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# Fitting competitive adsorption isotherms to the experimental distribution data in reversed-phase systems

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## Abstract

Distribution isotherms of phenol and resorcinol and *o*-cresol were determined between aqueous solutions with different concentrations of methanol and an octadecyl silica adsorbent. Single-component distribution data can be well described by either the Langmuir or the Jovanovic adsorption isotherms. The competitive Langmuir isotherm with single-component isotherm coefficients can describe moderately successfully the distribution in mixtures of phenol and *o*-cresol in 20–40% methanol, but it does not fit the experimental distribution data of the mixtures of phenol and resorcinol, which are better described by the competitive Jovanovic and the quadratic isotherms with single-component coefficients. Generally, the quality of the fit of the isotherms improves as the concentration of methanol in the solutions increases. The dependencies of the logarithms of the Langmuir isotherm coefficients and of the coefficients of quadratic and Jovanovic isotherms on the composition of the mobile phase can be described by second-degree polynomial equations over the range 0–40% methanol in water.

**Keywords:** Adsorption isotherms; Mobile phase composition; Phenol; Resorcinol; Cresols

## 1. Introduction

Few experimental distribution data of multicomponent samples between the liquid mobile phase and the solid column packing materials used in contemporary liquid chromatography have been published so far, but difficulties in selecting an adequate model for competitive adsorption equilibria have been clearly demonstrated [1]. The objective of the present work is to investigate possibilities of fitting various nonlinear isotherms to the experimental two-component data in reversed-phase liquid chromatography systems. For this purpose, we selected phenol, *o*-cresol and resorcinol as model compounds.

The composition of the mobile phase is the most

widely used tool for controlling the separation in liquid chromatography. The dependencies of the coefficients of the isotherms should be known to allow numerical calculations of the peak profiles and optimization of the effects of the mobile phase on the yield, purity and production rate under overloaded isocratic and gradient elution conditions. Recently, we have investigated the effect of the concentration of the organic modifier (methanol) in aqueous–organic mobile phases on the distribution of phenol and resorcinol between the stationary and the mobile phases and on the coefficients of some single- and two-component isotherm equations [2]. In the present work, we completed the data for these two compounds, compared it with new data sets acquired with mixtures of *o*-cresol and phenol and fitted other types of isotherms to this data.

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## 2. Theoretical

Several models have been suggested to describe the distribution of one sample component between the stationary and the mobile phases. The most common and the most simple nonlinear isotherm is the two-parameter Langmuir one [3]:

$$q = \frac{ac}{1 + bc} \quad (1)$$

Here,  $q$  is the concentration of the sample compound in the stationary phase;  $c$ , concentration in the mobile phase;  $a$ ,  $b$  are the coefficients of the isotherm ( $a = k_0/\Phi$ , where  $k_0$  is the capacity factor of the sample compound at infinite dilution, i.e., in analytical chromatography and  $b = a/q_s$ , where  $q_s$  is the column saturation capacity). If the Langmuir model does not fit well the experimental data, more complex isotherms can be used for this purpose, such as those based on bi-Langmuir [4], quadratic [5–7], Fowler [8] or Jovanovic [9] models.

Numerous and often complicated models have been suggested to describe the competitive equilibria involved between the components  $i$ ,  $j$  of a binary sample mixture and the adsorbent, yielding various competitive isotherm equations [10]. Competitive Langmuir isotherm with single-component Langmuir coefficients [11] is often used, but it is thermodynamically justified only if the column has the same saturation capacities for all sample components [1,3]:

$$q_i = \frac{a_i c_i}{1 + b_i c_i + b_j c_j} \quad (2)$$

More complex models have been suggested to account for the differences in column saturation capacities of the sample components, such as for example the competitive Fowler isotherm [6,7], the competitive quadratic isotherm which can be simplified by neglecting the terms with  $c_i^2$  to [6]:

$$q_i = \frac{a_i c_i + a_{ij} c_i c_j}{1 + b_i c_i + b_j c_j + b_{ij} c_i c_j} \quad (3)$$

or a thermodynamically more consistent LeVan–Vermeulen competitive isotherm [12].

In the competitive isotherm equations, Eqs. (2) and (3)  $a_i$ ,  $b_i$ ,  $a_j$ ,  $b_j$  are the single-component Langmuir coefficients of the sample components  $i$ ,  $j$ ,

whereas the coefficients  $a_{ij}$ ,  $b_{ij}$  in the quadratic isotherm account for competitive behaviour of sample compounds. Unfortunately, if the single-component Langmuir coefficients are used in the isotherm Eq. (3) or Eq. (4), poor fit to the experimental competitive distribution data is often obtained [2,6,13–16]. To overcome this problem, the coefficients evaluated from the competitive data have been used [2,5,6,17–19], which often differ significantly from the single-component isotherm coefficients and their values depend on the concentration ratio of the sample compounds, in contrast to their definition. Such isotherm equations are only empirical and do not allow fundamental interpretation of the distribution data.

