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Prediction of single and binary profiles in overloaded elution chromatography using various semi-ideal models

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ABSTRACT

Experimental band profiles of 2-phenylethanol and 3-phenylpropanol were recorded for pure components in different amounts and for binary mixtures at different compositions in reversed-phase chromatography. The injection function was also measured. These experimental profiles are compared with those calculated using different finite difference methods (*i.e.*, the Craig and Rouchon *et al.* models). The results show that it is important to take into account the true injection profile. The different calculation procedures in most instances give profiles which are in close agreement with the experimental data. The Craig model gives profiles which are generally sharper than those given by the Rouchon *et al.* model. Differences between the experimental and calculated profiles are ascribed to mathematical properties of the method implemented.

INTRODUCTION

In several previous instances, we have shown that single- and multi-component band profiles can be predicted accurately in isocratic elution chromatography, provided that the adsorption equilibrium isotherm, the column efficiency, the mobile phase flow velocity and the column dead volume are known accurately [1–4]. While it is relatively easy to account for single-component adsorption equilibrium data and the Langmuir isotherm is usually satisfactory, accurate representation of multi-component adsorption data is much more difficult. When severe overloading occurs at low concentration and when the column saturation capacities are equal, such as in chiral systems, the competitive Langmuir isotherm gives excellent results [3]. However, when the column saturation capacities differ the LeVan–Vermeulen isotherm [5] derived using the ideal adsorbed solution theory of Myers and Prausnitz [6] can give good results over a limited concentration range [7]. In the general case, however, and

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especially when the mobile phase concentration range studied exceeds 100 mM, it is difficult to achieve good representation of the competitive isotherm, unless empirical equations are used [8].

Band profiles can be calculated by solving the system of partial differential equations which express the conservation of the mass for each component. Usually it is assumed that the solutes in the mobile phase are at or near equilibrium with the solutes in the stationary phase at each point and at any time. Therefore, the compositions in the stationary and mobile phases are given by the equilibrium isotherm. As a closed-form solution of the system of partial differential equations cannot be derived, numerical solutions are calculated. Either finiti difference [9–12] or finite element [13] calculation procedures can be used. The latter are much faster than the former in instances where the problem has several space dimensions (*e.g.*, in aeronautics). This is not the case in chromatography, as we can assume the column to be one-dimensional [9].

The finite difference algorithms have a simple physical representation which makes them easy to understand [12]. The column is divided into a number of cells, in the space domain [9]. Time is also discretized. The values of the concentrations at all the points of this (t,z) grid are calculated successively, starting from the initial values (at time $t = 0$) and the values derived from the boundary condition. The boundary conditions give the values of concentrations imposed at the column inlet during the injection and throughout the course of the experiment. Axial dispersion which accounts for axial diffusion and the finite rate of the mass transfer in the column is introduced in this model as a consequence of the discretization of the time and space dimensions [9,12]. There is a finite number of segments considered in the grid during propagation of the concentration signal and this leads to averaging the concentration across the segments. The consequence of this is numerical or apparent dispersion of the solute band in the column.

The aim of this paper is to compare several semi-ideal models which can be used to predict individual band profiles in overloaded elution chromatography. For binary mixtures, the profiles calculated with the Craig model [14] and the Rouchon *et al.* model [15] are compared with experimental results. The Craig model is a physical model which has been used widely to calculate band profiles in overloaded elution [14,16,17]. An analogous procedure that gives faster computation times has also proven utility in predicting band profiles [2,9].

