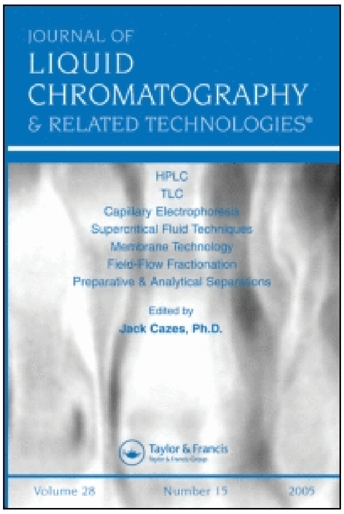

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Behavior of Some Predictive Isotherm Adsorption Models Describing the Multicomponent Equilibria of Phenol/*o*-Cresol in a Reversed-Phase Chromatographic System

Jorge E. García-Galdo[a]; Ulises J. Járegui-Haza[a]; Pavel Jandera[b]
[a] Departamento de Desarrollo Tecnológico, Centro de Química Farmacéutica (CQF), La Habana, Cuba [b] Department of Analytical Chemistry, University of Pardubice, Pardubice, Czech Republic

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Behavior of Some Predictive Isotherm Adsorption Models Describing the Multicomponent Equilibria of Phenol/*o*-Cresol in a Reversed-Phase Chromatographic System

Jorge E. García-Galdo and Ulises J. Jáuregui-Haza
Departamento de Desarrollo Tecnológico, Centro de Química
Farmacéutica (CQF), La Habana, Cuba

Pavel Jandera
Department of Analytical Chemistry, University of Pardubice,
Pardubice, Czech Republic

Abstract: The suitability of different isotherm adsorption models to describe two-component adsorption equilibria of phenol and *o*-cresol on a RP-18 column was studied in aqueous-organic mobile phases with three different concentrations of methanol (10%, 20% and 30%). The isotherm models employed take into account homogeneous or heterogeneous adsorbent surfaces and lateral interactions of adsorbed solutes. The reliability of the predicted two-component isotherm distribution data increases with increasing methanol concentration, both for models assuming homogeneous surface and lateral interactions between the adsorbed molecules and models considering both lateral interactions and surface heterogeneity. A modified Langmuir-Freundlich model enables the best prediction of the two-component equilibria from single-component experimental distribution data, but other models such as Jovanovic Freundlich, Fowler Guggenheim-Langmuir Freundlich, and Fowler Guggenheim-Jovanovic Freundlich models also enable satisfactory predictions.

Keywords: Adsorption isotherms, Phenol, *o*-Cresol, Two-component distribution equilibria

Address correspondence to Dr. Pavel Jandera, Department of Analytical Chemistry, University of Pardubice, Nám Čs Legií 565, 53210 Pardubice, Czech Republic. E-mail: pavel.jandera@upce.cz

INTRODUCTION

Chromatographic purification is becoming increasingly employed as a means of separating drugs from related impurities to produce pure compounds. In order to optimize and scale-up the preparative liquid chromatography (LC) unit operation, mathematical modeling can be used to save time, solvent consumption, and overall costs connected with tedious and time-consuming empirical method development based on trial and error approaches.[1] For calculation of elution bands profiles using non-linear chromatography models, the isotherm describing the adsorption equilibrium should be determined first, but the experimental measurement of the adsorption isotherms is not always straightforward.[1] For this reason, attempts are reported to determine the multi-component distribution data on the basis of single-component isotherm distribution data.[2–9] To solve this problem, reliable models are needed that allow prediction of binary or ternary distribution equilibria using the information obtained from single component isotherm data.[1,2,9–15] The adsorption isotherm models reported in the literature are based on various more or less simplifying assumptions.

Some models consider the essential sources of non-ideal behavior, like the adsorbate–adsorbate intermolecular interactions and the heterogeneity of the adsorbent surface. The Langmuir,[16] Le Van-Vermeulen,[17] Fowler,[18] Moreau,[19] Ruthven,[11] Kiselev,[15,20] Langmuir-Freundlich (LF),[11] Jovanovic-Freundlich (JF),[16] Fowler-Guggenheim/Langmuir-Freundlich (FG-LF),[12,16] Fowler-Guggenheim/Jovanovich-Freundlich (FG-JF),[16] and various models derived from the Adsorbed Solution Theory[9,13,21] can be used to predict binary equilibria from single-component isotherm data. Moreau, Ruthven, and Kiselev models are not completely predictive and assume some specific considerations.[15] With other models, it is necessary to apply combination rules for estimating the value of cross parameters that depend on the molecular size, such as in FG-LF, FG-JF, and one version of the Fowler model.[16] Quiñones and Guiochon have tested the reliability of several models predicting the multicomponent adsorption equilibrium of 2-phenyl ethanol and 3-phenyl ethanol on reversed-phase (RP) stationary phase. However, these models have not been validated or verified with enough experimental data and the results obtained are not entirely satisfactory.[15,16,22]

The coefficients of various isotherm models depend on the stationary phase and the mobile phase used for the separation, which should be taken into account in the optimization of chromatography process.[5,6,23,24] The composition of the mobile phase is frequently adjusted for the retention optimization in LC.[25] For instance, Guiochon[25] suggests that the retention factor for the first component should be approximately 2 to obtain maximum resolution between the critical feed components in preparative chromatography. Generally, simple equations relating the fraction volume of the organic modifier in the mobile phase with the isotherm parameters are employed in calculation routines to simulate chromatographic process.[26]

Many works focused on the effect of the organic modifier concentration on the retention, trying to elucidate the retention mechanism in RP-LC, see for example the recent work by Nikitas et al.[27,28] Jandera and Komers[6] investigated the effect of the organic modifier in aqueous-organic mobile phases on the adsorption isotherms based on Langmuir, quadratic, and Jovanovic models. The suitability of the models to correlate the binary equilibria of phenols in RP systems depends on the concentration of methanol in mobile phase. Further, models taking into account the effect of the mobile phase on the distribution of solutes between the stationary and the mobile phases have been studied in normal-phase systems considering the competition between the sample and the components of a mixed organic mobile phase.[5]

However, few predictive isotherm models have been tested experimentally at different mobile phase compositions. Further systematic studies are needed to elucidate the effect of mixed mobile phases on overloaded separations under non-linear isotherm conditions in RP or normal-phase LC systems. Such investigation could be helpful to develop a systematic approach for selecting optimum preparative conditions using empirical rules. In the present work, possibilities of using various predictive isotherm models to characterize and predict binary distribution equilibria of phenol and *o*-cresol from single-component distribution data on an octadecyl silica column at three modifiers concentration (10%, 20%, and 30%) are investigated.

THEORY

Several mathematical models have been developed to describe the distribution equilibrium between the concentration of one or more compounds between the solid phase *(q)* and the bulk liquid phase *(C)*. The simple Langmuir adsorption model[17] is most widely used to describe the adsorption equilibrium of a single compound. It has been derived assuming that one molecule is adsorbed per each adsorption site until monolayer coverage of a homogeneous adsorbent surface is achieved, and that the adsorbed molecules do not interact with one another. The model can be described by Eq. (1):

$$\theta = \left(\frac{q}{q_s}\right) = \frac{bc}{1 + bC} \quad (1)$$

Here θ is the fractional coverage, q_s is the adsorbent saturation capacity at the full coverage of the adsorbent surface, and b is the isotherm parameter.

The adsorption of a multi-component mixture can be characterized by the competitive Langmuir model[29] with the same meaning of the symbols as in Eq. (1); the subscripts, *i*, *j*, relate to the individual components of an *n*-component sample:

$$q_i = q_{si}\frac{b_i}{1+\sum_{j=1}^{n} b_j C_j} \tag{2}$$

The competitive Langmuir model is thermodynamically consistent only if the adsorbent saturation capacities are the same for all mixture components, $q_{s1} = q_{s2}$.[14,28] Such an assumption is unrealistic with mixtures of compounds with great differences in the size of molecules and calculations based on Eq. (2); using different values of q_s determined from single-component experimental data may result in erroneous results, especially at high concentrations.[11] To overcome the problem connected with different adsorbent saturation capacities, Le Van and Vermeulen suggested a model based on the ideal adsorption solution theory,[14] which—in case of a two-component mixture—can be described by Eqs. (3a)–(3d):

$$q_1 = \frac{q_s b_1 C_1}{1 + b_1C_1 + b_2C_2} + \Delta_{12} \tag{3a}$$

$$q_2 = \frac{q_s b_2 C_2}{1 + b_1C_1 + b_2C_2} - \Delta_{12} \tag{3b}$$

Where:

$$q_s = \frac{a_1C_1 + a_2C_2}{b_1C_1 + b_2C_2} \tag{3c}$$

$$\Delta_{12} = (q_{s1} - q_{s2})\frac{b_1b_2C_1C_2}{(b_1C_1 + b_2C_2)^2}\ln(1 + b_1C_1 + b_2C_2) \tag{3d}$$

The Le Van-Vermeulen model requires only Langmuir single component parameters for explicit calculation of the competitive distribution isotherms. If the differences between the saturation capacities *(q_s)* of the two components are not too large, the results using both the Langmuir and the Le Van-Vermeulen models are similar.

