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## Comparison of various isotherm models for predicting competitive adsorption data

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### ABSTRACT

Competitive adsorption isotherms were determined for 2-phenylethanol and 3-phenylpropanol on ODS-silica with methanol-water as the mobile phase. The experimental data were fitted to the Langmuir competitive isotherm, the second-order ideal adsorbed solution isotherm of LeVan and Vermeulen, the seven-parameter quadratic isotherm (ratio of two second-degree polynomials) and the competitive Fowler isotherm. The best results were obtained by adjusting the five parameters of the competitive Fowler isotherm by a non-linear regression. Unfortunately, this isotherm gives the mobile phase concentration as a function of the surface coverage and the equation cannot be inverted in closed form.

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### INTRODUCTION

Determination of competitive equilibrium isotherms is important in theoretical and experimental studies in order to evaluate the separation process. The isotherm is the fundamental thermodynamic property which has to be measured in order to permit the accurate prediction of the individual band profiles in non-linear chromatography [1]. Once the adsorption data have been obtained, however, they are put in a functional form by fitting to a model for use in the calculation of individual component profiles [2,3].

For single-component systems, several dynamic methods have been developed to measure adsorption isotherms accurately while avoiding the use of batch techniques, which are time consuming and require the use of large amounts of chemicals. The methods of elution by characteristic point (ECP) and frontal analysis (FA) are the most popular. ECP is based on using the rear boundary of a non-linear elution profile to measure the isotherm [1,4]. The main disadvantage of this

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method is that the experimental profile recorded deviates from the ideal profile because of the band broadening due to the finite efficiency of real columns. Thus an error is made in the calculation of the amount adsorbed. This deviation causes an error in the measured isotherm. However, with the modern, high-efficiency columns used in high-performance liquid chromatography (HPLC), this error remains acceptable. Another drawback is that separate detector calibration is required.

On the other hand, FA is based on making a series of step changes in the concentration of the mobile phase at the column inlet and writing an integral mass balance [5,6]. Compared with ECP, FA has the advantages that it does not require detector calibration and that the nature of the front (which is self-sharpening) makes the measurement independent of the column efficiency, as long as this efficiency exceeds about 100 theoretical plates. FA has the inconvenience of requiring a much larger amount of product than ECP. It has been shown that for high-efficiency columns ECP and FA give the same experimental isotherm [7].

Other methods have been proposed for the measurement of single-component isotherms, based on recording high-concentration band profiles and calculating the best-fit parameters to a known isotherm model [8–10]. Lastly, there are methods in which the isotherm is determined by the retention time of a small sample pulse injected on a concentration plateau [11].

For the measurement of binary and multi-component isotherms, several of these chromatographic methods can be applied. Frontal analysis has been extended and employed in the determination of two component competitive isotherms [12–14]. Step and pulse techniques have been suggested, using labelled compounds [11,15]. They are impractical for most organic compounds, for which labelled molecules are difficult and expensive to synthesize. Recently, a method based on analyzing the individual band profiles for a series of large-volume rectangular injections of binary mixtures has been proposed [16].

In the analysis of single-component isotherm data, several models can be used which accurately fit experimental isotherm data and provide a convenient means of obtaining an accurate prediction of the band profiles [17–19]. The Langmuir isotherm is the most common. The bi-Langmuir, Freundlich and Fowler isotherms [20,21] have also been used.

For the binary and multi-component cases, the competitive Langmuir isotherm model is often used, owing to its simplicity. However, this model, which does not satisfy the Gibbs–Duhem equation, lacks thermodynamic rigor. Further, the use of the Langmuir single-component parameters in the competitive model does not give an accurate prediction of overloaded elution profiles [16,22] and does not account well for the experimental competitive adsorption data [23]. A thermodynamically consistent competitive isotherm has been derived by LeVan and Vermeulen [24], who used the ideal adsorption solution (IAS) theory and introduced into the Langmuir equation an additional term accounting for the difference in column saturation capacities of the two components.

The Fowler isotherm can also be extended to binary mixtures and take into account the competitive behavior of the two components [20]. Statistical thermodynamic models have shown that the competitive isotherm should be the ratio of two polynomials of the same degree [25,26]. The Langmuir isotherm is the ratio of two first-degree polynomials. A better result is predicted with the use of the ratio of two

second-degree polynomials. Finally, a binary isotherm model based on ion-exchange formalism has been proposed by Velayudhan and Horváth [27]. None of these models has been used yet to account for competitive adsorption data and to calculate individual band profiles in non-linear chromatography.

In this paper, experimental adsorption data determined by two-component frontal analysis [12,14] are reported and a comparison is made between four of the competitive isotherm models listed above, the competitive Langmuir model, the quadratic isotherm model, the LeVan and Vermeulen IAS model and the competitive Fowler isotherm.

## THEORY

The classical equations of two-component frontal analysis [12,13,18] were used to derive the amount of the component adsorbed at equilibrium from the breakthrough curves recorded as the column response to step changes in the concentration.

Four isotherm models have been used to account for the measured experimental data. The simplest model is the competitive Langmuir isotherm model [28]:

$$q_1 = \frac{a_1 C_1}{1 + b_1 C_1 + b_2 C_2} \quad (1)$$

$$q_2 = \frac{a_2 C_2}{1 + b_1 C_1 + b_2 C_2} \quad (2)$$

where  $q_1$  and  $C_i$  are the concentrations of the  $i$ th component at equilibrium in the stationary and the mobile phase, respectively, and  $a_i$  and  $b_i$  are numerical coefficients, characteristic of the components and of the chromatographic system. The column saturation capacity is  $q_{i,s} = V_{sp} a_i / b_i$ , where  $V_{sp}$  is the volume of stationary phase contained in the column.

The Langmuir model has been corrected for its thermodynamic inconsistency by LeVan and Vermeulen [24], using the IAS theory. The first-order approximation of their equation is the Langmuir isotherm if the column saturation capacity is the same for the two components. If the column saturation capacity is different for the two components, the LeVan and Vermeulen isotherm is represented by a series which converges very rapidly and can be limited in most practical cases to its first two terms. The second-order approximation of their isotherm can be written as

$$q_1 = \frac{a_1 C_1 + a_2 C_2}{b_1 C_1 + b_2 C_2} \frac{b_1 C_1}{1 + b_1 C_1 + b_2 C_2} + \left( \frac{a_1}{b_1} - \frac{a_2}{b_2} \right) \frac{b_1 b_2 C_1 C_2}{(b_1 C_1 + b_2 C_2)^2} \ln(1 + b_1 C_1 + b_2 C_2) \quad (3)$$

$$q_2 = \frac{a_1 C_1 + a_2 C_2}{b_1 C_1 + b_2 C_2} \frac{b_2 C_2}{1 + b_1 C_1 + b_2 C_2} + \left( \frac{a_2}{b_2} - \frac{a_1}{b_1} \right) \frac{b_1 b_2 C_1 C_2}{(b_1 C_1 + b_2 C_2)^2} \ln(1 + b_1 C_1 + b_2 C_2) \quad (4)$$

Eqns. 1 and 2 (or 3 and 4) must be valid for any combination of mobile phase

concentrations of the two components ( $C_1, C_2$ ). Obviously, they must also be valid when one of these concentrations is zero. Thus, eqn. 1 (or 3) gives the Langmuir single-component isotherm for the first component when  $C_2 = 0$ . The coefficients  $a_i$  and  $b_i$  in eqns. 1–4 are the coefficients of the single-component Langmuir isotherms.