The Jovanovic isotherm was derived to account for monolayer, nonlocalized adsorption of the molecules of sample solutes [9]:

$$q = A_i (1 - e^{-a_i' c_i}) \quad (4)$$

and assuming the same settling times for the molecules of the compounds  $i$  and  $j$  [20] its two-component form can be written as:

$$q = A_i \cdot \frac{(e^{a_i' c_i} - 1)e^{a_{ij}' c_j}}{1 + (a_i' c_i - 1)e^{a_{ij}' c_j} + (e^{a_j' c_j} - 1)e^{a_{ij}' c_i}} \quad (5)$$

The coefficient  $A_i$  in Eqs. (4,5) is the column saturation capacity for sample component  $i$ . For low concentrations  $c$ , the first two terms of the Taylor expansion yield the Langmuir isotherm (Eq. (1)) with  $b = a_i'$  and  $a = A_i \cdot a_i'$ . If this approach is applied to the Eq. (6), Eq. (3) is obtained, with the single-component Langmuir coefficients  $a$ ,  $b$  of the compounds  $i$  and  $j$  as above and the coefficients  $a_{ij} = A_i a_i' a_{i,j}$ ,  $b_{ij} = (a_i' a_{i,j} + a_j' a_{j,i})$ .

The results of our recent experiments have shown that the plots of the logarithms of the Langmuir coefficients  $a$ ,  $b$  versus the concentration of methanol in the adsorbed solution deviate significantly from the straight lines. Second-degree polynomial equations can account for this behaviour [2]:

$$\log a = \log a_0 - m_a \varphi + d_a \varphi^2 \quad (6)$$

$$\log b = \log b_0 - m_b \varphi + d_b \varphi^2 \quad (7)$$

### 3. Experimental

#### 3.1. Chemicals

Phenol, resorcinol and *o*-cresol, all analytical grade, were obtained from Lachema, Brno, Czech Republic. Before the use, phenol was purified by distillation and *o*-cresol and resorcinol by crystallization from water and methanol, respectively.

Methanol of spectroscopic grade was obtained from Lachema. Water was doubly distilled in glass with addition of potassium permanganate. The solvents were filtered using a Millipore 0.45  $\mu\text{m}$  filter, mixed in the required ratios and degased by ultrasonication before the use. The sample solutions used for the determination of the distribution data were prepared by weighing the required amounts of the sample solutes and dissolving in the mobile phase.

#### 3.2. Instrumentation and methods

To acquire the data necessary for the determination of the equilibrium isotherms by frontal analysis method [21], an HP 1090M liquid chromatograph (Hewlett-Packard, Palo Alto, CA, USA) was used, equipped with a 3 DR gradient solvent delivery system and solvent reservoirs continuously stripped with helium to degas the mobile phase in one reservoir flask and the sample solution in the other one, an automatic sample injector, a column switching valve, a temperature-controlled column compartment, a diode-array UV detector and a data workstation. The ratio of the flow-rates of the two solutions 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 flow-rate (1 ml/min) and the column temperature (40°C) were kept constant during all the experiments. The eluate from the column used to measure the isotherm passed through an external LCD 2563 UV detector (Laboratory Instruments Works, Prague, Czech Republic) working at 289 nm and via a six-port column-switching valve to a high-speed analytical column the outlet of which was connected to the diode-array detector set at 254 nm. In this way, automated collection and analysis of the fractions was performed using a pre-set switching-valve

program to determine the concentrations of the two components in the eluate from the main column. The electrical output from the external detector was connected via an analog-digital convertor (760 Series Interface, Hewlett-Packard) to the data station of the chromatograph, so that the signals from both the diode-array and the external UV detectors were simultaneously processed.

The columns for measuring the isotherm data were glass-cartridge, 150 mm  $\times$  3.3 mm, packed with two different batches of Separon SGX C<sub>18</sub> material, 7  $\mu\text{m}$  particle size, obtained from Tessek, Prague, Czech Republic. The column dead volumes were evaluated from the record of the detector set to 200 nm after injection of pure methanol. A Hypersil ODS, 3  $\mu\text{m}$ , 60  $\times$  4.6 mm high-speed column was used for the analysis of the fractions of the eluate.

In each experiment the solute concentration in the stationary phase was determined from the appropriate integral mass balance equation [21], using (1) the experimental concentrations of the sample components at the plateaus of the frontal analysis curve and (2) the retention volumes corresponding to the inflection 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 [21] (0.35 ml). Solutions (0.1 mol/L) of the individual compounds were used for measuring single-component isotherms and sample mixtures containing phenol and resorcinol in concentration ratios 0.1:0.1, 0.1:0.02 and 0.02:0.1 mol/L for the determination of competitive isotherms. All experiments were repeated at least twice.

### 4. Results and discussion

#### 4.1. Single-component distribution data

Single-component distribution of phenols between the octadecylsilica material and water or aqueous methanol can be described by Langmuir as well as by Jovanovic isotherms (Eqs. (1) and (4)). The coefficients of the isotherms are given in Table 1. The Jovanovic isotherms fit the experimental data slightly better at higher sample concentrations in aqueous solutions with higher contents of methanol.