Jovanovic[30] developed another adsorption model describing monolayer adsorption on a homogeneous adsorbent surface in the absence of lateral interactions between adsorbed molecules.

$$\theta = 1 - e^{-KC} \tag{4}$$

The Jovanovic competitive model for the adsorption of a two-component mixture is represented by Eqs. (5a) and (5b):[16]

$$\theta_1 = \frac{K_1C_1}{K_1C_1 + K_2C_2}[1 - e^{-(K_1C_1+K_2C_2)}] \tag{5a}$$

$$\theta_2 = \frac{K_2C_2}{K_1C_1 + K_2C_2}[1 - e^{-(K_1C_1+K_2C_2)}] \tag{5b}$$

Fowler and Guggenheim[18] proposed the simplest model for localized monolayer adsorption with lateral interactions between the adsorbed molecules with the isotherm equation:

$$C = \frac{\theta}{K(1-\theta)} e^{-X\theta} \tag{6}$$

Here K is the adsorption isotherm parameter and χ is the lateral interaction parameter.

The programs for calculating band profiles in non-linear chromatography need the local values of the adsorbed phase concentrations at different positions in the column. It is impossible to inverse the Fowler model for direct analytical calculation of q as a function of C. Numerical methods necessary for calculations based on this model require considerable calculation time,[2] which is a drawback of these types of models.

Jaroniec et al.[27] proposed a competitive extension of the Fowler model resulting in Eqs. (7a, 7b):

$$\frac{1}{C_1}\frac{\theta_1}{1-(\theta_1+\theta_2)} = K_1 e^{-(X_1\theta_1+X_{12}\theta_2)} \tag{7a}$$

$$\frac{1}{C_2}\frac{\theta_2}{1-(\theta_1+\theta_2)} = K_2 e^{-(X_2\theta_2+X_{21}\theta_1)} \tag{7b}$$

Here the coefficients χ_{12} and χ_{21} account for the different influence of the molecules of the second component on the adsorption of the first sample component, and vice-versa. Quiñones and Guiochon[15] estimated the value of the cross parameters, χ_{12} and χ_{21}, using the geometric mean of the single component parameters obtained with single component experimental data:[29]

$$\chi_{12} = \chi_{21} = (\chi_1\chi_2)^{1/2} \tag{8}$$

In addition to Eq. (7), other extensions of the competitive Fowler model were reported.[2]

Moreau et al.[19] proposed other types of models that take into account possible lateral interactions between the solutes in the adsorbed phase. The models enable direct calculation of the stationary phase concentrations, so that numerical inverse solution is not necessary. If the interactions between the adsorbate molecules are limited to those between the adjacent molecules of the same type, the model is described by Eq. (9):

$$\theta = \frac{KC + b(KC)^2}{1 + 2KC + b(KC)^2} \tag{9}$$

where b is the adsorbate-adsorbate lateral interaction parameter defined as $b = e^{-E/RT}$.

Eqs. (10a) and (10b) characterize the adsorption of a binary mixture:[19]

$$\theta_1 = \frac{[K_1C_1 + b_{11}(K_1C_1)^2 + b_{12}K_1K_2C_1C_2]}{[1 + 2(K_1C_1 + K_2C_2 + b_{11}(K_1C_1)^2 + b_{22}(K_2C_2)^2 + 2b_{12}K_1K_2C_1C_2]} \tag{10a}$$

$$\theta_2 = \frac{[K_2C_2 + b_{22}(K_2C_2)^2 + b_{12}K_1K_2C_1C_2]}{[1 + 2(K_1C_1 + K_2C_2 + b_{11}(K_1C_1)^2 + b_{22}(K_2C_2)^2 + 2b_{12}K_1K_2C_1C_2]} \tag{10b}$$

The parameters b_{ii} can be obtained from single component adsorption data. The cross interaction coefficient, b_{12}, accounts for the interaction between the two different types of molecules in the adsorbed phase and must be determined from binary adsorption data.

Ruthven proposed a model considering the location of molecules in different cages, each containing a finite number of adsorbate molecules.[11] This model could describe successfully the adsorption on zeolites with a cage-like structure interconnected through small windows.[15] Assuming that each cage can accommodate up to two molecules:

$$\theta = \frac{KC + R(KC)^2}{1 + KC + (R/2)(KC)^2} \tag{11}$$

R is the parameter characterizing the adsorbate-adsorbate interactions in a cage.

The competitive equilibria may be expressed by means of the following equations:

$$\theta_1 = \frac{[K_1C_1 + R_{20}(K_1C_1)^2 + R_{11}(K_1C_1)(K_2C_2)]}{\left[\begin{array}{c} 1 + K_1C_1 + K_2C_2 + (R_{20}/2)(K_1C_1)^2 \\ +(R_{02}/2)(K_2C_2)^2 + R_{11}(K_1C_1)(K_2C_2) \end{array}\right]} \tag{12a}$$

$$\theta_2 = \frac{[K_2C_2 + R_{02}(K_2C_2)^2 + R_{11}(K_1C_1)(K_2C_2)]}{\left[\begin{array}{c} 1 + K_1C_1 + K_2C_2 + (R_{20}/2)(K_1C_1)^2 \\ +(R_{02}/2)(K_2C_2)^2 + R_{11}(K_1C_1)(K_2C_2) \end{array}\right]} \tag{12b}$$

Different versions of the Ruthven and Moreau models have been applied to predict binary equilibria.[15].

The surface heterogeneity is another source of non-ideal behavior during the adsorption process.[12] Many mathematical equations have been developed to describe adsorption on heterogeneous surfaces without considering lateral interactions.[12]

The Langmuir-Freundlich (LF)[11,12] isotherm model has been applied successfully to the correlation of two-component distribution equilibrium data. The model contains a parameter (ν) that accounts for heterogeneous surfaces, similar to the Freundlich[31] model parameter.

$$\theta_t = \frac{(aC)^v}{1 + (aC)^v} \tag{13}$$

Jaroniec et al.[12] proposed the following expressions to characterize the adsorption of a binary mixture:

$$\theta_{t1} = \frac{a_1C_1}{a_1C_1 + a_2C_2}\frac{(a_1C_1 + a_2C_2)^{\bar{v}}}{[1 + (a_1C_1 + a_2C_2)^{\bar{v}}]} \tag{14a}$$

$$\theta_{t2} = \frac{a_2C_2}{a_1C_1 + a_2C_2}\frac{(a_1C_1 + a_2C_2)^{\bar{v}}}{[1 + (a_1C_1 + a_2C_2)^{\bar{v}}]} \tag{14b}$$

Equations (14a) and (14b) assume that the two-component heterogeneity parameter ν can be calculated as the arithmetic mean of the single component parameters.[16]

Based on the simple Langmuir two-component adsorption model, Eqs. (15a) and (15b) were proposed for the LF two-component adsorption equilibrium:[11]

$$\theta_{t1} = \frac{(a_1C_1)^{v_1}}{1 + (a_1C_1)^{v_1} + (a_2C_2)^{v_2}} \tag{15a}$$

$$\theta_{t2} = \frac{(a_2C_2)^{v_2}}{1 + (a_1C_1)^{v_1} + (a_2C_2)^{v_2}} \tag{15b}$$

Semi-empirical single-component Jovanovic-Freundlich (JF) model considering non-homogeneous adsorption surface, has been applied successfully to correlate the adsorption of some chlorinated hydrocarbons on a micro porous silica gel at different temperatures:[32]

$$\theta_t = 1 - e^{-(aC)^v} \tag{16}$$

This model reduces to the Jovanovic model (Eq. 4) if the adsorbent surface is homogeneous ($\nu = 1$).