The third isotherm we used is the quadratic isotherm, suggested by statistical thermodynamics and for which different derivations have been discussed [23,25]:

$$q_1 = \frac{a_1 C_1 + a_{12} C_1 C_2}{1 + b_1 C_1 + b_2 C_2 + b_{12} C_1 C_2} \quad (5)$$

$$q_2 = \frac{a_2 C_2 + a_{21} C_1 C_2}{1 + b_1 C_1 + b_2 C_2 + b_{21} C_1 C_2} \quad (6)$$

where  $b_{12} = b_{21}$ . In eqns. 5 and 6, the coefficients  $a_i$  and  $b_i$  are the same as in the single-component isotherm of the  $i$ th component. The coefficients  $a_{ij}$  and  $b_{ij}$  have to be determined for the binary mixture.

The last isotherm we used is the competitive Fowler isotherm [20]:

$$\frac{1}{C_1} \cdot \frac{\theta_1}{1 - (\theta_1 + \theta_2)} = b_0 e^{-\chi_1(\theta_1 + \theta_2)} \quad (7)$$

$$\frac{1}{C_2} \cdot \frac{\theta_2}{1 - (\theta_1 + \theta_2)} = b_0 e^{-\chi_2(\theta_1 + \theta_2)} \quad (8)$$

where  $\theta_i$  is the ratio  $q_i/q_{s,i}$  of the stationary phase concentration of the  $i$ th component to its column saturation capacity and  $\chi_i$  is a numerical coefficient. For a binary mixture, this isotherm has five parameters ( $q_{s,1}, q_{s,2}, \chi_1, \chi_2$  and  $b_0$ ).

Each isotherm model was tested (i) by using the single-component parameters of the corresponding model (Langmuir or Fowler) in a mixing model and by adjusting the other parameters, when needed (*i.e.*, with the quadratic isotherm model) using a non-linear least-squares fitting method and (ii) by empirically fitting the corresponding equations to the isotherm data and determining the best values of the parameters, using a non-linear least-squares fitting method.

The non-linear least-squares fit was accomplished using the SAS library and the SYSNLIN procedure, so that the parameters calculated give the least error for both components. Success with this method depends considerably on the choice of a suitable initial solution. We have found that searching empirically for an acceptable set of solutions using “what if” calculations carried out with the 123 spreadsheet (Lotus Development, Cambridge, MA, U.S.A.) and its graphics module permits the rapid selection of a satisfactory initial solution for the SAS program.

The absolute error between the data points and the best parameter isotherm given by each model was calculated by

$$E_i = \sum_{j=1}^n (q_{\text{exp},j} - q_{t,j})^2 \quad (9)$$

where  $i$  is the component number and  $j$  stands for the rank of the data point. This error was calculated for each model and the results were compared.

## EXPERIMENTAL

### *Equipment*

Frontal analysis was performed by pumping the mobile phase with a Gilson (Middleton, WI, U.S.A.) Model 302 pump through a ten-port Valco (Houston, TX, U.S.A.) pneumatically actuated valve fitted with two 2-ml sample loops, a column and a detector. The column was immersed in a Haake (Saddlebrook, NJ, U.S.A.) water-bath. Step changes in the solute concentration were made by switching the Valco valve after filling the proper loop with a solution of the sample in the mobile phase at the required concentration. The effluent composition was monitored by a Spectroflow 757 variable-wavelength UV detector (Applied Biosystems, Ramsey, NJ, U.S.A.) at 272 nm. The effluent was sampled using a four-port electrically actuated Valco valve with an internal 2- $\mu$ l loop.

The quantitative composition at each plateau was determined by an on-line HPLC unit consisting of a Beckman (Berkeley, CA, U.S.A.) Model 110B pump, the Valco four-port valve, a YMC (Morris Plains, NJ, U.S.A.) cartridge column and a Spectroflow Model 757 UV detector set at 254 nm. Both UV analog signals were digitized through a Gilson Model 621 system interface box and monitored using the 714 controller software on an IBM (Armonk, NY, U.S.A.) Model 50Z PS/2 computer.

### *Columns and chemicals*

The adsorption column was packed in-house at 7000 p.s.i. with 10- $\mu$ m Spherical ODS-silica from Vydac (Hesperia, CA, U.S.A.) in a 250  $\times$  2.1 mm I.D. column. A 3- $\mu$ m YMS 5  $\times$  0.46 cm I.D. cartridge column was used for on-line analysis.

2-Phenylethanol and 3-phenylpropanol were purchased from Fluka (Ronkonkoma, NY, U.S.A.). Methanol and water were purchased from Burdick and Jackson (Muskegon, MI, U.S.A.). All these products were used without further purification. The mobile phase was methanol-water (50:50). Concentrations are reported in mg/ml; a concentration of 1 mg/ml is 8.2 mM for 2-phenylethanol and 7.4 mM for 3-phenylpropanol.

### *Procedures*

Step changes in the solute concentrations were made in the mobile phase stream at the column inlet. The composition of the column effluent was monitored. Fig. 1 illustrates two typical frontal steps from which the amount adsorbed was calculated. The trace obtained from monitoring the effluents exhibits a primary plateau and a sub-plateau for each step. The concentration of the primary plateaux is known and the composition of the effluent at each sub-plateau was determined by on-line analysis. Samples were taken on-line, at the point where the arrow is drawn, on both the primary plateau and the sub-plateaux.

The chromatograms are shown in the upper part of Fig. 1. Note that the concentration of the 2-phenylethanol, the first component, at each sub-plateau is greater than that at the primary plateau. This is due to the displacement effect of the second component on the first. However, the concentration of 3-phenylpropanol, the second component, at the sub-plateaux is lower than that on the primary plateau.

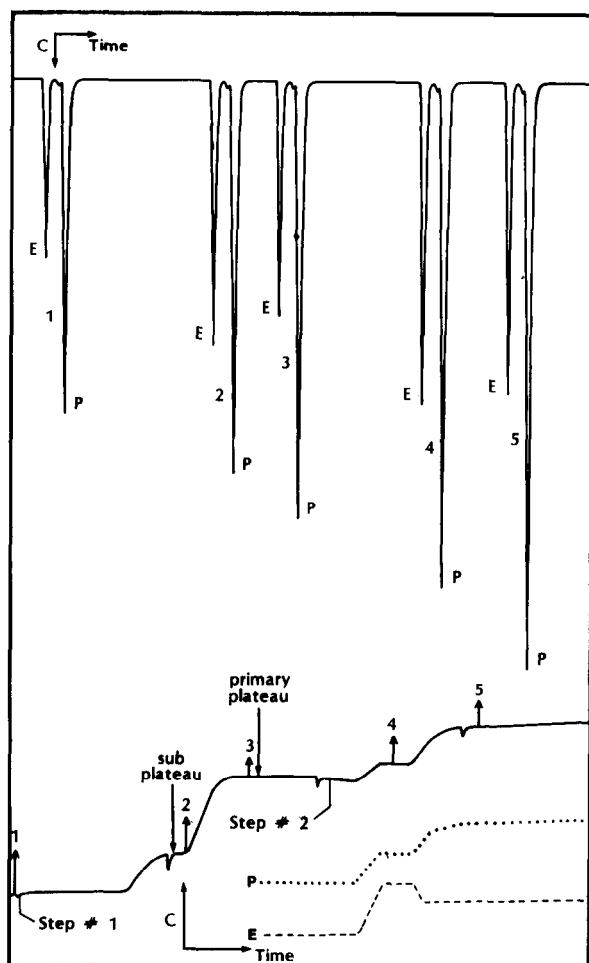


Fig. 1. Frontal profiles and effluent chromatograms. Bottom traces: frontal analysis. Solid line, detector profile in frontal analysis; dotted line, reconstructed profile for 3-phenylpropanol; dashed line, reconstructed profile for 2-phenylethanol. The arrows 1-5 indicate the times when an eluate sample was collected and analyzed. Top trace: analysis of the eluate samples taken during frontal analysis.

## RESULTS AND DISCUSSION

The pure component adsorption isotherms of 2-phenylethanol and 3-phenylpropanol were measured as described above. The two series of data are plotted in Fig. 2 (symbols). A non-linear least-squares analysis of these experimental data to the Langmuir Isotherm shows an excellent fit to the pure component data over the whole concentration range (Fig. 2, solid lines).