THEORY

Mass balance equation

The individual band profiles are obtained as the solution of the mass balance equation for each component i in a chromatographic column [9,11]:

$$F \cdot \frac{\partial q_i}{\partial t} + \frac{\partial C_i}{\partial t} + u_0 \cdot \frac{\partial C_i}{\partial z} = D_a \cdot \frac{\partial^2 C_i}{\partial z^2} \tag{1}$$

where q_i and C_i are the stationary and the mobile phase concentrations of each component at equilibrium, z and t are the column length and time, respectively, F is the phase ratio, u_0 the linear mobile phase velocity and D_a the apparent diffusion

coefficient. The apparent diffusion coefficient is related to the column height equivalent to a theoretical plate (HETP, H) under linear conditions by

$$D_a = \frac{HL}{2t_0} \tag{2}$$

where L is the column length and t_0 is the dead time.

Eqn. 1 represents the semi-ideal model of chromatography. It assumes the mass transfer kinetics in the column are fast and deviation from equilibrium is small [11]. The equilibrium concentrations of each component i in the two phases are related according to the functional form of the isotherm:

$$q_i = f(C_i) \tag{3}$$

In elution chromatography, the initial conditions are an empty column [$C_i(z,0) = 0$] and the boundary condition usually corresponds to the injection of a rectangular pulse of concentration C_i^0 and width t_p.

There is no closed-form solution for this problem when the number of components is two or greater. A numerical solution has to be calculated and several approaches are possible [11]. The simplest approach considers the migration of the chromatographic bands along the column as the propagation of a signal through a grid [12]. The numerical solution of the semi-ideal model consist of solving eqn. 1 with $D_a = 0$. When $D_a = 0$, the solution to eqn. 1 is called the ideal model. Two procedures are worthy of special consideration [12]. They are the Rouchon *et al.* [15] and the Craig model. In the Rouchon *et al.* model, the propagation requires that part of the cell content is frozen in time, which has no physical meaning. However, this procedure leads to fast computations. The partial differential equation in eqn. 1 is replaced by the following finite difference equantion:

$$u_0 \cdot \frac{C_{z,t} - C_{z-1,t}}{\Delta z} + \frac{C_{z-1,t} - C_{z-1,t-1}}{\Delta t} + F \cdot \frac{q_{z-1,t} - q_{z-1,t-1}}{\Delta t} = 0 \tag{4}$$

In the Craig model, where the propagation scheme resembles closely the separation process and implements the Craig machine, eqn. 1 is replaced by another finite difference equation:

$$u_0 \cdot \frac{C_{z,t-1} - C_{z-1,t-1}}{\Delta z} + \frac{C_{z,t} - C_{z,t-1}}{\Delta t} + F \cdot \frac{q_{z,t} - q_{z,t-1}}{\Delta t} = 0 \tag{5}$$

Numerical errors are made and they accumulate during the integration of the mass balance equation, because the increments Δz and Δt are finite. It can be shown that the overall contribution of these errors to the solution obtained is as a first approximation equal to the addition of a diffusion term of the mass balance equation. The coefficient D_a of this numerical diffusion term is related to the characteristics of the calculation by the equation for the Rouchon *et al.* [15] method:

$$D_a = \frac{\Delta z u_0}{2}(a - 1) \tag{6}$$

and for the Craig method:

$$D_a = \frac{\Delta z u_0}{2}(1 - a) \tag{7}$$

where a is the Courant number:

$$a = \frac{u_0 \Delta t}{(1 + k')\Delta z} \tag{8}$$

The theory of partial differential equations shows that in order to obtain a stable numerical solution, the Courant number must be larger than 1 in the Rouchon *et al.* [15] model and smaller than 1 in the Craig model. With $a = 1$ for the single-component system, the solution to the ideal model is obtained. By comparing eqns. 2 and 6–7 a relationship between the values of the HETP, the space and the time increment can be derived. For the Rouchon *et al.* [15] model this relationship is

$$H = -\Delta z + \frac{u_0}{1 + k'}\Delta t \tag{9}$$

and for the Craig model

$$H = \frac{k' \Delta z}{1 + k'} \tag{10}$$

In the Craig model, the linear velocity is related directly to the space and time increment:

$$u_0 = \frac{\Delta z}{\Delta t} \tag{11}$$

Proper selection of the space and time increments permits adjustment of the apparent column HETP to the value required to model exactly the experimental system. This results is rigorous for single-component bands in linear chromatography. For binary mixtures in non-linear chromatography, the consequence of eqns. 8 and 9 is that the HETP can be adjusted exactly to the amount of band spreading for one component. However, the efficiency (the apparent dispersion) of the two bands cannot be controlled independently. Moreover, eqns 8 and 9 do not give a realistic relationship between the column HETP and the retention factor. This effect is negligible for the prediction of single-component bands and small for many two-component problems, especially when the relative retention is small.

Another calculation method, the control diffusion procedure, has been presented [12]. In this method, small values of the space and time increments are selected, such that the extent of the numerical diffusion does not exceed the required amount of apparent diffusion for any of the component. Then, a diffusion term is added to the

finite difference equations (eqns. 4 and 5) representing the amount of diffusion missing for each component. This is calculated according to Fick's second law:

$$\frac{\partial C}{\partial t} = D_p \cdot \frac{\partial^2 C}{\partial z^2} \tag{12}$$

The apparent diffusion coefficient D_p is chosen so that $D_p = D_a - D_n$, where D_a is the required value of the apparent dispersion coefficient (eqn. 2) and D_n is the numerical diffusion resulting from the choice of the space and time increments and the local k' [12].

Isotherm model

The single-component isotherm data were fitted to the Langmuir equation:

$$q = \frac{aC}{1 + bC} \tag{13}$$

The values of the parameters are summarized in Table I.

The isotherm for the binary mixture was measured using the method of the hodograph transform [4] as applied to the competitive Langmuir isotherm model:

$$q_i = \frac{a_i C_i}{1 + \sum b_i C_i} \tag{14}$$

For practical purposes it is convenient to define the column saturation capacity

$$CSC = \frac{\sum_{i=1}^{n} \frac{a_i}{b_i} \cdot V_{sp}}{n} \tag{15}$$

as the maximum amount adsorbed as a monolayer on the surface of the stationary phase. Then the amount of sample injected can be made independent of the size of the column by using the loading factor:

$$L_{f,i} = \frac{m_i}{CSC} \tag{16}$$

where m_i is the amount of sample component i injected.

TABLE I

SUMMARY OF SINGLE-COMPONENT ISOTHERM DATA FOR 2-PHENYLETHANOL AND 3-PHENYLPROPANOL

Parameter	Column 1		Column 2	
	Phenylethanol	Phenylpropanol	Phenylethanol	Phenylpropanol
HETP (cm)	0.0167		0.009	
t_0 (s)	180		176	
k'	0.72	1.31	0.71	1.42
a (ml/ml)	1.92	3.55	1.94	3.41
b (ml/mg)	0.0148	0.0255	0.0218	0.0592
CSC^a	140	150	109	70

[a] Defined by eqn. 15.

EXPERIMENTAL

The isotherm data and the individual band profiles for large-sized samples were determined using a modular chromatograph expecially assembled for this purpose.

Apparatus

The modular liquid chromatograph was assembled from two Waters Assoc. (Milford, MA, USA) Model 510 pumps, a Valco (Houston, TX, USA) six-port electrically actuated valve fitted with a 100-μl sample loop and a Kratos Spectroflow (ABI, Ramsey, NJ, USA) variable-wavelength UV detector set at 272 nm for the measurement of the band profiles. The pumps were controlled and the detector signal was monitored via a Waters System Interface Module (SIM), using the Waters Maxima 860 Dynamic Solutions (Ventura, CA, USA) software installed on an NEC APCIV Powermate 2 microcomputer. The electrical outputs of the valve and the detector were connected to the SIM box for automatic data acquisition.

Products

Two 25 × 0.46 cm I.D. columns were packed in-house, at 9000 p.s.i., using 10-μm Vydac (Hesperia, CA, USA) octadecylsilica as stationary phase. The characteristics of these two columns are summarized in Table I. The flow-rate in all the experiments was 1.0 ml/min.