The JF model can be extended to describe two-component adsorption equilibrium according to Jaroniec et al.[12] as follows:

$$\theta_{t1} = \frac{a_1C_1}{a_1C_1 + a_2C_2}[1 - e^{-(a_1C_1+a_2C_2)^{\bar{v}}}] \tag{17a}$$

$$\theta_{t2} = \frac{a_2C_2}{a_1C_1 + a_2C_2}[1 - e^{-(a_1C_1+a_2C_2)^{\bar{v}}}] \tag{17b}$$

The model is rigorous if the heterogeneity parameters of both components are approximately equal.

Recently, two predictive models that consider lateral interactions and the surface heterogeneity were published.[12,16] The Fowler-Guggenheim/Langmuir-Freundlich (FG-LF) and the Fowler-Guggenheim/Jovanovic-Freundlich (FG-JF) models are described by complex implicit functions and have been validated in only a few experimental systems. Quiñones and Guiochon[16] verified these models experimentally for the competitive adsorption of 2-phenyl ethanol and 3-phenyl ethanol. These models gave the best predictive results among all models tested, but their incorporation into the calculation routines for the band profiles prediction requires considerable calculation time.[16] Recently, Kaczmarski and Antos[35] proposed a calculation algorithm for non-linear chromatography using these models.

The single component FG-LF[12] model is quantitatively described by Eq. (18):

$$\theta_t = \frac{(aCe^{X\theta_t})^{v}}{1 + (aCe^{X\theta_t})^{v}} \tag{18}$$

and the two-component distribution FG-LG model by Eqs (19a) and (19b):

$$\theta_{t1} = \phi_1 \frac{[a_1C_1e^{X_1\theta_{t1}+X_{12}\theta_{t2}} + a_2C_2e^{X_{21}\theta_{t1}+X_2\theta_{t2}}]^{\bar{v}}}{\{1 + [a_1C_1e^{X_1\theta_{t1}+X_{12}\theta_{t2}} + a_2C_2e^{X_{21}\theta_{t1}+X_2\theta_{t2}}]^{\bar{v}}\}} \tag{19a}$$

$$\theta_{t2} = \phi_2 \frac{[a_1C_1e^{X_1\theta_{t1}+X_{12}\theta_{t2}} + a_2C_2e^{X_{21}\theta_{t1}+X_2\theta_{t2}}]^{\bar{v}}}{\{1 + [a_1C_1e^{X_1\theta_{t1}+X_{12}\theta_{t2}} + a_2C_2e^{X_{21}\theta_{t1}+X_2\theta_{t2}}]^{\bar{v}}\}} \tag{19b}$$

with:

$$\phi_1 = \frac{a_1C_1e^{X_1\theta_{t1}+X_{12}\theta_{t2}}}{[a_1C_1e^{X_1\theta_{t1}+X_{12}\theta_{t2}} + a_2C_2e^{X_{21}\theta_{t1}+X_2\theta_{t2}}]} \tag{19c}$$

$$\phi_2 = \frac{a_2C_2e^{X_{21}\theta_{t1}+X_2\theta_{t2}}}{[a_1C_1e^{X_1\theta_{t1}+X_{12}\theta_{t2}} + a_2C_2e^{X_{21}\theta_{t1}+X}]} \tag{19d}$$

Quiñones and Guiochon[16] derived the FG-JF model by extending the JF model using the procedure used by Jaroniec et al.[12] for the derivation of the FG-LF model.

$$\theta_t = 1 - e^{-(aCe^{X\theta_t})^{\bar{v}}} \tag{20}$$

The two-component model is described by Eqs. (21a) and (21b):

$$\theta_{t1} = \phi_1\{1 - e^{-[a_1C_1e^{X_1\theta_{t1}+X_{12}\theta_{t2}} + a_2C_2e^{X_{21}\theta_{t1}+X_2\theta_{t2}}]^{\bar{v}}}\} \tag{21a}$$

$$\theta_{t2} = \phi_2\{1 - e^{-[a_1C_1e^{X_1\theta_{t1}+X_{12}\theta_{t2}} + a_2C_2e^{X_{21}\theta_{t1}+X_2\theta_{t2}}]^{\bar{v}}}\} \tag{21b}$$

EXPERIMENTAL

Materials and Instrumentation

The experimental data used in this work were previously reported.[6] Phenol and *o*-cresol, all analytical grade, were obtained from Lachema (Brno, Czech Republic). Before use, phenol was purified by distillation and *o*-cresol by crystallization from methanol. Methanol, HPLC grade, was obtained from Merck (Darmstadt, Germany). De-ionized water was doubly distilled in a glass vessel. The solvents were filtered over a Millipore 0.45 μm filter. The mobile phases were prepared by mixing their components in the required ratios and degassed by ultrasonication before use. For the determination of the distribution data the required amounts of solutes were weighed and dissolved in the mobile phase to prepare 0.1 mol/L solutions, either of pure compounds or of binary mixtures (1:1).

A Hewlett-Packard 1090 liquid chromatograph (Palo Alto, CA, USA) was used in all experiments. The adsorption equilibrium of phenol and *o*-cresol was measured on a Separon SGX C-18 (7 μm particle size) glass cartridge column, 150 × 3.3 mm i.d. (Tessek, Prague, Czech Republic) in aqueous solutions of methanol at three different concentrations (10%, 20%, and 30%) at 40°C.

Methods

The frontal analysis approach used for the determination of the distribution isotherm data was described earlier.[6,36] The ratio of the flow rates of the mobile phase and of the solution of a sample compound was adjusted from 0 to 100% in successive 10% steps. Time was allowed for the stabilization of the detector signal after each concentration change. The solute concentration in the stationary phase was determined from the integral mass balance equation using the experimental concentrations of the sample compounds, at the plateaus of the frontal analysis curve and the retention (breakthrough) volumes corresponding to the inflections points on the breakthrough curve, corrected for the volume of the tubing between the mixing point of the liquids pumped in each channel and the column top (0.35 mL). The steps on the frontal analysis curve were steep and the inflection points were close enough to the half-heights of the steps so that possible errors in the breakthrough volumes were lower than 0.01 mL, which was within the limits of the accuracy of the instrumental determination of the elution volumes. Various isotherm models were fitted to the experimental distribution data by nonlinear regression using a corrected Newton method. The best single-component isotherm coefficients were obtained by minimizing the sum of the squares of the residuals (RSS):[22]

$$\mathrm{RSS} = \sum_{i=1}^{n} (q_{ex,i} - q_{t,i})^2 \qquad (22)$$

$q_{ex,i}$ and $q_{t,i}$ are the experimental and calculated values for each data point, respectively.

The Fowler, FG-LF and FG-JF models are implicit with respect to the surface coverage, so that the adsorbed concentrations cannot be calculated directly using the model equations. The solution was possible after inversion of each model with respect to the adsorbed concentration using a Gauss-Jacobi numerical method.[37] To compare models with different numbers of isotherm parameters the Fisher's test was used.[38] The best model provides the highest value of the Fisher parameter F:

$$F = \frac{(n - l) \sum_{i=1}^{n} (q_{ex,i} - \overline{q_{ex}})^2}{(n - 1) \sum_{i=1}^{n} (q_{ex,i} - q_{t,j})} \qquad (23)$$

l is the total number of adjusted parameters of the model and $\overline{q_{ex}}$ is the mean value of the experimental adsorbed phase concentration.

According to Eq. (23), F decreases with the increasing number of parameters of the model tested. As different numbers of the isotherm model parameters are accounted for in the definition, the ability of various models to account for a set of adsorption data can be compared on the basis of the values of the corresponding F factors.

RESULTS AND DISCUSSION

The following model equations were selected to study the behavior of adsorption isotherms describing the adsorption equilibrium of the phenol/*o*-cresol system on silica RP-18: Langmuir (Eqs. 1 and 2), Fowler (Eqs. 6, and 7), Jovanovic (Eqs. 4, 5), JF (Eqs. 16, 17), LF (Eqs. 13–15), Ruthven (Eqs. 11, 12), Le Van Vermeulen (Eq. 3), Moreau (Eqs. 9, 10), FG-LF (Eqs. 20, 21) and FG-JF (Eqs. 18, 19). The single component experimental data for each methanol concentration tested were fitted to the models considering different sources of non-ideal behavior. The parameters obtained were used to predict binary equilibria with multicomponent models. The results of nonlinear regression analysis and the prediction of the binary equilibria using these models are presented in Tables 1–10. The values of RSS (Eq. 22) for single-component and two-component (the values in the parentheses) distribution data are also reported in the tables, together with the global RSS calculated as the sum of the contributions of both single component and binary data for each model. Tables 1–10 also show the calculated F-test values.