The coefficients of the Langmuir isotherm de-

Table 1

Coefficients of single-component isotherms of resorcinol (R), phenol (P) and *o*-cresol (C) on C<sub>18</sub> columns 1 and 2; 1 = Langmuir isotherm (Eq. (1)), 2 = Jovanovic isotherm (Eq. (4))

% Methanol	0	10	20	30	40
<i>Column 1, R</i>					
$k'_{0,exp}$	2.54	1.14	0.53	0.24	0.06
1 <i>a</i>	6.32	2.60	1.55	0.92	0.60
<i>b</i>	13.00	7.74	5.19	3.21	2.33
$q_s$	0.48	0.34	0.30	0.29	0.26
$k'_{0,lang}$	2.57	1.06	0.63	0.37	0.24
2 $A_i$	0.34	0.25	0.20	0.19	0.17
$a'_i$	16.42	9.89	7.34	4.84	3.35
$k'_{0,jov}$	2.27	1.00	0.60	0.37	0.23
<i>Column 1, P</i>					
$k'_{0,exp}$	7.51	3.02	2.17	1.28	0.71
1 <i>a</i>	20.32	7.05	4.35	2.85	1.78
<i>b</i>	17.23	6.72	4.32	3.20	2.05
$q_s$	1.18	1.05	1.01	0.89	0.87
$k'_{0,lang}$	8.26	2.87	1.77	1.16	0.72
2 $A_i$	0.88	0.69	0.62	0.53	0.52
$a'_i$	19.18	9.66	6.72	5.23	3.34
$k'_{0,jov}$	6.86	2.71	1.70	1.13	0.71
<i>Column 2, P</i>					
$k'_{0,exp}$		7.05	4.00	2.36	1.41
1 <i>a</i>		17.80	9.13	5.40	3.15
<i>b</i>		9.11	4.92	2.85	1.62
$q_s$		1.95	1.86	1.89	1.54
$k'_{0,lang}$		8.34	4.28	2.53	1.48
2 $A_i$		1.30	1.13	1.11	1.17
$a'_i$		12.77	7.98	5.02	2.70
$k'_{0,jov}$		7.78	4.23	2.61	1.48
<i>Column 2, C</i>					
$k'_{0,exp}$		19.86	10.48	5.55	3.00
1 <i>a</i>		38.66	21.56	12.48	6.78
<i>b</i>		16.17	10.96	7.50	4.21
$q_s$		2.39	1.97	1.67	1.62
$k'_{0,lang}$		18.11	10.10	5.85	3.18
2 $A_i$		1.73	1.36	1.09	0.97
$a'_i$		19.09	14.30	10.73	6.83
$k'_{0,jov}$		15.47	9.11	5.48	3.11

$k'_0$  = capacity factor at infinite dilution-conditions of linear (analytical) chromatography; exp = experimental; calculated from Langmuir and Jovanovic isotherms: Langmuir  $k'_0 = aV_s/V_m$ ; Jovanovic  $k'_0 = A_i a'_i V_s/V_m$ .

$V_s$  and  $V_m$  = volumes of the stationary and of the mobile phases in the column.

crease as the concentration of methanol is increased, in agreement with Eqs. (6) and (7) (Fig. 1). The correlation coefficients of these equations are 0.999

or better. The column saturation capacities for the individual phenols also decrease with increasing concentration of methanol. Because the value of the capacity factor of methanol on a C<sub>18</sub> column in water is equal to 1 or less, methanol can hardly displace sample compounds which are much more strongly retained. Solvation and solubility effects in the stationary and in the mobile phases can significantly decrease the sorption in reversed-phase systems as the concentration of methanol in the solvent increases. These effects are not adequately accounted for by any pure adsorption model.

The saturation capacities generally increase as the polarities of the solutes decrease, but for phenol and *o*-cresol are close to each other with differences of less than 25%. On the other hand, the saturation capacities for resorcinol are much lower than for phenol, possibly because resorcinol with two hydroxy groups is much more polar and the second phenolic group hinders the access of the molecules of resorcinol to the surface of the adsorbent.

The differences between the Langmuir coefficients and the saturation capacities for phenol measured with different batches of the columns used are very significant (approximately twice as large for column 2 than for column 1). Different phase ratios were found for these columns, which indicates that different types of silica or different surface coverage with bonded material could have been used in their production.

Also the coefficients of the Jovanovic isotherms decrease as the concentration of methanol increases. In contrast to the Langmuir coefficients, simple second-degree polynomial equations describe these dependencies more adequately than their semilogarithmic forms (Fig. 2):

$$A_i = A_{0i} - A_{1i}\varphi + A_{2i}\varphi^2 \quad (8)$$

$$a'_i = a_{0i} - a_{1i}\varphi + a_{2i}\varphi^2 \quad (9)$$

The correlation coefficients for these equations are 0.999 or better with column 2 and 0.97–0.99 with column 1. The column saturation capacities and the capacity factors at linear (analytical) chromatography conditions,  $k'_0$ , calculated from the Jovanovic coefficients are in most cases lower than the corresponding data found from the Langmuir isotherms