The solutes were 2-phenylethanol and 3-phenylpropanol purchased from Fluka (Ronkonkoma, NY, USA) and 2,6-dimethylphenol, purchased from Aldrich (Milwaukee, WI). The mobile phase was a mixture of methanol and water, purchased from Burdick and Jackson (Muskegon, MI, USA). All chemicals were used as received.

Procedures

The single-component elution profiles were derived from the detector trace and from a calibration graph determined by pumping directly into the detector a known concentration of sample. The detector response was strongly non-linear in the region of interest [18].

For binary mixtures, the individual component profiles were obtained by collecting fractions every 3 s with subsequent reanalysis using a Model 232/401 Automatic Sample Processor from Gilson (Middletown, WI, USA) [19]. With a linear calibration graph quantitative analysis of each sample was done using the Maxima software.

The injection profile was determined by placing the sample valve between the column and the detector, which permits a mobile phase stream with a stable flow. The concentrated samples of 2-phenylethanol were injected and their profiles recorded. Fig. 1 shows a typical results, with the corresponding ideal, rectangular profile overlaid. It can be seen that the measured profile gives a sharp front and diffuse rear boundary owing to dispersion in the tubes. Moreover, the maximum concentration injected is lower than that of the prepared sample solution. The measured injection profile was fitted to one half of the Gaussian function and this function form was used in the inlet boundary condition of the finite difference algorithms.

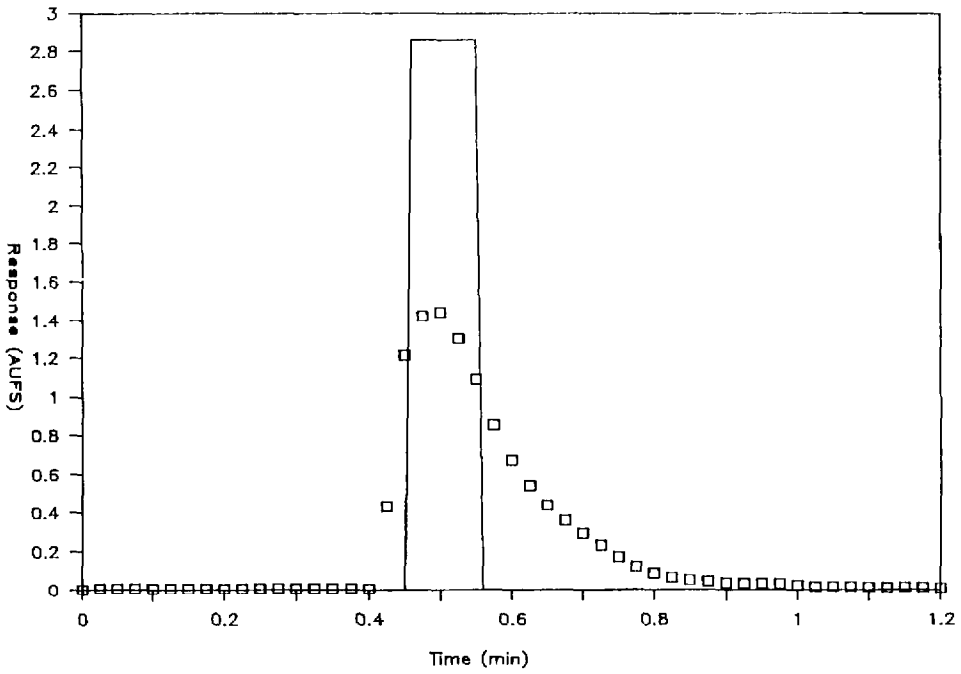

Fig. 1. Injection profile for a large-volume sample. Symbols, experimental profile; solid line, rectangular profile.

