the Langmuir model. Unfortunately, it is necessary to have competitive adsorption data available in order to identify the interaction parameters present in these models. So far, the competitive Fowler isotherm model remains the best in terms of the prediction of the competitive data from the analysis of single-component data, as previously reported [6]. This model is the simplest model of localized adsorption with non-specific lateral attractive interactions between the adsorbed molecules. It does not consider any interactions in the liquid phase [32]. The Jovanovic models, on the other hand, do not take into account the interactions between adsorbed molecules.

Thus, models which take into account adsorbate–adsorbate interactions in both phases, such as the 11-parameter quadratic model, appear to be the strongest candidates to solve the present problem. The empirical fit of the experimental data to these models, although a practical procedure of parameter identification, does not give, in general, a low value of the RSS. This is true even with the Fowler model. In most cases, the estimation of the single-component data is severely sacrificed. The only reasonable exception seems to be the 11-parameter quadratic model which accounts well for the whole set of experimental data, giving a fairly low value of the RSS. This model is explicit with respect to the mobile phase concentrations of both components. This eliminates the serious, practical drawback associated with the use of the Fowler isotherm model, which is due to the need for its numerical inversion in each loop of the programs which calculates band profiles in non-linear chromatography and to the corresponding increase of CPU time required.

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