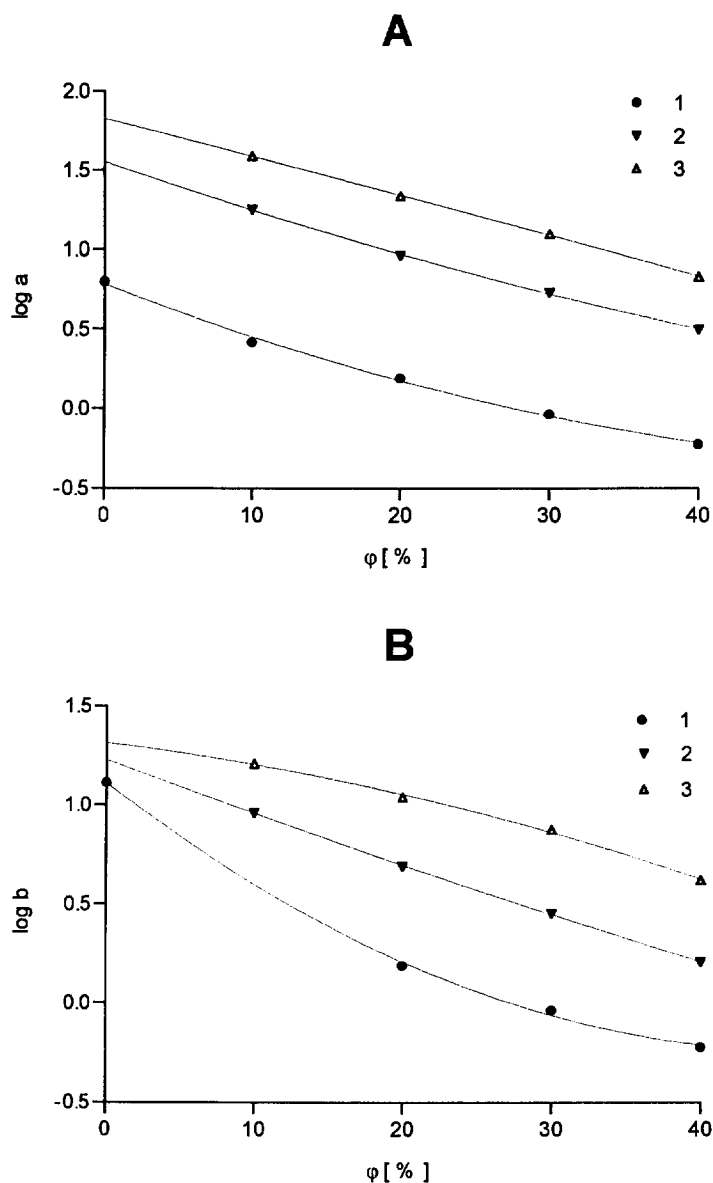


Fig. 1. Coefficients  $a$  (A) and  $b$  (B) of single-component Langmuir isotherms of resorcinol (1), phenol (2) and *o*-cresol (3) in mobile phases with different concentrations of methanol in water,  $\varphi$  (% v/v) on a Separon SGX C<sub>18</sub> column.

(Table 1). The agreement of the  $k'_0$  values calculated from the two isotherms with the experimental capacity factors determined after injection of low amounts of sample compounds and the calculated  $k'_0$  generally improves as the concentration of methanol in the mobile phase increases.

#### 4.2. Two-component distribution data

If single-component Langmuir, Jovanovic or quadratic isotherms are fitted to the two-component distribution data at a constant concentration ratio of the sample components, very good fit is obtained.