RESULTS AND DISCUSSION

Adsorption equilibrium isotherms were determined on the two columns using the classical techniques of frontal analysis for single components [1, 20, 21] and by the method of the Hodograph transform for binary mixtures [22]. The single-component parameters are given in Table I and the isotherms of phenylethanol and phenylpropanol are shown in Fig. 2. The differences between the isotherms measured on the two columns are almost negligible at low concentrations but significant at high concentrations. The values of the slope of the isotherm at the concentration origin (*i.e.*, the coefficient a) differ by less than 1% for 2-phenylethanol and by 4% for 3-phenylpropanol. Therefore, the isotherms corresponding to each component on both columns are tangential. In contrast, the isotherm curvature (*i.e.*, the coefficients b) differs by more than 50% between the two columns. This result suggests that columns for preparative liquid chromatography may be even more difficult to reproduce than analytical columns.

The values of the average hodograph parameters [4] employed in the prediction of the binary mixtures using the Craig, Rouchon *et al.* [15] and control diffusion models are $a_1 = 1.924$ ml/ml, $a_2 = 3.554$ ml/ml, $b_1 = 3.044$ ml/mmol and, $b_2 = 3.69$ ml/mmol.

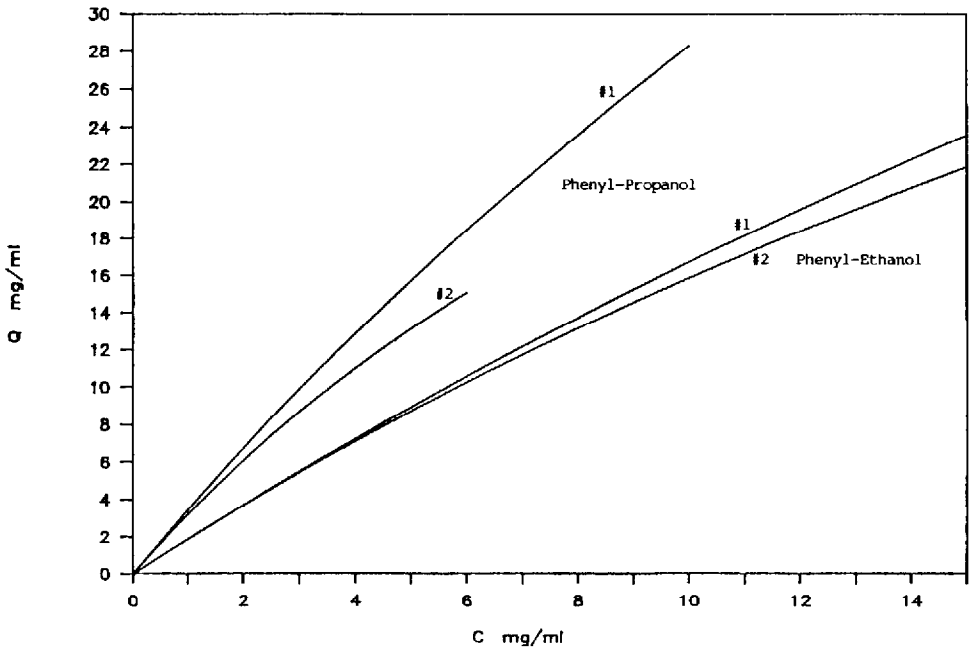

Fig. 2. Reproducibility of experimental isotherm data for phenylethanol and 3-phenylpropanol on two columns packed with C_{18}-bonded silica.