Models Based on the Assumption of Homogeneous Adsorbent Surface

The Langmuir model is widely used to represent single component distribution data. In many cases, particularly for single solute RPLC data, the

Table 1. Results of non-linear regression analysis of the two-component adsorption data of phenol and *o*-cresol mixture in 10% aqueous methanol using models assuming homogeneous adsorbent surface

			RSS			
Section	Model	Parameters	Phenol	*o*-Cresol	Global RSS	F cal
(1)	Langmuir equations (1–2) $q_{s1} = q_{s2}$	$A_1 = 8.038$, $b_1 = 5.042$, $q_{s1} = q_{s2} = 1.594$, $a_2 = 15.120$, $b_2 = 9.483$	0.00019 (0.0528)	0.0011 (0.0142)	0.0682	26.75
(2)	Langmuir equations (1–2)	$A_1 = 7.736$, $b_1 = 4.329$, $q_{s1} = 1.787$, $a_2 = 15.287$, $b_2 = 9.754$, $q_{s2} = 1.567$	0.00009 (0.0598)	0.00109 (0.0076)	0.0686	26.61
(3)	Le Van Vermeulen equations (3)	$A_1 = 7.736$, $b_1 = 4.329$, $q_{s1} = 1.787$, $a_2 = 15.287$, $b_2 = 9.754$, $q_{s2} = 1.567$	0.00009 (0.0483)	0.0011 (0.0118)	0.0613	29.75
(4)	Jovanovic equations (4–5)	$q_{s1} = 1.043$, $K_1 = 7.281$, $q_{s2} = 1.0213$, $K_2 = 14.046$	0.00013 (0.0612)	0.0018 (0.0220)	0.0851	21.45

Table 2. Results of non-linear regression analysis of the two-component adsorption data of phenol and *o*-cresol mixture in 20% aqueous methanol using models assuming homogeneous adsorbent surface

			RSS			
Section	Model	Parameters	Phenol	*o*-Cresol	Global RSS	F cal
(1)	Langmuir equations (1–2) $q_{s1} = q_{s2}$	$a_1 = 5.187$, $b_1 = 3.306$, $q_{s1} = q_{s2} = 1.583$, $a_2 = 9.273$, $b_2 = 5.842$	0.00003 (0.0250)	0.00015 (0.0031)	0.0283	35.92
(2)	Langmuir equations (1–2)	$a_1 = 5.187$, $b_1 = 3.153$, $q_{s1} = 1.645$, $a_2 = 9.273$, $b_2 = 5.892$, $q_{s2} = 1.574$	0.00002 (0.0242)	0.00015 (0.0026)	0.0269	37.69
(3)	Le Van Vermeulen equation (3)	$a_1 = 5.187$, $b_1 = 3.153$, $q_{s1} = 1.645$, $a_2 = 9.273$, $b_2 = 5.892$, $q_{s2} = 1.574$	0.00002 (0.0227)	0.00015 (0.0031)	0.0259	39.16
(4)	Jovanovic equations (4–5)	$q_{s1} = 0.927$, $K_1 = 5.532$, $q_{s2} = 0.953$, $K_2 = 9.443$	0.00003 (0.0258)	0.00025 (0.0063)	0.0324	31.34

Table 3. Results of non-linear regression analysis of the two-component adsorption data of phenol and *o*-cresol mixture in 30% aqueous methanol using models assuming homogeneous adsorbent surface

			RSS			
Section	Model	Parameters	Phenol	*o*-Cresol	Global RSS	F cal
(1)	Langmuir $q_{s1} = q_{s2}$ equations (1–2)	$a_1 = 3.905$, $b_1 = 2.103$, $q_{s1} = q_{s2} = 1.857$, $a_2 = 5.754$, $b_2 = 3.099$	0.00005 (0.0084)	0.00004 (0.0005)	0.0089	65.55
(2)	Langmuir equations (1–2)	$a_1 = 3.766$, $b_1 = 1.557$, $q_{s1} = 2.419$, $a_2 = 5.820$, $b_2 = 3.299$, $q_{s2} = 1.764$	0.00001 (0.0082)	0.00003 (0.0005)	0.0088	66.43
(3)	Le Van Vermeulen equation (3)	$a_1 = 3.766$, $b_1 = 1.557$, $q_{s1} = 2.419$, $a_2 = 5.820$, $b_2 = 3.299$, $q_{s2} = 1.764$	0.00001 (0.0055)	0.00003 (0.0001)	0.0057	102.97
(4)	Jovanovic equations (4–5)	$q_{s1} = 1.293$, $K_1 = 2.903$, $q_{s2} = 0.992$, $K_2 = 5.810$	0.00001 (0.0087)	0.00004 (0.0003)	0.0091	64.41

Table 4. Results of non-linear regression analysis of the two-component adsorption data of phenol and *o*-cresol mixture in 10% aqueous methanol using models assuming homogeneous adsorbent surface and lateral interactions between the adsorbed molecules

			RSS			
Section	Model	Parameters	Phenol	*o*-Cresol	Global RSS	F cal
(1)	Fowler equations (6–7)	$q_{s1} = 6.120$, $\chi_1 = -3.384$, $K_1 = 1.284$, $q_{s2} = 13.302$, $\chi_2 = -12.387$, $K_2 = 1.284$	0.000048 (0.0049)	0.000412 (0.0429)	0.0483	35.90
(2)	Moreau equations (9–10)	$q_{s1} = 2.320$, $K_1 = 3.363$, $b_1 = 0.6125$, $q_{s2} = 2.054$, $K_2 = 7.696$, $b_2 = 0.513$, $b_{12} = b_2$	0.00007 (0.059)	0.0008 (0.0057)	0.0662	26.20
(3)	Moreau equations (9–10)	$q_{s1} = 2.320$, $K_1 = 3.363$, $b_1 = 0.612$, $q_{s2} = 2.054$, $K_2 = 7.696$, $b_2 = 0.513$, $b_{12} = b_1$	0.000075 (0.0498)	0.0008 (0.0046)	0.0553	31.38
(4)	Ruthven equations (11–12)	$q_{s1} = 1.179$, $K_1 = 6.616$, $R_1 = 0.295$, $q_{s2} = 1.027$, $K_2 = 15.392$, $R_2 = 0.256$, $R_{12} = R_1$	0.000075 (0.0522)	0.0008 (0.0044)	0.0575	30.17
(5)	Ruthven equations (11–12)	$q_{s1} = 1.179$, $K_1 = 6.616$, $R_1 = 0.295$, $q_{s2} = 1.027$, $K_2 = 15.392$, $R_2 = 0.256$, $R_{12} = R_2$	0.000075 (0.0600)	0.0008 (0.0052)	0.0661	26.23

Table 5. Results of non-linear regression analysis of the two-component adsorption data of phenol and *o*-cresol mixture in 20% aqueous methanol using models assuming homogeneous adsorbent surface and lateral interactions between the adsorbed molecules

			RSS			
Section	Model	Parameter	Phenol	*o*-Cresol	Global RSS	F cal
(1)	Fowler equations (6–7)	$q_{s1} = 10.597$, $\chi_1 = -6.764$, $K_1 = 0.498$, $q_{s2} = 10.678$, $\chi_2 = -8.262$, $K_2 = 0.912$	0.00001 (0.0187)	0.00006 (0.0012)	0.0199	48.48
(2)	Moreau equations (9–10)	$q_{s1} = 2.175$, $K_1 = 2.396$, $b_1 = 0.610$, $q_{s2} = 2.076$, $K_2 = 4.531$, $b_2 = 0.565$, $b_{12} = b_2$	0.00002 (0.0236)	0.0001 (0.0020)	0.0257	37.47
(3)	Moreau equations (9–10)	$q_{s1} = 2.175$, $K_1 = 2.396$, $b_1 = 0.610$, $q_{s2} = 2.076$, $K_2 = 4.531$, $b_2 = 0.565$, $b_{12} = b_1$	0.00002 (0.0219)	0.0001 (0.0017)	0.0238	40.60
(4)	Ruthven equations (11–12)	$q_{s1} = 1.086$, $K_1 = 4.798$, $R_1 = 0.306$, $q_{s2} = 1.038$, $K_2 = 9.056$, $R_2 = 0.282$, $R_{12} = R_1$	0.00002 (0.0218)	0.0001 (0.0017)	0.0237	40.77
(5)	Ruthven equations (11–12)	$q_{s1} = 1.086$, $K_1 = 4.798$, $R_1 = 0.306$, $q_{s2} = 1.038$, $K_2 = 9.056$, $R_2 = 0.282$, $R_{12} = R_2$	0.00002 (0.0236)	0.0001 (0.0020)	0.0258	37.46