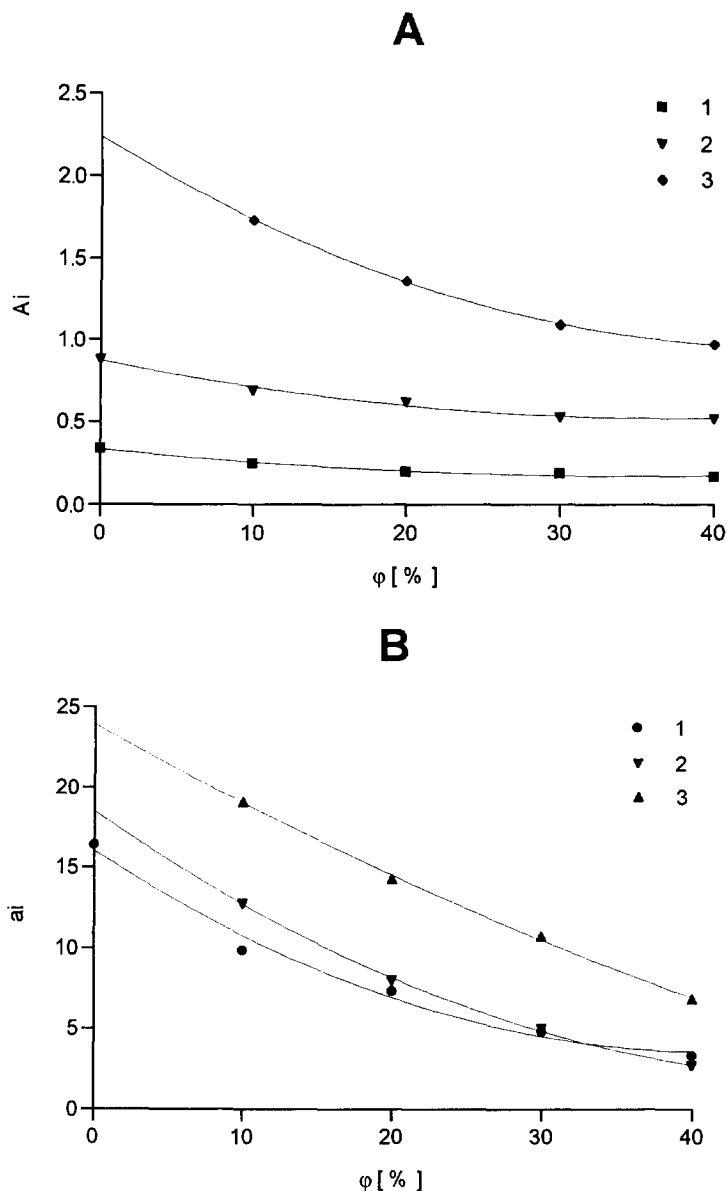


Fig. 2. Coefficients  $A_i$  (A) and  $a'_i$  (B) of single-component Jovanovic isotherms of resorcinol (1), phenol (2) and *o*-cresol (3) in mobile phases with different concentrations of methanol in water,  $\phi$  (% v/v) on a Separon SGX C<sub>18</sub> column.

However, this fit is not very useful in practice, as different coefficients of the isotherms apply at different concentration ratios of the sample compounds.

The single-component Langmuir ( $a$ ,  $b$ ) or Jovanovic ( $A_i$ ,  $a'_i$ ) coefficients were used in the equations of corresponding competitive isotherms and the coefficients  $a_{ij}$ ,  $b_{ij}$  of the quadratic (Eq. (3))

and  $a_{i,j}$ ,  $a_{j,i}$  of the Jovanovic (Eq. (5)) isotherms were determined as the best-fit parameters using nonlinear regression analysis of the whole set of the experimental data at three different concentration ratios of phenols in the binary sample mixtures (0.1:0.02, 0.1:0.1 and 0.02:0.1 mol/L), so that the values of the competitive isotherm coefficients apply

for varying concentration ratios of the sample components. The experimental distribution of phenol and *o*-cresol (points) in solutions with different concentrations of methanol are compared with the competitive Langmuir (full lines), quadratic (dashed lines) and Jovanovic (dash-dotted lines) isotherms of

phenol and *o*-cresol (Fig. 3) and of resorcinol and phenol (Fig. 4). Only the data for the 0.1:0.1 mol/L ratios are shown in Figs. 3 and 4.

The competitive Langmuir isotherm fits reasonably well the two-component distribution data of phenol and *o*-cresol in 30% and in 40% methanol on

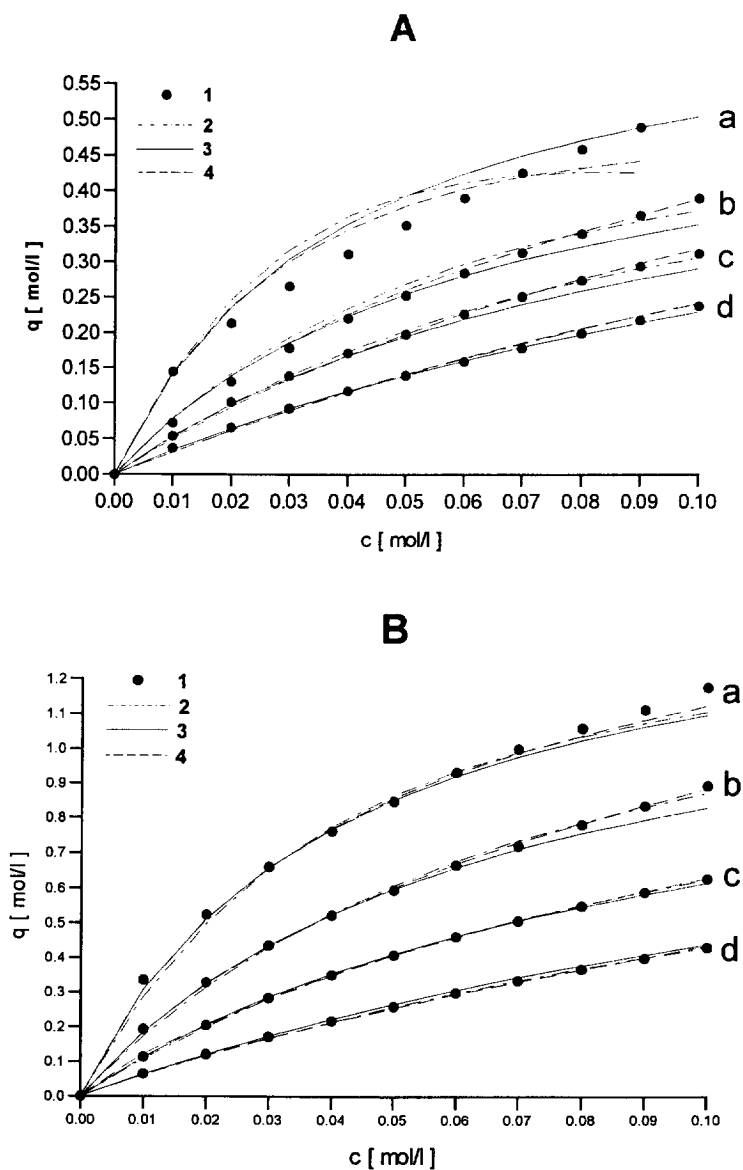


Fig. 3. Competitive Jovanovic (2-dash-dotted lines), competitive Langmuir (3-full lines) and quadratic (4-dashed lines) isotherms fitted to the two-component distribution experimental data (1-points) of phenol (A) and *o*-cresol (B) on a Separon SGX  $C_{18}$  column in 10% (a), 20% (b), 30% (c) and 40% (d) methanol at the concentration ratio of phenol and resorcinol 0.1:0.1 mol/L.  $c$ ,  $q$  = Concentration of the sample compounds in the mobile and in the stationary phases, respectively.