Competitive isotherm data were obtained under conditions of increasing total sample concentration, but at a constant ratio of the concentrations of the two components. The ratios of the 2-phenylethanol (PE) to 3-phenylpropanol (PP)

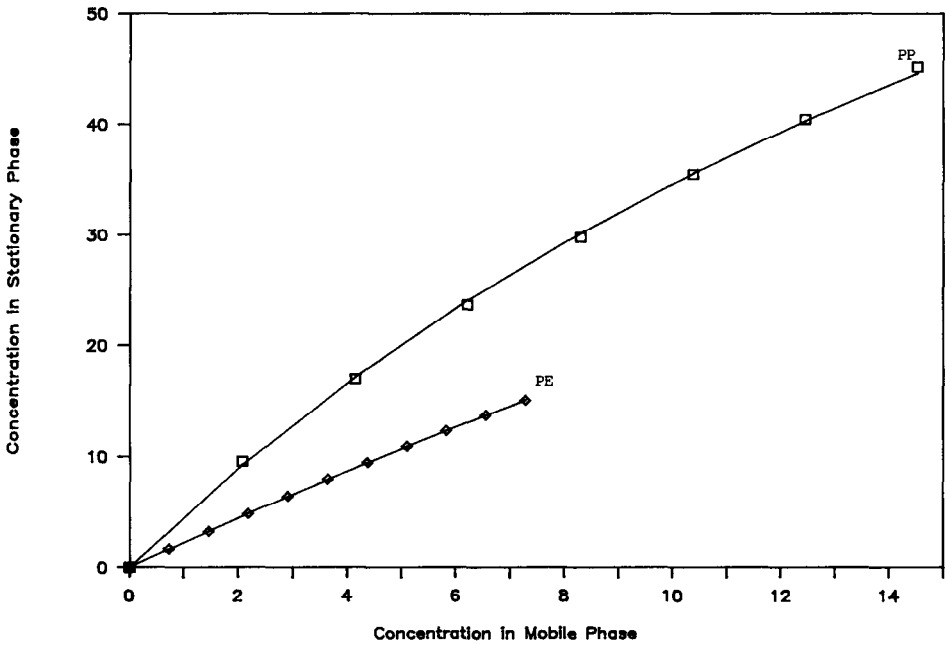


Fig. 2. Experimental single-component data for  $\diamond$  = 2-phenylethanol and  $\square$  = 3-phenylpropanol, fitted to single-component Langmuir model (solid lines). All concentrations in mg/ml. Experimental conditions: 250  $\times$  2.1 mm I.D. column packed with 10- $\mu$ m Vydac ODS-silica; mobile phase, methanol-water (50:50); flow-rate 0.25 ml/min.

TABLE I  
SUMMARY OF ISOTHERM PARAMETERS

Isotherm	Parameters		
Competitive Langmuir (single-component)	$a_1 = 2.3$ $b_1 = 0.015$	$a_2 = 4.82$ $b_2 = 0.039$	
Competitive Langmuir (best-fit parameters)	$a_1 = 2.4$ $b_1 = 0.022$	$a_2 = 3.83$ $b_2 = 0.01913$	
Quadratic isotherm (three floating parameters)	$a_1 = 2.30$ $a_{1,2} = 0.030$ $b_1 = 0.015$	$a_2 = 4.82$ $a_{21} = -0.20$ $b_2 = 0.039$	$b_{1,2} = 0.0$
Quadratic isotherm (seven floating parameters)	$a_1 = 2.3$ $a_{1,2} = 0.020$ $b_1 = 0.021$	$a_2 = 3.85$ $a_{2,1} = -0.075$ $b_2 = 0.022$	$b_{1,2} = 0.0$
Fowler isotherm (single-component, six parameters)	$q_{s,1} = 154$ $\chi_1 = 0.0048$ $b_1 = 0.0149$	$q_{s,2} = 138$ $\chi_2 = 0.029$ $b_2 = 0.0335$	
Fowler isotherm (single-component, five parameters)	$q_{s,1} = 104$ $\chi_1 = 0.366$ $b_1 = 0.0242$	$q_{s,2} = 187$ $\chi_2 = 0.378$ $b_2 = 0.0242$	
Fowler isotherm (best-fit parameters)	$q_{s,1} = 105$ $\chi_1 = 0.338$	$q_{s,2} = 160$ $\chi_2 = 0.366$	$b = 0.0242$

concentration investigated were 1:1, 1:3 and 3:1. The experimental data are shown as symbols in Figs. 3–10, where they are compared with the predictions of the various isotherms studied (solid lines). In each figure, (a) shows the isotherms of 2-phenylethanol and (b) those of 3-phenylpropanol.

The competitive Langmuir model (eqns. 1 and 2) was used first to account for the competitive adsorption data. The parameters  $a_1$ ,  $a_2$ ,  $b_1$  and  $b_2$  were obtained by regression to the single-component data (Fig. 2). They are reported in Table I. The comparison between the prediction of this competitive isotherm and the experimental data is shown in Fig. 3. For 2-phenylethanol (Fig. 3a), very good agreement is observed with the experimental data, except for the 1:3 mixture at high concentrations. However, for 3-phenylpropanol (Fig. 3b), strong deviations are observed. The adsorbed amount of 3-phenylpropanol determined experimentally is 20–30% less than that predicted by the competitive Langmuir model.

As the column saturation capacities are not equal for the two components (153 and 124 mg/ml for PE and PP, respectively), the LeVan and Vermeulen model [24] was tried. However, in the region for which data were taken, this model gives results (not shown) that were virtually the same as the competitive Langmuir isotherm. This is explained by the relatively small difference in column saturation capacities between the two components (20%) and the small curvature of the isotherm in the concentration range investigated, although measurements were made in nearly the whole accessible range, which is limited by the solubility of 3-phenylpropanol.

In order to try to improve the isotherm prediction, the competitive Langmuir model was used empirically. The values of the coefficients  $a_i$  and  $b_i$  in eqns. 1 and 2 that give the least error for the entire set of adsorption data (*i.e.*, the two-single component isotherms and the six mixed isotherms) were determined from a non-linear fit. As summarized in Table I,  $a_1$  does not change,  $a_2$  decreases by 20%,  $b_1$  increases by 50% and  $b_2$  decreases by 50%. Fig. 4a shows that there is hardly any change in the already very good fit for 2-phenylethanol (*cf.*, Fig. 3a), except for a substantial improvement of the fit in the high concentration range of the 1:3 mixture data. On the other hand, Fig. 4b shows a marked improvement in the fit for 3-phenylpropanol. The sum of errors reported in Table II has decreased from 287 to 47 (mg/ml)<sup>2</sup>. Still, the experimental data for the 1:3 and the 1:1 PE–PP mixtures are 8–10% lower than predicted by the model (Fig. 4b). Further, this improvement has been achieved at the cost of a less satisfactory fit of the single-component adsorption data by the competitive isotherm (see Fig. 7, dashed line).