Table 6. Results of non-linear regression analysis of the two-component adsorption data of phenol and *o*-cresol mixture in 30% aqueous methanol using models assuming homogeneous adsorbent surface and lateral interactions between the adsorbed molecules

			RSS			
Section	Model	Parameters	Phenol	*o*-Cresol	Global RSS	F cal
(1)	Fowler equations (6–7)	$q_{s1} = 12.201$, $\chi_1 = -4.575$, $K_1 = 0.310$, $q_{s2} = 11.928$, $\chi_2 = -7.280$, $K_2 = 0.498$	0.00001 (0.0047)	0.00002 (0.0003)	0.0050	110.10
(2)	Moreau equations (9–10)	$q_{s1} = 3.023$, $K_1 = 1.248$, $b_1 = 0.715$, $q_{s2} = 2.320$, $K_2 = 2.528$, $b_2 = 0.605$, $b_{12} = b_2$	0.00001 (0.0082)	0.00003 (0.0004)	0.0086	64.19
(3)	Moreau equations (9–10)	$q_{s1} = 3.023$, $K_1 = 1.248$, $b_1 = 0.715$, $q_{s2} = 2.319$, $K_2 = 2.528$, $b_2 = 0.605$, $b_{12} = b_1$	0.00001 (0.0068)	0.00003 (0.0006)	0.0074	74.61
(4)	Ruthven equations (11–12)	$q_{s1} = 1.569$, $K_1 = 2.404$, $R_1 = 0.334$, $q_{s2} = 1.162$, $K_2 = 5.6$, $R_2 = 0.301$, $R_{12} = R_1$	0.00001 (0.0074)	0.00003 (0.0007)	0.0081	68.86
(5)	Ruthven equations (11–12)	$q_{s1} = 1.569$, $K_1 = 2.404$, $R_1 = 0.334$, $q_{s2} = 1.162$, $K_2 = 5.046$, $R_2 = 0.301$, $R_{12} = R_2$	0.00001 (0.0082)	0.00003 (0.0005)	0.0088	63.00

Langmuir model provides correlation in good agreement with the experimental data.[1] In addition to the Langmuir model, Tables 1–3 show the results of the correlations of single component data and the prediction of the binary equilibria given by Jovanovic and Le Van Vermeulen models for three compositions of methanol in mobile phase.

The Le Van Vermeulen model with the single-component Langmuir experimental parameters was applied to predict two-component equilibria, as it should yield better predictions than the competitive Langmuir model as the differences between the column saturation capacities for phenol and *o*-cresol, q_{s1} and q_{s2}, are significant (Table 1).[2]

Tables 1–3 show the calculated parameters of the Langmuir model obtained, assuming the same adsorption capacities for both phenol and *o*-cresol (section 1), and the results obtained without this simplifying assumption (section 2). Similar results were found with both calculation approaches, because the differences between q_{s1} and q_{s2} are relatively small. In both cases, the parameters, b, obtained by nonlinear regression, decreases with increasing concentration of methanol in the mobile phase. Similar results are observed with the Jovanovic model (Tables 1–3). Simple polynomial or semi logarithmic equations can satisfactorily describe the plots of the isotherm parameter *versus* the modifier concentration in the mobile phase.[6,27] The results (the values of the Fisher parameter F) in Tables 1–3 show that the Langmuir model prediction of the multi-component distribution data from the single-component isotherm parameters is comparable or slightly better than the prediction based on the Jovanovic model for all the three mobile phases (10%, 20%, and 30% methanol).

The Le Van Vermeulen model (Tables 1–3) gives better prediction of the two-component distribution data than the Langmuir model. The differences between the parameter F calculated for both models are most significant with 30% methanol mobile phase, where the difference between q_{s1} and q_{s2} is the greatest. The value of the parameter F calculated for the models assuming homogeneous adsorbent surface suggest that the Le Van Vermeulen model, in spite of its relative simplicity, can satisfactorily describe the experimental single-component and multi-component data of phenol and *o*-cresol in the concentration range 10–30% methanol in the aqueous-organic liquid phase.

The agreement of the experimental two-component distribution data with the theoretically predicted isotherms improve with increasing methanol concentration in the mobile phase for all homogeneous surface models tested (Langmuir, Jovanovic, and Le Van Vermeulen), see global values of RSS in Tables 1–3. The fit of the single-component isotherm data is better with pure phenol than with pure *o*-cresol. On the contrary, the prediction of the adsorbed concentrations of *o*-cresol from binary mixtures using the two-component adsorption models is better than with phenol.

Table 7. Results of non-linear regression analysis of the two-component adsorption data of phenol and *o*-cresol mixture in 10% aqueous methanol assuming heterogeneous adsorbent surface (LF and JF models)

			RSS			
Section	Model	Parameters	Phenol	*o*-Cresol	Global RSS	F cal
(1)	LF, condition 1 equations (13,14)	$q_{s1} = 3.250$, $a_1 = 1.677$, $v_1 = 0.899$, $q_{s2} = 3.678$, $a_2 = 1.849$, $v_2 = 0.772$	0.000002 (0.0052)	0.00005 (0.0792)	0.0845	20.51
(2)	LF, condition 1 equations (13,15)	$q_{s1} = 3.250$, $a_1 = 1.677$, $v_1 = 0.899$, $q_{s2} = 3.678$, $a_2 = 1.849$, $v_2 = 0.772$	0.000002 (0.00239)	0.00005 (0.0017)	0.0040	432.39
(3)	LF, condition 2 equations (13,14)	$q_{s1} = q_{s2} = 3.586$, $a_1 = 1.443$, $v_1 = 0.890$, $a_2 = 1.941$, $v_2 = 0.775$	0.000003 (0.0039)	0.00005 (0.0524)	0.0563	31.61
(4)	LF, condition 2 equations (13,15)	$q_{s1} = q_{s2} = 3.586$, $a_1 = 1.443$, $v_1 = 0.890$, $a_2 = 1.941$, $v_2 = 0.7751$	0.000003 (0.0026)	0.00005 (0.00216)	0.004775	372.60

(5)	LF, condition 3 equations (13, 14)	$q_{s1} = q_{s2} = 2.002$, $a_1 = 3.293$, $v_1 = v_2 = 0.915$, $a_2 = 6.162$	0.000430 (0.0452)	0.000534 (0.0088)	0.0550	56.05
(6)	LF, condition 3 equations (13, 15)	$q_{s1} = q_{s2} = 2.002$, $a_1 = 3.293$, $v_1 = v_2 = 0.915$, $a_2 = 6.162$	0.0004 (0.0281)	0.0005 (0.0063)	0.0353	87.38
(7)	JF, condition 1 equations (16, 17)	$q_{s1} = 1.847$, $a_1 = 3.086$, $v_1 = 0.894$, $q_{s2} = 2.164$, $a_2 = 3.527$, $v_2 = 0.764$	0.000002 (0.0042)	0.00005 (0.0569)	0.0611	28.36
(8)	JF, condition 2 equations (16, 17)	$q_{s1} = q_{s2} = 2.106$, $a_1 = 2.538$, $v_1 = 0.881$, $a_2 = 3.703$, $v_2 = 0.768$	0.000004 (0.0055)	0.00005 (0.0315)	0.0371	48.01
(9)	JF, condition 3 equations (16, 17)	$q_{s1} = q_{s2} = 1.308$, $a_1 = 4.814$, $v_1 = v_2 = 0.881$, $a_2 = 8.999$	0.0004 (0.0471)	0.0006 (0.0108)	0.0590	52.38

Table 8. Results of non-linear regression analysis of the two-component adsorption data of phenol and *o*-cresol mixture in 20% aqueous methanol assuming heterogeneous adsorbent surface (LF and JF models)