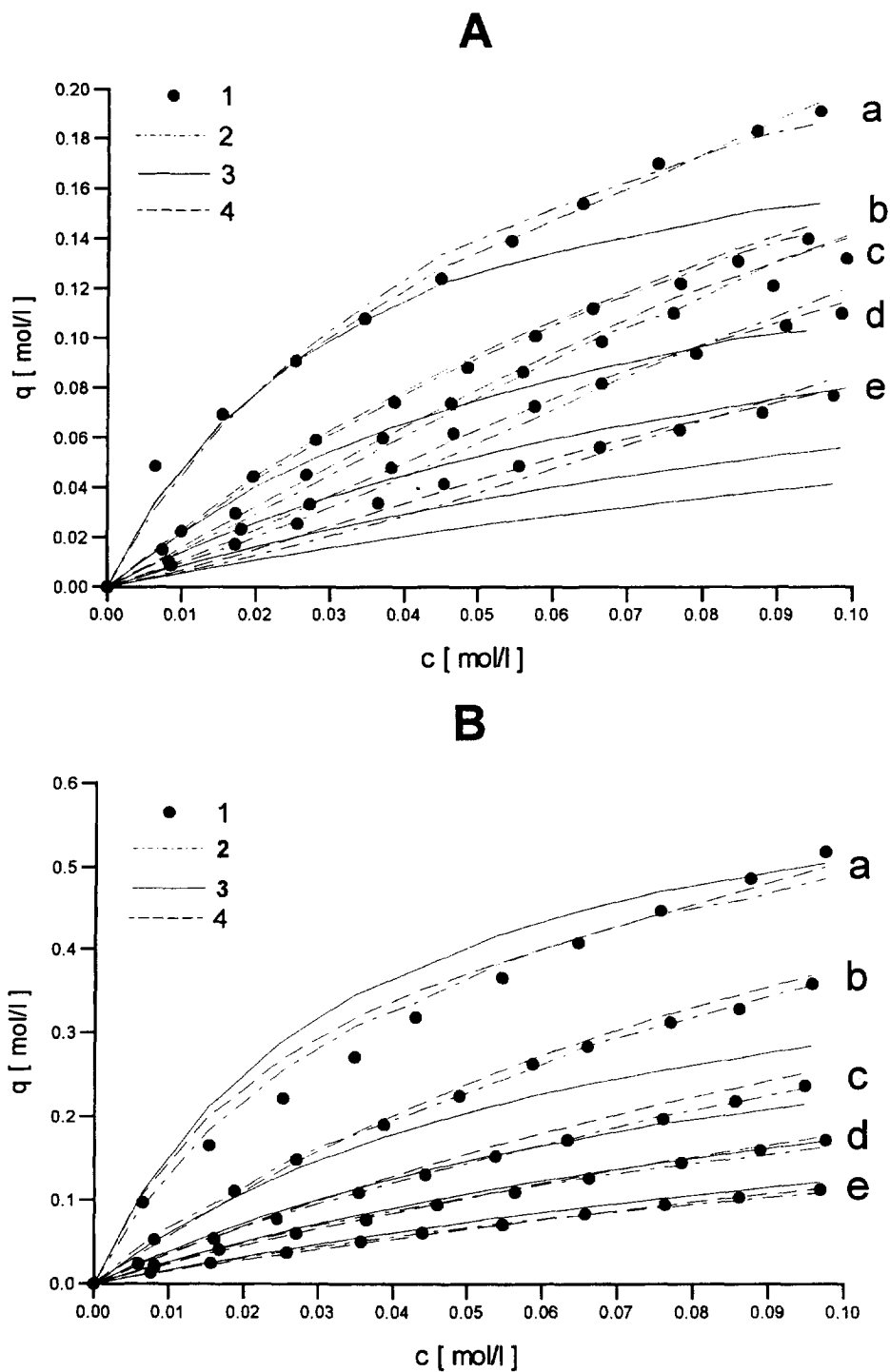


Fig. 4. Competitive isotherms fitted to the two-component distribution experimental data of phenol (A) and resorcinol (B) on a Separon SGX  $C_{18}$  column in water (a), 10% (b), 20% (c), 30% (d) and 40% (e) methanol at the concentration ratio of phenol and resorcinol 0.1:0.1 mol/L.  $c$ ,  $q$  = Concentration of the sample compounds in the mobile and in the stationary phases, respectively. The meaning of symbols is as in Fig. 3.



column 2, but significant deviations from the experimental data are observed in solutions with lower concentrations of methanol, and this isotherm fails to describe the two-component distribution data of phenol and resorcinol on column 1. This behaviour can be explained by large differences in their saturation capacities (Table 1), as the model of the competitive Langmuir isotherm is based on the assumptions of equal saturation capacities of the column for all sample components.