The experimental data were then fitted to the quadratic competitive isotherm, given by eqns. 5 and 6 (Fig. 5). Keeping with the rigor of this isotherm, the coefficients  $a_1$ ,  $a_2$ ,  $b_1$  and  $b_2$  derived from the single-component adsorption data were used and the coefficients  $a_{12}$ ,  $a_{21}$  and  $b_{12}$  were determined by minimizing the error between the experimental and theoretical data. Surprisingly, although this model has seven parameters instead of four, the results are not much better than those of the competitive Langmuir model. For 2-phenylethanol (Fig. 5a) the model predicts nearly the same amount of component adsorbed at equilibrium as the competitive Langmuir isotherm derived from the single-component adsorption data (compare Figs. 3a and 5a) for the 3:1 and the 1:1 mixtures. The results are slightly better for the 1:3 mixture. For 3-phenylpropanol, the results are slightly better for the 1:3 mixture and somewhat better for the 1:1 mixture. The improvement is significant for the 3:1 mixture (compare



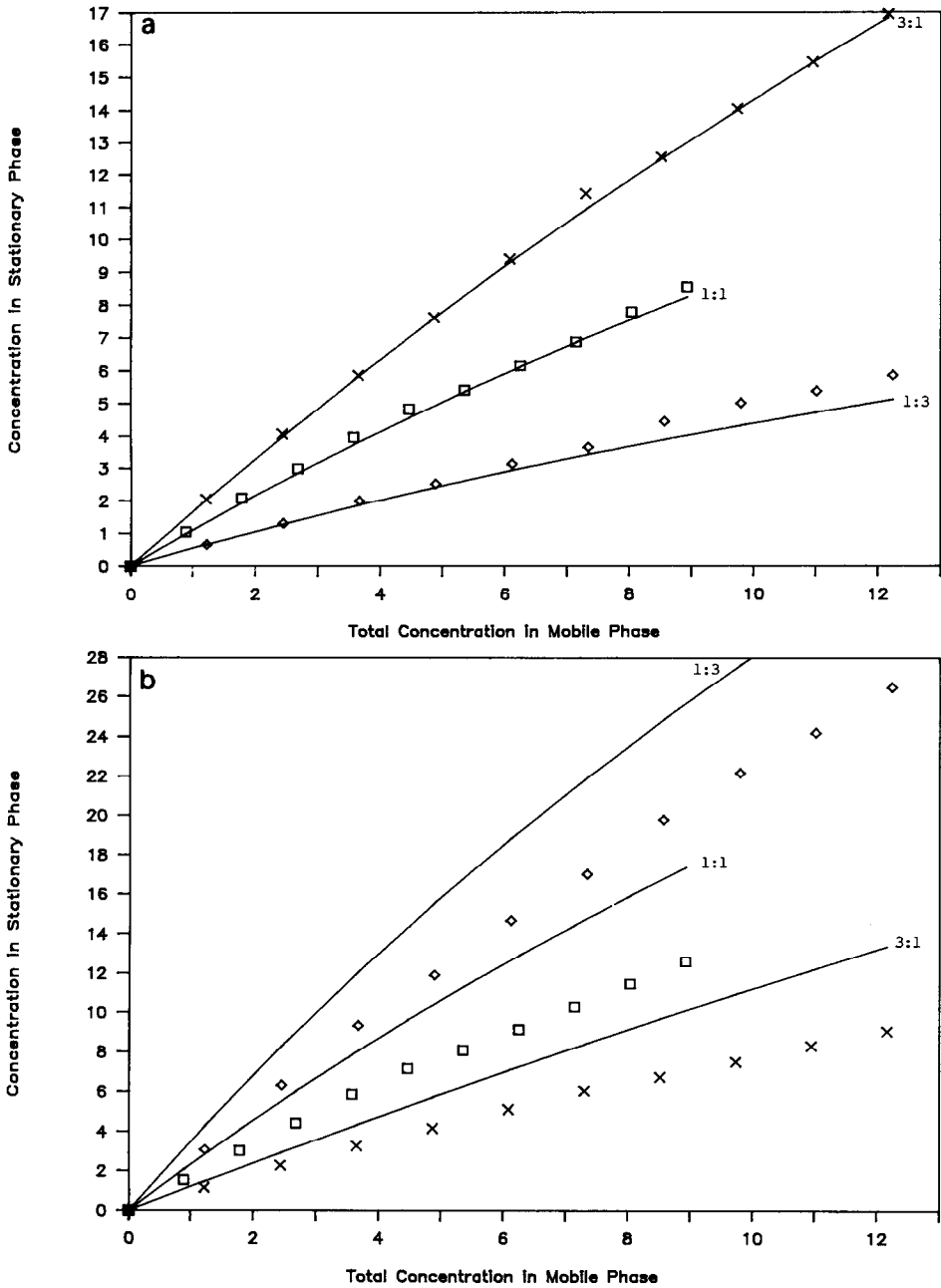


Fig. 3. Comparison of competitive isotherm experimental data and the competitive Langmuir isotherm with single-component parameters. All concentrations in mg/ml. Experimental conditions: see text and Fig. 2. Competitive adsorption data for  $\diamond = 1:3$ ,  $\square = 1:1$  and  $\times = 3:1$  mixtures. (a) 2-phenylethanol; (b) 3-phenylpropanol.

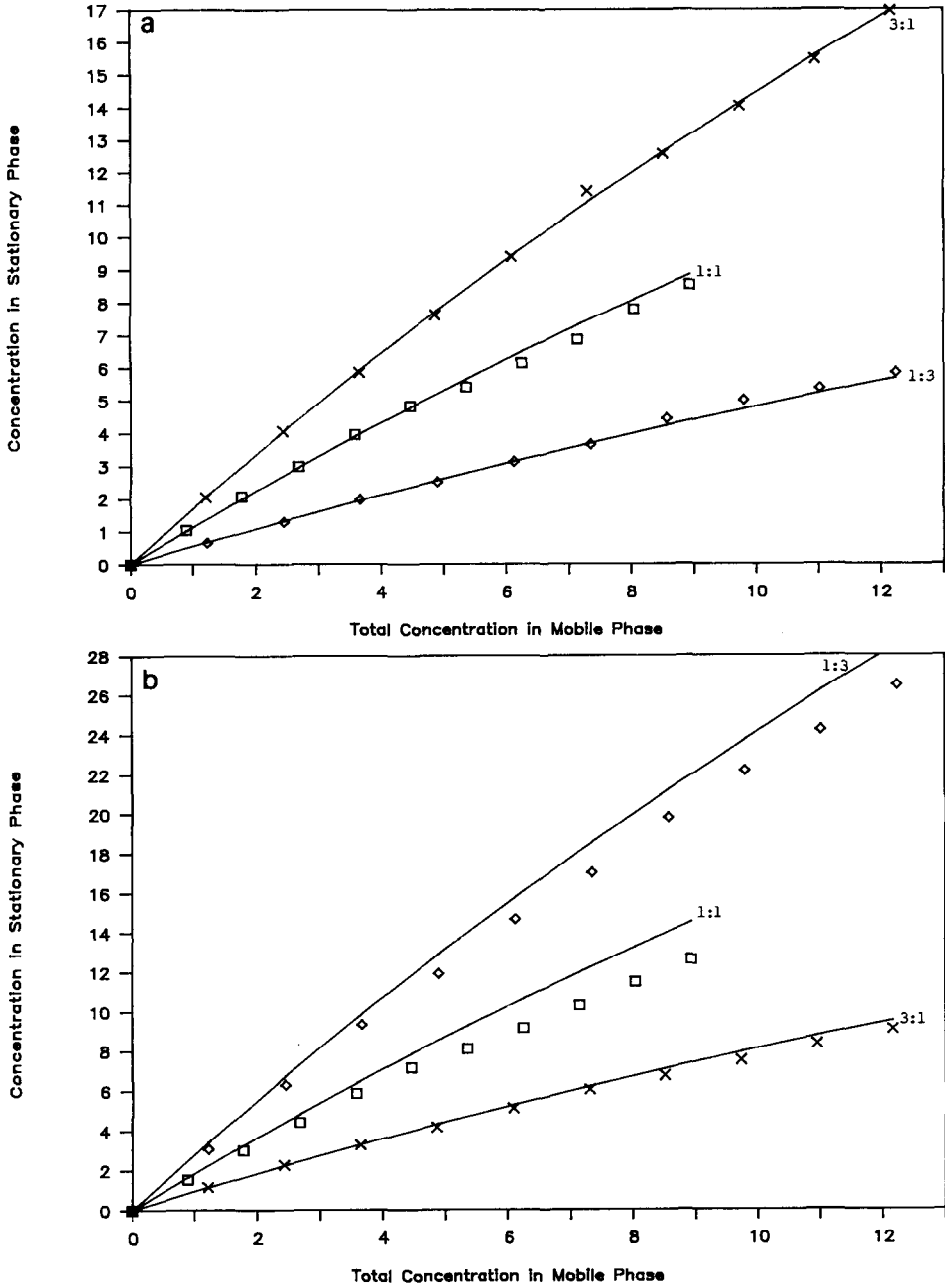


Fig. 4. Comparison of competitive isotherm experimental data and the competitive Langmuir isotherm with the best-fit Parameters. All concentrations in mg/ml. Experimental conditions: see text and Fig. 2. Same experimental data (symbols) as in Fig. 3. (a) 2-phenylethanol, (b) 3-phenylpropanol.