			RSS			
Section	Model	Parameters	Phenol	*o*-Cresol	Global RSS	F cal
(1)	LF, condition 1 equations (13, 14)	$q_{s1} = 2.712$, $a_1 = 1.503$, $v_1 = 0.932$, $q_{s2} = 2.646$, $a_2 = 2.415$, $v_2 = 0.882$	0.000002 (0.0075)	0.000003 (0.0055)	0.0129	74.69
(2)	LF, condition 1 equations (13, 15)	$q_{s1} = 2.712$, $a_1 = 1.503$, $v_1 = 0.932$, $q_{s2} = 2.646$, $a_2 = 2.415$, $v_2 = 0.882$	0.000002 (0.0056)	0.000003 (0.0003)	0.0059	162.44
(3)	LF, condition 2 equations (13, 14)	$q_{s1} = q_{s2} = 2.666$, $a_1 = 1.541$, $v_1 = 0.934$ $a_2 = 2.386$, $v_2 = 0.881$	0.000002 (0.0068)	0.000003 (0.0064)	0.0131	75.47
(4)	LF, condition 2 equations (13, 15)	$q_{s1} = q_{s2} = 2.666$, $a_1 = 1.541$, $v_1 = 0.934$ $a_2 = 2.386$, $v_2 = 0.881$	0.000002 (0.0054)	0.000003 (0.0003)	0.0057	173.24

(5)	LF, condition 3 equations (13, 14)	$q_{s1} = q_{s2} = 1.987$, $a_1 = 2.258$, $\nu_1 = \nu_2 = 0.943$, $a_2 = 3.977$	0.00005 (0.0204)	0.00005 (0.0019)	0.0224	76.76
(6)	LF, condition 3 equations (13, 15)	$q_{s1} = q_{s2} = 1.987$, $a_1 = 2.258$, $\nu_1 = \nu_2 = 0.943$, $a_2 = 3.977$	0.00005 (0.0133)	0.00005 (0.0010)	0.0144	119.38
(7)	JF, condition 1 equations (16, 17)	$q_{s1} = 1.46104$, $a_1 = 2.90251$, $\nu_1 = 0.93134$, $q_{s2} = 1.55800$, $a_2 = 4.24799$, $\nu_2 = 0.87299$	0.000002 (0.0077)	0.000004 (0.0063)	0.0140	68.76
(8)	JF, condition 2 equations (16, 17)	$q_{s1} = q_{s2} = 1.552$, $a_1 = 2.672$, $\nu_1 = 0.926$, $a_2 = 4.276$, $\nu_2 = 0.874$	0.000002 (0.0090)	0.000004 (0.0044)	0.0135	73.58
(9)	JF, condition 3 equations (16, 17)	$q_{s1} = q_{s2} = 1.218$, $a_1 = 3.613$, $\nu_1 = \nu_2 = 0.928$, $a_2 = 6.363$	0.000056 (0.0212)	0.00005 (0.0024)	0.0236	72.81

Table 9. Results of non-linear regression analysis of the two-component adsorption data of phenol and *o*-cresol mixture in 10% aqueous methanol assuming heterogeneous adsorbent surface (LF and JF models)

			RSS			
Section	Model	Parameters	Phenol	*o*-Cresol	Global RSS	F cal
(1)	LF, condition 1 equations (13, 14)	$q_{s1} = 5.854$, $a_1 = 0.506$, $\nu_1 = 0.947$, $q_{s2} = 2.766$, $a_2 = 1.677$, $\nu_2 = 0.933$	0.000004 (0.0067)	0.000006 (0.0021)	0.0089	62.52
(2)	LF, condition 1 equations (13, 15)	$q_{s1} = 5.854$, $a_1 = 0.506$, $\nu_1 = 0.947$, $q_{s2} = 2.766$, $a_2 = 1.677$, $\nu_2 = 0.933$	0.000004 (0.0026)	0.000006 (0.0042)	0.0068	81.34
(3)	LF, condition 2 equations (13, 14)	$q_{s1} = q_{s2} = 3.134$, $a_1 = 1.103$, $\nu_1 = 0.977$, $a_2 = 1.399$, $\nu_2 = 0.922$	0.000007 (0.0007)	0.000007 (0.0020)	0.0027	210.71
(4)	LF, condition 2 equations (13, 15)	$q_{s1} = q_{s2} = 3.134$, $a_1 = 1.103$, $\nu_1 = 0.977$, $a_2 = 1.399$, $\nu_2 = 0.922$	0.000007 (0.0015)	0.000007 (0.0011)	0.0026	219.20

(5)	LF, condition 3 equations (13, 14)	$q_{s1} = q_{s2} = 2.029$, $a_1 = 1.846$, $\nu_1 = \nu_2 = 0.986$, $a_2 = 2.717$	0.00005 (0.0063)	0.00003 (0.0002)	0.0066	149.44
(6)	LF, condition 3 equations (13, 15)	$q_{s1} = q_{s2} = 2.029$, $a_1 = 1.846$, $\nu_1 = \nu_2 = 0.986$, $a_2 = 2.717$	0.00005 (0.0055)	0.00003 (0.0002)	0.0058	170.03
(7)	JF, condition 1 equations (16, 17)	$q_{s1} = 2.958$, $a_1 = 1.041$, $\nu_1 = 0.948$, $q_{s2} = 1.568$, $a_2 = 3.017$, $\nu_2 = 0.928$	0.000004 (0.0057)	0.000007 (0.0017)	0.0073	75.50
(8)	JF, condition 2 equations (16, 17)	$q_{s1} = q_{s2} = 1.732$, $a_1 = 1.998$, $\nu_1 = 0.973$, $a_2 = 2.626$, $\nu_2 = 0.918$	0.000006 (0.0012)	0.000008 (0.0011)	0.0023	246.20
(9)	JF, condition 3 equations (16, 17)	$q_{s1} = q_{s2} = 1.174$, $a_1 = 3.132$, $\nu_1 = \nu_2 = 0.978$, $a_2 = 4.612$	0.000049 (0.0067)	0.000035 (0.0002)	0.0070	140.41

Table 10. Results of non-linear regression analysis of the two-component adsorption data of phenol and *o*-cresol mixture for mobile phases with 10%, 20% and 30% methanol using FG-LF and FG-JF models

			RSS			
Section	Model	Parameters	Phenol	*o*-Cresol	Global RSS	F cal
(1)	FG-JF equations (19–20)10% methanol	$q_{s1} = q_{s2} = 7.676$, $a_1 = 0.458$, $\chi_1 = -0.491$ $\nu_1 = \nu_2 = 0.836$, $a_2 = 1.053$, $\chi_2 = -4.051$	0.00004 (0.015)	0.00007 (0.001)	0.0158	109.61
(2)	FG-LF equations (21–22) 10% methanol	$q_{s1} = q_{s2} = 12.012$, $a_1 = 0.273$, $\chi_1 = -0.650$ $\nu_1 = \nu_2 = 0.839$, $a_2 = 0.626$, $\chi_2 = -6.177$	0.00004 (0.0144)	0.00007 (0.0011)	0.0156	111.32
(3)	FG-JF equations (19-20) 20% methanol	$q_{s1} = q_{s2} = 7.458$, $a_1 = 0.462$, $\chi_1 = -2.048$ $\nu_1 = \nu_2 = 0.913$, $a_2 = 0.885$, $\chi_2 = -3.984$	0.000004 (0.014)	0.000002 (0.0003)	0.0140	68.87

(4)	FG-LF equations (21–22) 20% methanol	$q_{s1} = q_{s2} = 11.856$, $a_1 = 0.289$, $\chi_1 = -3.463$, $\nu_1 = \nu_2 = 0.919$, $a_2 = 0.551$, $\chi_2 = -6.351$	0.000003 (0.0142)	0.000003 (0.0003)	0.0146	66.13
(5)	FG-JF equations (19–20) 30% methanol	$q_{s1} = q_{s2} = 12.534$, $a_1 = 0.223$, $\chi_1 = -1.643$, $\nu_1 = \nu_2 = 0.945$, $a_2 = 0.356$, $\chi_2 = -5.514$	0.000004 (0.0024)	0.000006 (0.0012)	0.0036	153.56
(6)	FG-LF equations (21–22) 30% methanol	$q_{s1} = q_{s2} = 10.174$, $a_1 = 0.283$, $\chi_1 = -0.886$, $\nu_1 = \nu_2 = 0.948$, $a_2 = 0.4519$, $\chi_2 = -3.971$	0.000004 (0.0024)	0.000006 (0.0012)	0.0036	155.32

Models with Lateral Interactions Between the Molecules Adsorbed on a Homogeneous Surface

The Fowler, Moreau and Ruthven models were selected to study the effects accounting for the lateral interactions between the adsorbed molecules of phenol and *o*-cresol on the accuracy of prediction of two-component distribution in the present chromatographic phase system. The results are presented in Tables 4–6.