The values of the coefficients of the quadratic and of the competitive Jovanovic isotherms for the phenols studied are given in Table 2. These data are the best-fit parameters and are not attributed to any physical meaning, so that the isotherms are only empirical ones, having the form of competitive Jovanovic or quadratic equations.

The competitive quadratic and Jovanovic isotherms provide good fit to the competitive distribution data of phenol and *o*-cresol on column 2 in all solvents, except for phenol in 10% methanol and the

quadratic isotherm yields slightly better agreement with the experiment at high concentrations of the sample components. Very significant improvement was observed when the empirical competitive Jovanovic and quadratic isotherms were fitted to the competitive distribution data for phenol and resorcinol on column 1. The empirical Jovanovic isotherm describes better than the quadratic isotherm the experimental distribution data of phenol. On the other hand, the empirical competitive quadratic isotherm fits the experimental data for resorcinol slightly better than the Jovanovic isotherm. However, from the fit of these isotherms to the experimental data, no conclusions can be made about the validity of any theoretical model.

The second-order approximation of the LeVan–Vermeulen isotherm with the coefficients of the individual Langmuir isotherms (the graphs are not shown in Figs. 3 and 4) does not fit the experimental data of phenols.

Fig. 5 shows the dependencies of the formal competitive Jovanovic parameters  $a_{i,j}$  and  $a_{j,i}$  on the concentration of methanol. To first approximation, these plots can be described by second degree polynomial equations similar to the dependence of the parameter  $a'_i$  by Eq. (9). The correlation coefficients of these equations are 0.91–0.998 for column 1 and 0.89–0.94 for column 2. The determination of the mathematical form of such dependencies for all parameters of the competitive isotherms is essential for calculation of band profiles in overloaded gradient elution chromatography. On the other hand, the coefficients of the quadratic isotherms are either low or do not show significant dependence on the concentration of methanol.

Fig. 6 compares the experimental band profiles (1) of a 550  $\mu$ l sample containing 0.1 mol/L of each phenol (P) and *o*-cresol (C) on column 2 in 30% methanol with the band profiles predicted using the competitive Langmuir (2) and quadratic (3) isotherms at two different concentrations of methanol. The experimental band profiles were measured at 286 nm and recalculated to the concentration response using individual calibration curves for each sample compound. The competitive Langmuir isotherm, except for slightly underestimated height of the peak of *o*-cresol and tailing of the peak of

Table 2  
Coefficients of two-component isotherms of resorcinol (R), phenol (P) and *o*-cresol (C) on  $C_{18}$  columns 1 and 2; 1=competitive quadratic isotherm (Eq. (3)), 2=competitive Jovanovic isotherm (Eq. (5))

% Met-		0	10	20	30	40
hanol						
<i>Column 1, R</i>						
1	$a_{ij}$	2.02	0.01	0.40	0.22	0.00
	$b_{ij}$	24.64	1.22	9.05	7.01	0.63
2	$a_{i,j}$	5.82	7.95	8.91	10.48	9.52
	$a_{j,i}$	-1.94	-0.81	-26.41	-36.23	-49.04
<i>Column 1, P</i>						
1	$a_{ji}$	0.00	0.00	0.00	0.00	0.00
	$b_{ji}$	1.78	1.09	1.17	1.24	1.30
2	$a_{i,j}$	-26.35	-4.96	-19.44	-17.36	-16.54
	$a_{j,i}$	-11.64	-2.70	-2.45	-2.39	-2.56
<i>Column 2, P</i>						
1	$a_{ij}$		25.65	14.74	11.70	13.95
	$b_{ij}$		101.64	11.98	-10.69	27.90
2	$a_{i,j}$		11.90	6.50	6.88	5.99
	$a_{j,i}$		10.67	1.93	2.23	1.58
<i>Column 2, C</i>						
1	$a_{ji}$		-13.9	-20.8	-12.8	-13.8
	$b_{ji}$		-20.2	-42.9	-24.7	-30.2
2	$a_{i,j}$		8.82	2.68	1.70	-4.64
	$a_{j,i}$		7.98	3.87	2.14	-2.02