TABLE II  
SUMMARY OF ERRORS (mg/ml)<sup>2</sup>

The error is given as the sum of the squares of the differences between the calculated and the experimental concentrations (eqn. 9). The values in parentheses were derived using only the six competitive isotherms. For the other values, the summation is extended to the two single-component isotherms.

Isotherm	2-Phenylethanol	3-Phenylpropanol
Competitive Langmuir (single-component)	2.4	287
Competitive Langmuir (best-fit parameters)	1.98 (1.78)	47 (16.4)
Quadratic isotherm (three floating parameters)	1.26	75.8
Quadratic isotherm (seven floating parameters)	1.15 (0.93)	56.9 (8.3)
Fowler isotherm (single-component)	0.7 (0.5)	12.9 (12.6)
Fowler isotherm (best-fit parameters)	0.7 (0.56)	34.1 (0.77)

Figs. 3b and 5b). Overall, the fits are better (see Table II) but still not completely satisfactory. As seen in Fig. 4b, the Langmuir isotherm does not account accurately for the decrease in the slope of the 3-phenylpropanol competitive isotherm with increasing 2-phenylethanol concentration. A correction to that slope is supplied by the quadratic isotherm, using a best value of  $a_{21}$  which is negative, but the correction is insufficient.

We then used the quadratic isotherm as an empirical model. A non-linear regression was used to calculate the set of coefficients which minimize the sum of the errors (eqn. 9). Fig. 6 gives the best results in terms of the isotherms predicted. The agreement is excellent for 2-phenylethanol, with a slightly better fit than with the Langmuir models (Fig. 6a and Table II). For the 3-phenylpropanol data also the agreement is very good (Fig. 6b), much better than when the data are fitted to the competitive Langmuir isotherm equation (Table II). This situation was to be expected as the new isotherm has seven parameters instead of four.

We compare in Fig. 7 the single-component isotherms predicted by the competitive isotherm eqns. 1, 2 and 5, 6 ( $C_1 = 0$  or  $C_2 = 0$ ) with the experimental data with empirically optimized coefficients. The fit with the experimental data is now less good than with the single-component Langmuir isotherms (Fig. 2). The advantage of the competitive Langmuir isotherm and the quadratic isotherm with single-component Langmuir isotherm coefficients is that these isotherms fit very well the experimental data obtained for the single-component equilibrium isotherms. As in all curve-fitting processes, however, we lose some and gain some in fitting the whole set of data on the competitive isotherm equations and optimizing the coefficients. The fit of the competitive equilibrium data is greatly improved at the expense of the fit of the single-component equilibrium data. Nevertheless, the fit of single-component equilibrium data with either the Langmuir competitive isotherm or the quadratic isotherm is still very good for 2-phenylethanol (Fig. 7). For 3-phenylpropanol, the quality of the fit is still acceptable, especially at high concentrations for the Langmuir isotherm. At low

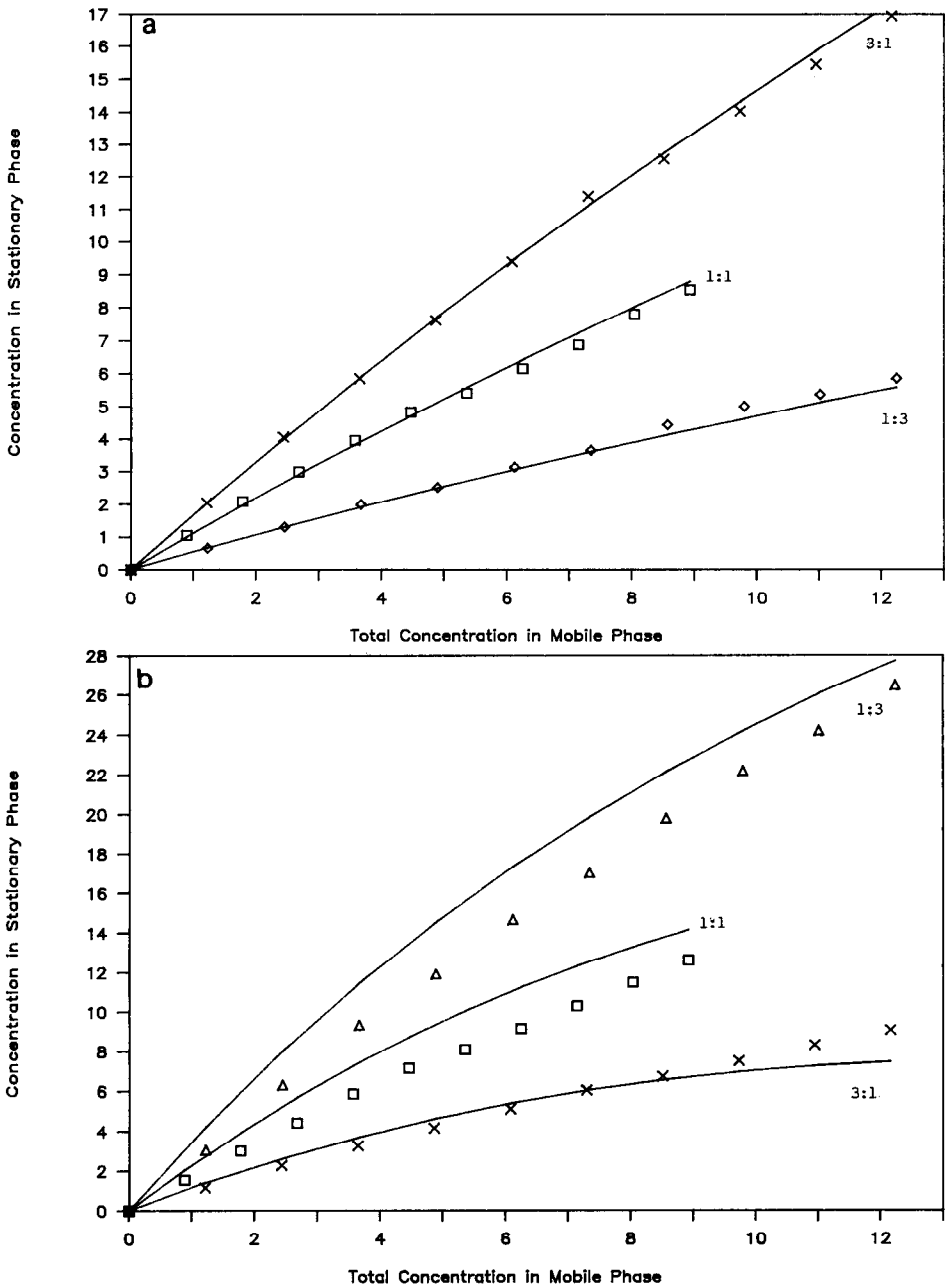


Fig. 5. Comparison of competitive isotherm experimental data and the prediction of the quadratic isotherm with three floating parameters. All concentrations in mg/ml. Experimental conditions: see text and Fig. 2. Same experimental data (symbols) as in Fig. 3.  $\Delta$  = 1:3 mixture. (a) 2-phenylethanol; (b) 3-phenylpropanol.