The Fowler competitive model (Eqs. 7a, 7b) better fits the experimental single-component and two-component distribution data than the models that do not account for lateral intermolecular interactions. The *F* parameter values calculated for the Fowler model are higher than those of the Langmuir, Jovanovic, and Le Van Vermeulen models for each methanol concentration. For the validity of the model, the values of the parameters K_1, K_2 need not be the same for the mixture components. The cross lateral interaction parameters are determined as the geometric mean of the parameters obtained with experimental data for pure compounds (Eq. 8). This approximation provides good results when the size or the polarities of the components are not very different.[16] The molecular volumes of phenol and *o*-cresol are 352 A^3 and 399 A^3, respectively, and the surface areas of phenol and *o*-cresol are 219 A^2 and 247 A^2, respectively. These values were determined using the modeling and molecular simulation program Hyper Chem 7. The calculated differences between the molecular volumes and areas of the two solutes are relatively small, which justifies using the Fowler competitive model in this particular case.

The global RSS decreases with increasing methanol concentration (Tables 4–6). The negative sign of the values of the lateral interaction parameters calculated by the Fowler model may be possibly attributed to the attractive hydrogen-bond interactions between the adsorbed molecules of phenolic compounds.

The Moreau (Eqs. 10a, 10b) and the Ruthven (Eqs. 12a, 12b) models are described by explicit equations enabling direct calculations of adsorbed concentrations, which is advantageous for the numerical calculations of the chromatographic band profiles. With both models, the same sign of the parameters of lateral interactions were obtained (Tables 4–6). We assumed for both models that the cross lateral interaction parameter, b_{12} or R_{12}, are equal to the molecular interaction parameters of either phenol, b_1 or R_1, or *o*-cresol, b_2 or R_2. Quiñones et al.[15] previously applied this procedure to describe the adsorption of 2-phenyl ethanol and 3-phenyl propanol on a C-18 RP column. The global RSS are lowest considering $b_{12} = b_1$ or $R_{12} = R_1$ (Tables 4–6). This may indicate that the phenol adsorbate-adsorbate lateral interactions on the stationary phase may dominate over the lateral interactions of *o*-cresol. The results are slightly better than those obtained with the Langmuir, Jovanovic, and Le Van Vermeulen models for mobile phases containing 10% and 20% methanol.

With 30% methanol, the Le Van Vermeulen model gives better predictions (Table 3).

Generally, the accuracy of predictions of all the lateral-interaction models improves (higher values of the parameter F) with increasing concentration of methanol in the mobile phase.

Models Taking into Account the Adsorbent Surface Heterogeneity

The results obtained by applying the LF and JF models that take into account the adsorbent surface heterogeneity to characterize the adsorption of binary mixtures of phenol with *o*-cresol are shown in Tables 7–9. Two versions of the competitive LF model (Eqs. 14a, 14b, and Eqs. 15a, 15b, respectively) and a competitive extension of the JF model (Eqs. 17a, 17b) were tested for fitting the experimental data, under three different conditions: 1) The adsorption (saturation) capacity parameters (q_s) need not be equal for the two components in a binary mixture. The competitive surface heterogeneity parameters of the JF (Eqs. 17a, 17b) or LF (Eqs. 14a, 14b) models are calculated as the arithmetic mean of the heterogeneity parameters for pure phenol and *o*-cresol, $\nu = (\nu_1 + \nu_2)/2$ (Tables 7–9). The competitive LF model version described by Eqs. 15a, 15b employs the values of the surface heterogeneity parameter determined for each component from single component distribution experimental data. 2) The adsorption (saturation) capacity parameters are the same for both phenol and *o*-cresol ($q_{s1} = q_{s2}$). The competitive heterogeneity surface parameter is calculated as in case 1 (Tables 7–9). 3) Equal heterogeneity surface and the adsorption (saturation) capacity parameters are assumed for both phenol and *o*-cresol ($\nu = \nu_1 = \nu_2$), $q_s = q_{s1} = q_{s2}$ (Tables 7–9).

The values of the surface heterogeneity coefficients obtained for each condition indicate that the surface is not completely homogenous ($\nu < 1$). The values of this parameter calculated by LF and JF models at the same experimental conditions are similar and are getting closer to 1 as the concentration of methanol in the mobile phase increases, suggesting that the role of the surface heterogeneity increases in mobile phases with lower concentrations of organic solvents. Hence, the JF and LF models provide the best description of the experimental distribution data for mobile phases with 30% methanol.

In mobile phases with 10% methanol, the single-component LF model (Eq. 13) and the competitive LF model version described by Eqs. 15a, 15b (Table 7) describe better the distribution data.

The best data fit is obtained assuming different q_{s1} and q_{s2} and $\nu_1 \neq \nu_2$ (Table 7). Figure 1 shows the agreement between the experimental (points) and predicted (LF model, lines) single-component (A) and two-component (B) distribution data of phenol and *o*-cresol in 10% methanol. The fit of the

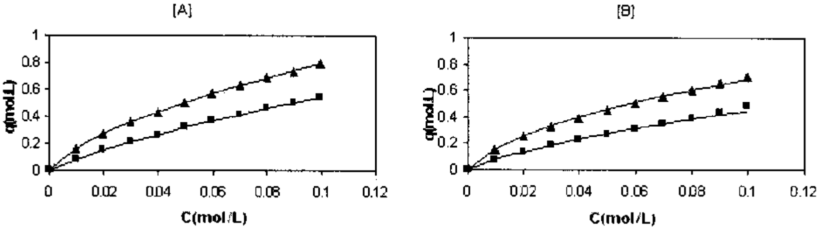

Figure 1. Experimental and calculated adsorption isotherms of phenol and *o*-cresol. Mobile phase: 10% aqueous methanol, 40°C. A: single component isotherms; B: Two-component isotherm for 1:1 phenol–*o*-cresol mixtures. Symbols ■: experimental data for phenol, ▲: experimental data for *o*-cresol. Solid lines: isotherms calculated using LF model (Eqs. 13, 15a, 15b).

single component data to the model is excellent and the prediction of the binary equilibria using this isotherm adsorption model is satisfactory.

Good results are also obtained considering $q_1 = q_{s2}$ (condition 2). The values of the parameter *F* calculated with the LF model (Eqs. 15a, 15b) for both conditions 1 and 2 are better than with the models that consider lateral interactions on homogenous surfaces. The *F*-values in Table 7 show that, for the experimental data measured with 10% methanol, the LF model (Eqs. 15a, 15b) provides excellent prediction of single-component adsorption isotherm data.

On the contrary, the LF competitive model with equal or average heterogeneity parameter values (Eqs. 14a, 14b) gives worse predictions for 10% than for higher methanol concentrations. For condition 1 (Table 7) the LF model (Eqs. 14a, 14b), provides lower *F*-values than the models assuming homogeneous adsorbent surface. The JF model (Eqs 17a, 17b) with condition 1 (section 7) gives poorer results (lower *F*-values) than the Le Van Vermeulen model. With both JF and LF models, the prediction of two-component distribution in 10% methanol slightly improves, assuming both $q_{s1} = q_{s2}$, $\nu_1 = \nu_2$ (condition 3, sections 5 and 9).

For mobile phase with 20% methanol, the fit of single component experimental data to LF model (Eq. 13) is excellent. The two-component distribution experimental data are described satisfactorily by LF model using Eqs. (15a) and (15b). The best results are obtained assuming equal saturation adsorption capacities for phenol and *o*-cresol (condition 2), as demonstrated by the values of the parameter *F* in Table 8. Fig. 2A illustrates the accuracy of the fit of the single component data to the LF model; Fig. 2B the agreement of the two-component distribution data predicted with LF competition model (Eqs. 15a, 15b, condition 2), using the isotherm parameters listed in Table 8.