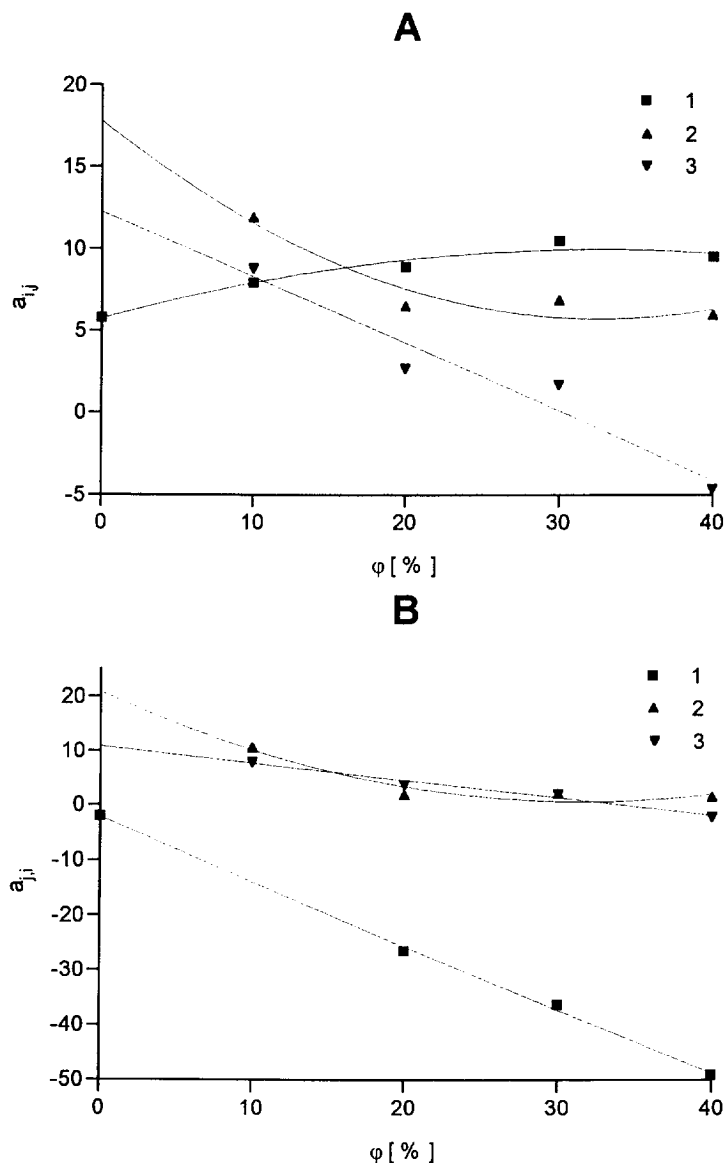


Fig. 5. Coefficients  $a_{i,j}$  (A) and  $a_{j,i}$  (B) of competitive Jovanovic isotherms of resorcinol (1), phenol (2) and *o*-cresol (3) in mobile phases with different concentrations of methanol in water,  $\phi$  (% v/v) on a Separon SGX C<sub>18</sub> column.

phenol, provides acceptable agreement between the experimental and the predicted band profiles. The quadratic isotherm provides a similar shape for the band profiles, except for the front of the band of phenol shifted to approximately 0.05 min higher elution times and slightly lower and more tailing peak of *o*-cresol.

## 5. Conclusions

Suitability of various competitive isotherms to describe the two-component distribution data of phenols in reversed-phase systems depends on the column saturation capacities for the individual components and on the concentration of methanol in the

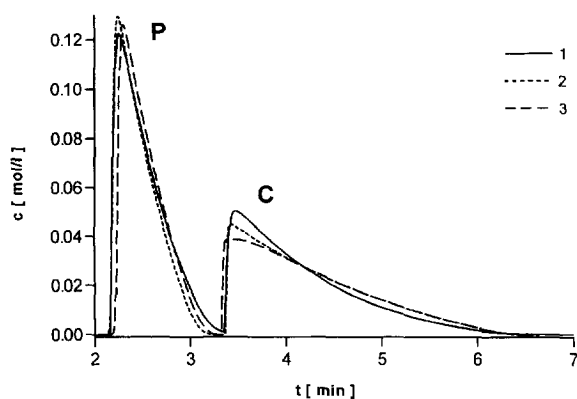


Fig. 6. Experimental (1-solid line, calculated from the calibrated detector response) and simulated (2, 3) band profiles of phenol (P) and *o*-cresol (C) in overloaded chromatography on a Separon SGX column in 30% methanol as the mobile phase. Sample volume: 550  $\mu$ l, concentration of each compound 0.1 mol/L. Flow-rate: 1 ml/min. Isotherms used for simulation: competitive Langmuir (2-dotted line) and quadratic (3-dashed line).

sample solvent. The fit of the competitive Langmuir isotherm to the experimental distribution data improves as the polarities of phenols decrease and as the concentration of methanol in the sample solvent increases. This isotherm fails to describe the distribution of a polar dihydroxybenzene, for which significantly lower saturation capacity was found than for monohydroxybenzenes. On the other hand, it can suitably describe the behaviour of monohydroxybenzenes, especially in solvents with higher concentrations of methanol. For the distribution of compounds with different column saturation capacities, the competitive Jovanovic or the quadratic isotherms can adequately describe the two-component distribution data, except for phenol in pure water or 10% methanol. The competitive distribution isotherms can be used to calculate simulated overloaded band profiles.

The dependencies of the Langmuir and of the Jovanovic single-component and competitive isotherms on the concentration of methanol can be described by simple second-order polynomial equations to allow calculations of sample bands in overloaded gradient elution separations. On the other hand, it is not possible on the basis of the results obtained to decide which model controls the behaviour in the system studied—the Langmuir or the

Jovanovic one. From the practical point of view, physico-chemical interpretation of the isotherm is irrelevant with respect to the simulation of the band profiles under overloaded column conditions and any mathematical function can be used as long as it correlates the experimental results [1].

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