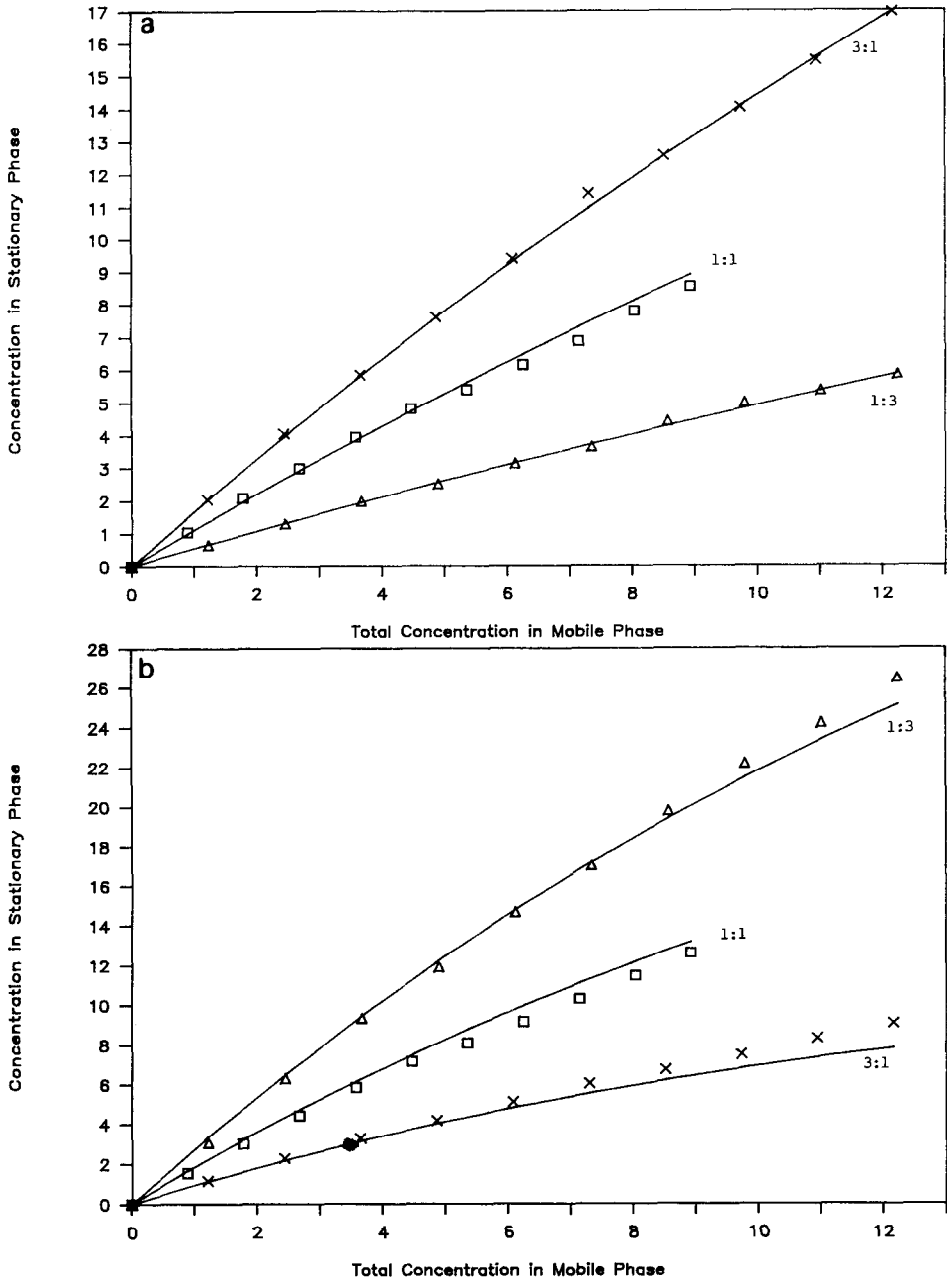


Fig. 6. Comparison of competitive isotherm experimental data and the prediction of the quadratic isotherm with seven floating parameters. All concentrations in mg/ml. Experimental conditions: see text and Fig. 2. Same experimental data (symbols) as in Fig. 3.  $\Delta$  = 1:3 mixture. (a) 2-phenylethanol; (b) 3-phenylpropanol.

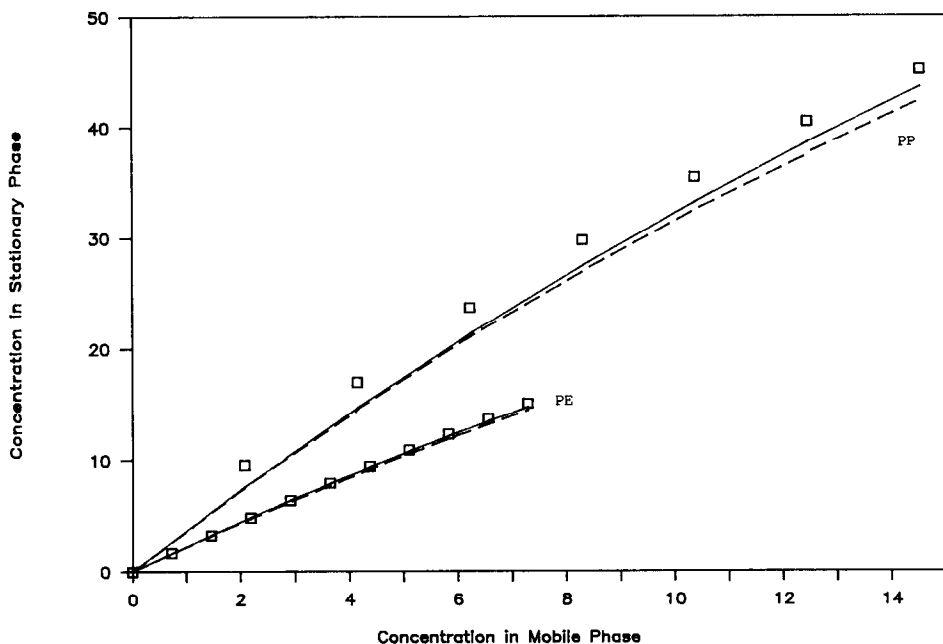


Fig. 7. Comparison of single-component experimental data with the best-fit competitive Langmuir model (solid line) and the quadratic seven floating parameters (dashed line) isotherm. All concentrations in mg/ml. Experimental conditions: see text and Fig. 2. Same experimental data as in Fig. 2.

concentrations for the Langmuir isotherm and over the whole concentration range for the quadratic isotherm, the amount of 3-phenylpropanol adsorbed at equilibrium is significantly higher than that predicted by the “best” isotherm.

Finally, the data were fitted to the Fowler isotherm (eqns. 7 and 8). For single-component isotherms, the agreement is excellent, as good as with the Langmuir isotherm (*cf.*, Figs. 2 and 8). In the case of competitive isotherms, however, the coefficient  $b$  must be the same for both components. Therefore, if we want to use the single-component Fowler isotherm parameters in a competitive Fowler isotherm, we must introduce this condition ( $b_1 = b_2$ ) in the fitting calculation of the single-component data. We then obtain different numerical values for the coefficients, but the fit remains very good. Only these latter isotherms are shown in Fig. 8, for the sake of clarity. The two sets of isotherms would be almost impossible to distinguish. In Fig. 8, and in subsequent figures dealing with the competitive equilibrium data, we have plotted the concentration in the mobile phase *versus* that in the stationary phase at equilibrium, following the form of eqns. 7 and 8, and to illustrate the practical drawback of the Fowler isotherm, *i.e.*, the impossibility of inverting its equation in closed form.