The predicted competitive data for phenol show some negative deviations from the experimental results (points) in the high concentration range.

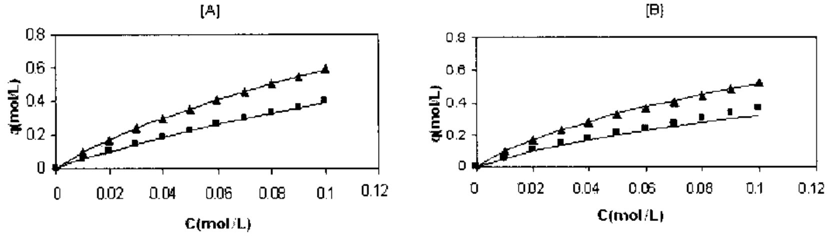

Figure 2. Experimental and calculated adsorption isotherms of phenol and *o*-cresol. Mobile phase: 20% aqueous methanol, 40°C. A: single component isotherms; B: Two-component isotherm for 1:1 phenol–*o*-cresol mixtures. Symbols ■: experimental data for phenol, ▲: experimental data for *o*-cresol. Solid lines: isotherms calculated using LF model (Eqs. 13, 15a, 15b).

On the other hand, the JF model (Sections 7, 8, 9 in Tables 7–9) provides poorer predictions of the multicomponent distribution than the LF model, especially with the heterogeneity parameter of Eqs. (17a, 17b) calculated as the arithmetic mean of the heterogeneity parameters of pure phenol and *o*-cresol.

For the mobile phase with 30% methanol, the JF model provides the best description of the experimental distribution data of phenol and *o*-cresol (condition 2, Table 9), although the LF model offers a satisfactory data fit using conditions 1 and 3. Fig. 3A illustrates the fit of the model to single component data, and Fig. 3B the agreement of the two-component experimental distribution data with the predicted JF model isotherm using the parameters reported in Table 9, section 8. In contrast to the data measured in 10% and 20% methanol, the fit of the JF model to the experimental distribution data in mobile phases with 30% methanol is the best among all models tested.

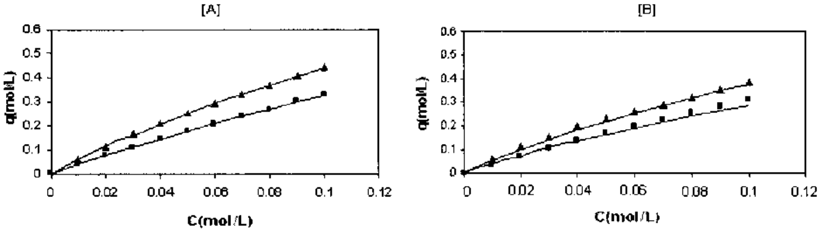

Figure 3. Experimental and calculated adsorption isotherms for phenol and *o*-cresol in mobile phases with 30% methanol at 40°C. A: single component experimental and calculated isotherms of phenol and *o*-cresol. B: Experimental and calculated data for a two-component mixture of phenol and *o*-cresol (1:1). Symbols ■: experimental data for phenol, ▲: experimental data for *o*-cresol. Solid lines correspond to the isotherms calculated with JF model.

The isotherms with the parameters accounting for the adsorption surface heterogeneity allow a better characterization of the competitive distribution of phenol and *o*-cresol system in comparison to the models assuming homogeneous adsorbent surface and lateral interactions on the adsorbed phase.

Models that Account for Adsorbent Surface Heterogeneity and Lateral Intermolecular Interactions

The FG-LF and FG-JF models account for two sources of non-ideality: the lateral intermolecular interactions and the heterogeneity of the adsorbent surface. The results of the non-linear regression analysis of the experimental data using these two models and the prediction of the binary equilibria using both models are presented in Table 10, sections 1–6. In all cases, equal heterogeneity and lateral interactions parameters were assumed for phenol and *o*-cresol, $q_{s1} = q_{s2}$, and $\nu_1 = \nu_2$.

The heterogeneity parameters of phenol and *o*-cresol $\nu_i < 1$, and are similar for each methanol concentration, and indicate that the surface is not completely homogeneous. As with LF and JF models (Tables 7–9), they increase with increasing methanol concentration in the mobile phase. The lateral interaction parameters, X_i, posses a negative sign, in agreement with the data fitted to the Fowler model (Tables 4–6). In all mobile phases the lateral interaction parameters are more negative for the molecules of *o*-cresol than for phenol molecules.

The global RSS decreases with increasing methanol concentration in the mobile phase. In 10% methanol, the parameter F is higher than with other models, except for the LF competitive model (Eqs. 15a, 15b, in Table 7, sections 2 and 4). For mobile phases with 20% and 30% methanol, the results are still satisfactory, but slightly worse than with the models assuming only the adsorbent surface heterogeneity. The F-parameters are very similar for both FG-LF and FG-JF models at any methanol concentration in the mobile phase. The accuracy of the data fit does not improve by using the surface heterogeneity parameters calculated as the geometric mean of the single component parameters.

CONCLUSIONS

Several theoretical adsorption models were compared with respect to their suitability to characterize single-component and two-component distribution data of phenol and *o*-cresol on a C_{18} column. The experimental distribution data were determined at three different concentrations of methanol in aqueous-organic mobile phases. As a rule, the fit of the data to various models and the accuracy of prediction of solute distribution in two-component mixed samples improves with increasing methanol concentration, particularly for adsorption models taking into account adsorbent surface heterogeneity, lateral interactions between adsorbed molecules, or both lateral interactions and surface heterogeneity.

Of the simple models assuming homogeneous adsorbent surface and absence of lateral intermolecular interactions, the Le Van Vermeulen model provides isotherms in best agreement with the experiment for each methanol concentration in the mobile phase. The differences between the results obtained with the Langmuir and the Le Van Vermeulen models can be attributed to different saturation adsorption capacities for phenol and *o*-cresol.

Of the models assuming homogeneous adsorbent surface and lateral interactions between the adsorbed molecules, the Fowler model gives better agreement between the calculated and experimental isotherm data than the Ruthven and Moreau models. The negative sign of the adsorbate-adsorbate interaction parameter implies important attractive forces (probably hydrogen-bonding interactions) between the adsorbed molecules.

The JF, and especially the LF models of adsorption on heterogeneous adsorbent surface, provide low RSS values and better fit to the experiment and more accurate prediction of the two-component distribution data of phenol and *o*-cresol than all other models tested in this work.

Both FG-LF and FG-JF models provide satisfactory descriptions of the experimental distribution data, but the *F* parameters are lower than those obtained with the LF model. It seems that in the present system the effects of the adsorbent surface heterogeneity are more important than the lateral interactions between adsorbed molecules. However, neglecting the differences in the molecular volumes and areas of phenol and *o*-cresol in the calculations of the heterogeneity and lateral interaction parameters may affect the accuracy of the calculations using the FG-LF and FG-JF models.

ABBREVIATIONS

q: Concentration of the component in the stationary phase [mol/L].

C: Concentration of the component in the liquid phase [mol/L].

q_s: Saturation capacity of the column [mol/L].

θ: Surface coverage, $\theta = q/q_s$

a: Coefficient of the Langmuir isotherm ($a = b \cdot q_s$), (Eqs. 3a, 3b, 3c and 3d).

b: Coefficient of the Langmuir isotherm model, It is the ratio of the adsorption and desorption rate constants, Eqs. (1–3). [L/mol]

R: Lateral interaction parameter in Eqs. (11), (12a) and (12b) (Ruthven model).

K: Numerical parameter of the models: Jovanovic (Eqs. 4, 5a and 5b), Fowler (Eqs. 6, 7a and 7b), Moreau (Eqs. 9, 10a and 10b) and Ruthven (11, 12a and 12b). Henry constant is equal to the product $q_s \cdot K$. [L/mol]

χ: Lateral interaction parameter (It is taking into account in the models: Fowler (Eqs 6, 7a and 7b), FGLF (Eqs. 19, 20a and 20b) and FGJF (Eqs. 21, 22a, 22b).

γ: Heterogeneity parameter (It appears in the models: LF (Eqs. 13, 14a, 14b, 15a and 15b), JF (Eqs. 16, 17a and 17b), FG-LF (Eqs. 19, 20a and 20b) and FG-JF (Eqs. 21, 22a and 22b).

i, j: relate to the individual components of an n-component sample.

n: number of components.

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