In Fig. 9a and b we show the competitive isotherms obtained by introducing in eqns. 7 and 8 the best values of the “single-component” Fowler isotherm coefficients just obtained. The results are satisfactory, as shown by the error reported in Table II. The fit achieved is as good as with the quadratic seven floating parameter or with the

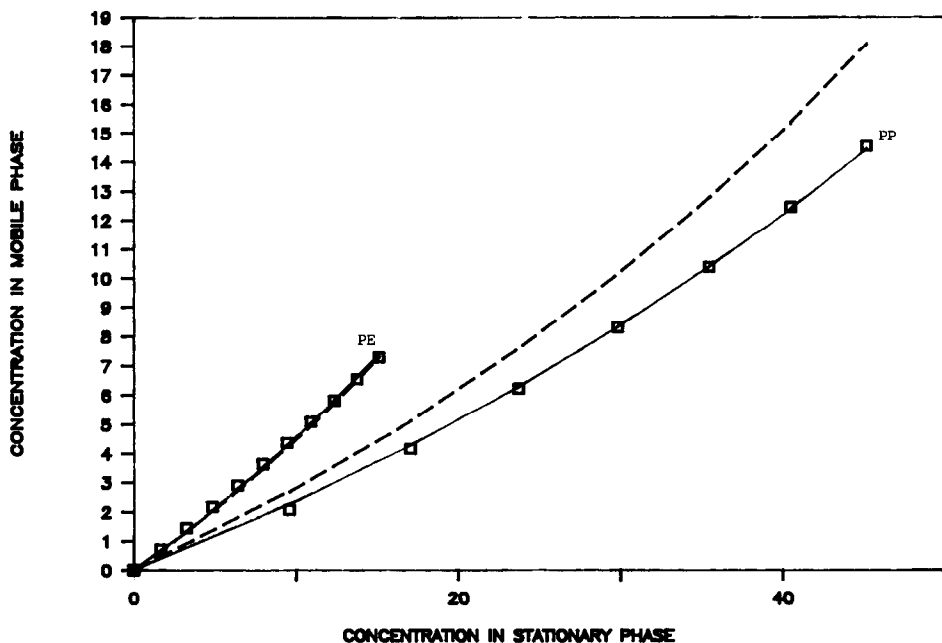


Fig. 8. Comparison of single-component data with five-parameter best-fit single-component Fowler model (solid lines) and best-fit competitive Fowler model (dashed lines). All concentrations in mg/ml. Experimental conditions: see text and Fig. 2. Same experimental data as in Fig. 2.

competitive Langmuir isotherms for 2-phenylethanol. For 3-phenylpropanol, the fit is nearly as good as for 2-phenylethanol, a considerable improvement over the results provided by the other isotherms using single-component isotherm coefficients (*cf.*, Figs. 3b, 5b and 9b).

Last, we show in Fig. 10a and b the competitive isotherms obtained by fitting the experimental data to the competitive Fowler isotherm. The agreement is excellent for both components, except for the high concentration points in the 1:1 mixture data. The single-component isotherm predicted by the competitive Fowler isotherm now obtained (*i.e.*, by making  $C_1$  or  $C_2$  equal to zero in eqn. 7 or 8, respectively, with the numerical coefficients in the last line of Table I) agrees well with experimental data for 2-phenylethanol (Fig. 8, dashed line). For 3-phenylpropanol, substantial disagreement is again observed. The amount adsorbed at equilibrium predicted by this isotherm is about 15% less than measured (Fig. 8).

## CONCLUSIONS

The problem of finding a good model to predict the competitive adsorption behavior of the components of a mixture based on the use of single-component data is a major one in multi-component non-linear chromatography. It is important because the individual band profiles in chromatography are very sensitive to small deviations of the isotherms from linear behavior [2], so we need a very good model. The problem is

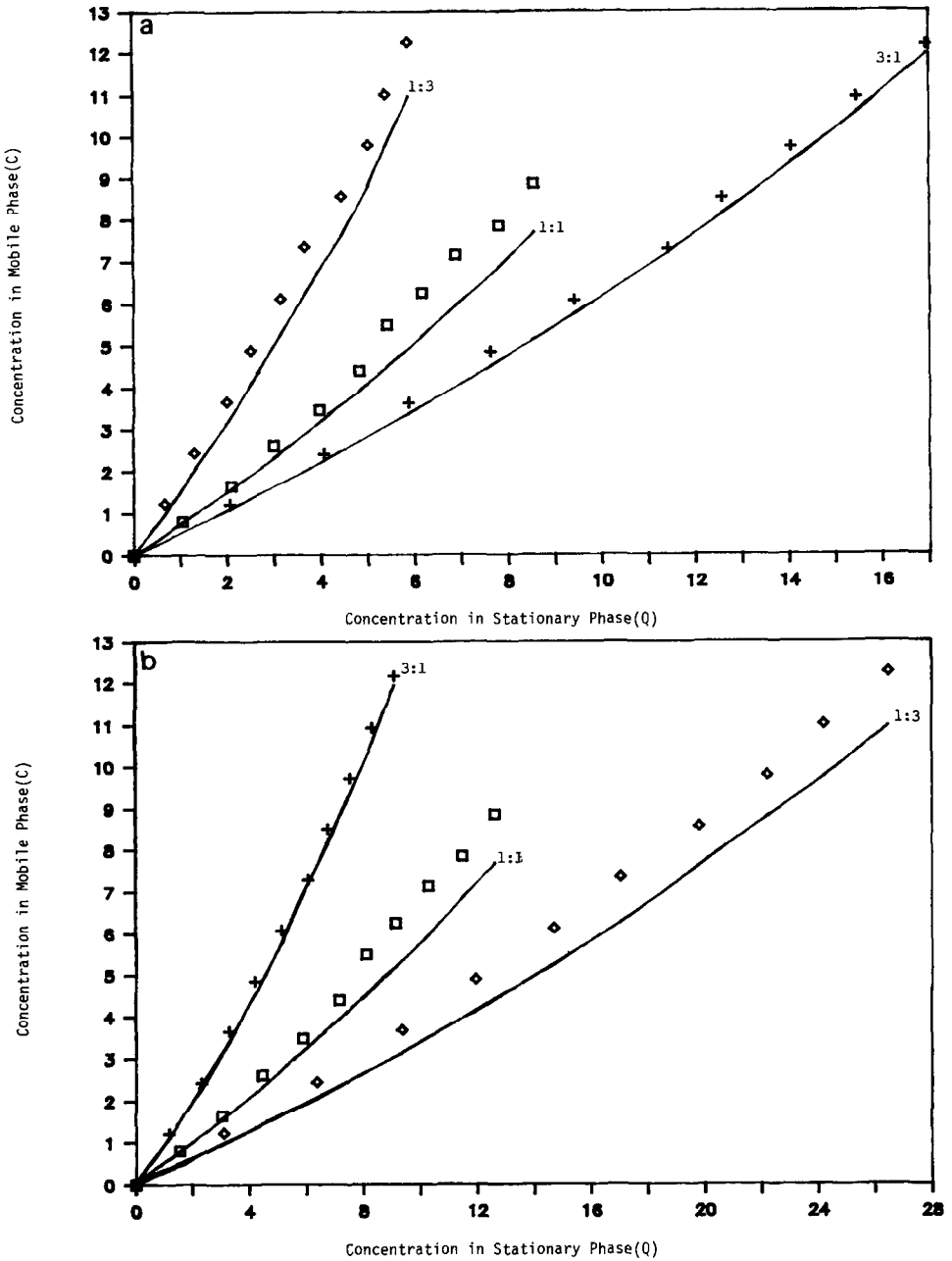


Fig. 9. Comparison of the competitive isotherm experimental data and the prediction of the competitive Fowler isotherm with the single-component parameters (five parameters). All concentrations in mg/ml. Experimental conditions: see text and Fig. 2. Same experimental data as in Fig. 3. (a) 2-phenylethanol; (b) 3-phenylpropanol.



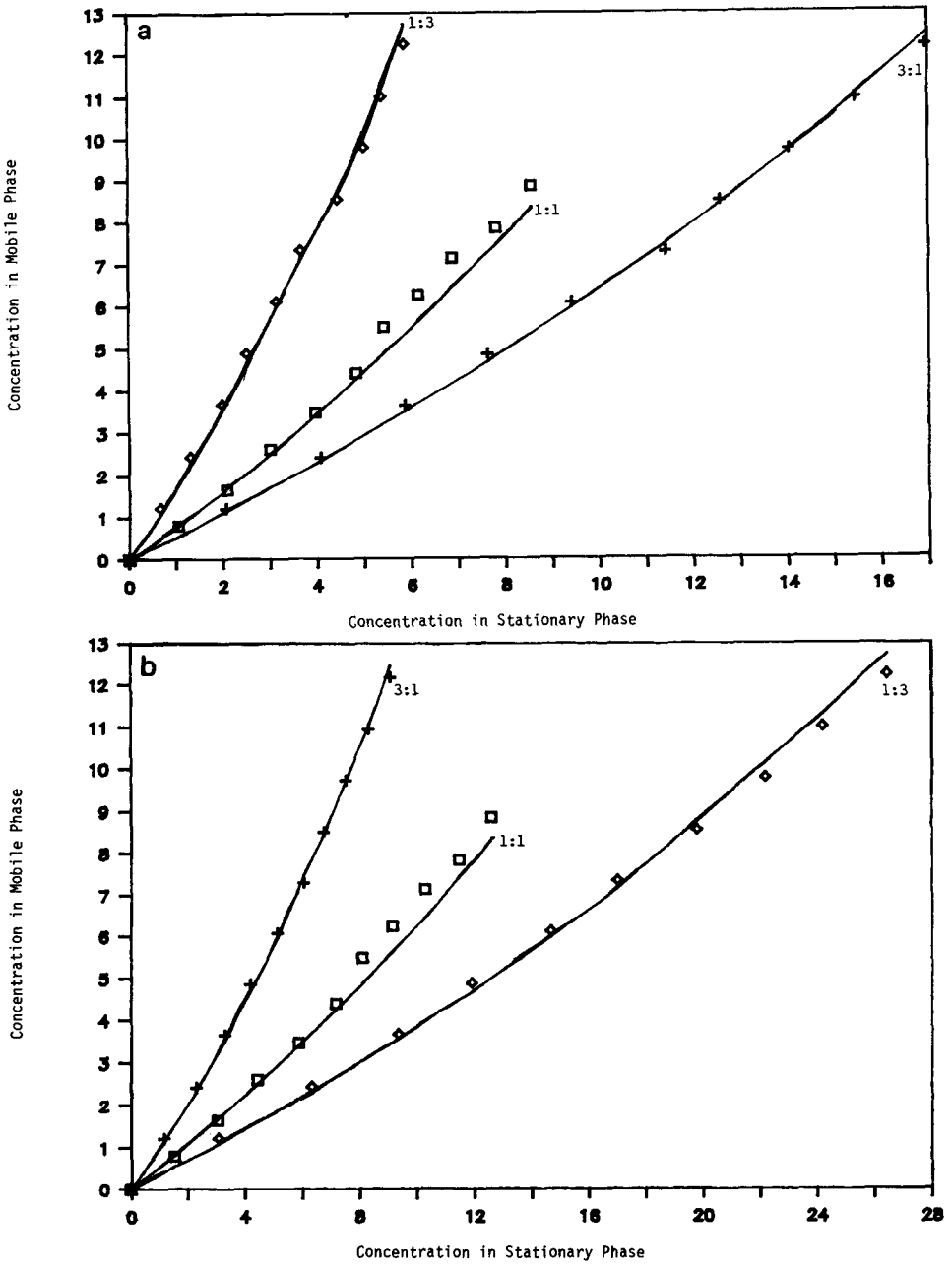


Fig. 10. Comparison of the competitive isotherm experimental data and the prediction of the competitive Fowler isotherm with the best-fit parameters. All concentrations in mg/ml. Experimental conditions: see text and Fig. 2. Same experimental data as in Fig. 3. (a) 2-phenylethanol; (b) 3-phenylpropanol.

important also from the practical point of view, because it is much easier and faster to collect single-component data than competitive adsorption data.

The solution of this problem in a particular case was the main aim of this work and it remains unsolved. None of the isotherms available gives results which are completely satisfactory. The second aim, in case the first could not be achieved, as has happened, was to find an isotherm model which could be fitted to a whole set of experimental data and account for them empirically.

The results presented here and our conclusions are restricted to one specific case. They can reasonably be expected to apply to many pairs of monofunctional homologues in reversed-phase liquid chromatography, but not far beyond. This is but a small fraction of the separation problems encountered in preparative chromatography.

The IAS model, although thermodynamically more sound than the Langmuir competitive isotherm, does not give significantly better results than the empirical Langmuir model in this case, essentially because the difference in column saturation capacities is small and the range of coverage (*i.e.*, concentrations reported to the saturation capacity) investigated remains low. In spite of its soundness and increased complexity, the quadratic isotherm did not give much improved results.

Our experiments showed that the apparent  $a$  parameter of the isotherms (*i.e.*, the slope of the competitive isotherm at the origin) decreases in the presence of an increasing amount of the other component. As it is more significant for 3-phenylpropanol than for 2-phenylethanol, it was more difficult to obtain a good fit for the former. This explains why the quadratic isotherm with seven floating parameters gives much better results than that with three floating parameters. In the latter instance, the only way to adjust the slopes of the competitive isotherms would be by choosing a negative value of  $a_{1,2}$ , but if the full correction to the slope were made, the fit would degrade rapidly with increasing concentrations. The addition of three new parameters to the model does not improve the number of degrees of freedom much. In the former instance, the selection of a value of  $a_2$  lower than that given by the single-component Langmuir isotherm permits a much better overall fit of the data.

Although the quadratic isotherm with seven floating parameters gives a good fit of the experimental data, there is significant doubt regarding the theoretical meaning of this result. As the pure component data are well accounted for by a Langmuir isotherm, adsorbate-adsorbate interactions are low between the molecules of the pure components. As the two components are homologues, there is no reason to think that adsorbate-adsorbate interactions between a molecule of 2-phenylethanol and a molecule of 3-phenylpropanol are any stronger than these interactions between two molecules of either 2-phenylethanol or 3-phenylpropanol. This would mean that the origin of the deviation from competitive Langmuir behavior lies in the non-ideal behavior of the mobile phase solution rather than in adsorbate-adsorbate interactions.

Of all the models investigated here, only the competitive Fowler isotherm accounts accurately enough for this effect. With optimized values of the five parameters, it accounts very well for the whole set of experimental data. This is especially noteworthy in the case of 3-phenylpropanol (Table II). Model error is observed, however, at high concentrations of 3-phenylpropanol and a systematic error of about 15% in the single-component isotherm of this compound is observed. The five

coefficients of the competitive Fowler isotherm are much easier to determine in practice than the seven parameters of the quadratic isotherm. The adjustment of the parameter  $b$  is the most critical, while changes in  $\chi_1$  and  $\chi_2$  have much less importance.

The excellent results obtained with the Fowler isotherm are only mildly satisfying. Eqns. 7 and 8 cannot be inverted and solved for  $q_1$  and  $q_2$ . The programs calculating band profiles in non-linear chromatography, however, need the local values of these stationary phase concentrations [2,29]. Their calculation as a function of  $C_1$  and  $C_2$  by numerical inversion of the two isotherm equations in each loop of the program, or even their search in a precalculated table, would increase markedly the CPU time required.

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