Single-component profiles

Single-component elution band profiles at increasing sample size were measured on both columns for 2-phenylethanol, 3-phenylpropanol and 2,6-dimethylphenol. Some of the profiles recorded on column 2 are shown in Figs. 3 (2-phenylethanol), 4 (3-phenylpropanol) and 5 (2,6-dimethylphenol). The single-component profiles for column 1 have been reported previously [2,23] and in all instances the agreement between the calculated and experimental profiles is good. The hump on the back of the 3-phenylpropanol peaks (Fig. 4) is due to a calibration problem. The detector response is very non-linear in the concentration range sampled and the polynomial used to fit the response is not a monotonic function in its first derivative. The serious tail at the end of the 2,6-dimethylphenol band is probably due to the interaction between the acidic hydroxyl group of the phenol molecule and some unreacted silanol groups at the surface of the silica. The adsorption data and the band profiles might be better accounted for by a biLangmuir isotherm, as has been reported previously [3,24,25].

Two-component band profiles

The individual band profiles of 2-phenylethanol and 3-phenylpropanol were determined experimentally for three different binary mixtures having relative compositions 1:1, 1:3 and 3:1. The volume of sample injected and the amounts of each component are reported in Table II. The total sample size is *ca.* 28% of the average of the column saturation capacities for the two compounds. This corresponds to a high degree of column overload.

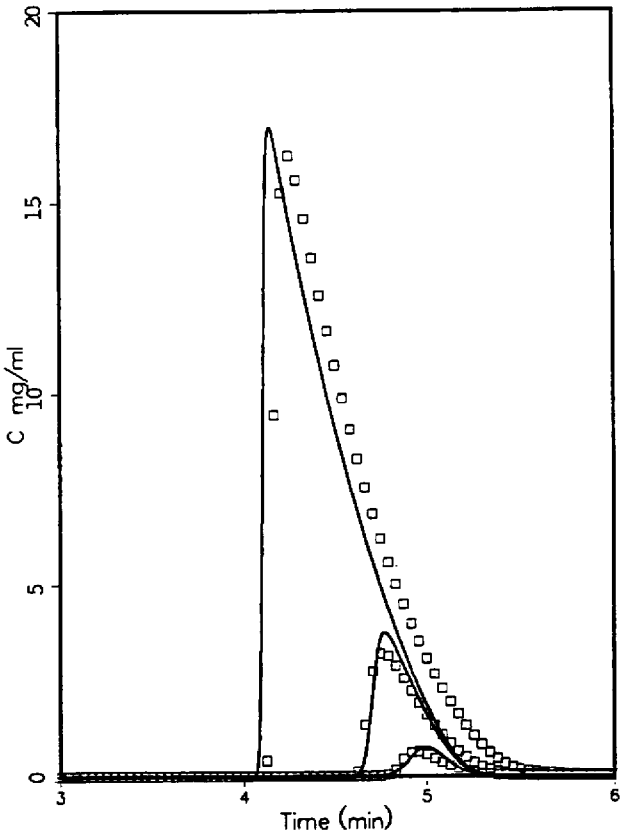

Fig. 3. Overloaded elution band profiles of samples of 2-phenylethanol on C_{18}-bonded silica. Symbols, experimental; solid lines, theoretical. 0.2 mg = 0.2% of CSC; 1.2 mg = 1% of CSC; 8.6 mg = 7.9% of CSC.

In the following sections, a comparison is made between various theoretical models and experimental data for binary mixtures on column 1.

Effect of the injection function using the semi-ideal model. Fig. 6 compares the theoretical profiles calculated assuming a rectangular profile (dashed lines) and the measured injection profile (solid lines) according to the Rouchon *et al.* [15] implementation of the semi-ideal model for 1:1, 1:3 and 3:1 mixtures. In many respects, the differences in the theoretical profiles predicted under these conditions are relatively minor, but they are not completely insignificant. In general, the profiles obtained with the experimentally correct injection profile give rise to shorter, broader peaks. The diffuse injection profile gives rise to slightly more diffuse exit profiles. Therefore, there is more interference and better agreement with the experimental data.

This comparison illustrates the influence that the injection profile may have on the resolution between bands in preparative chromatography. It is notable, but not extremely important, especially in view of displacement effects. Reducing the tailing will permit gains in the recovery yield and the production rate.

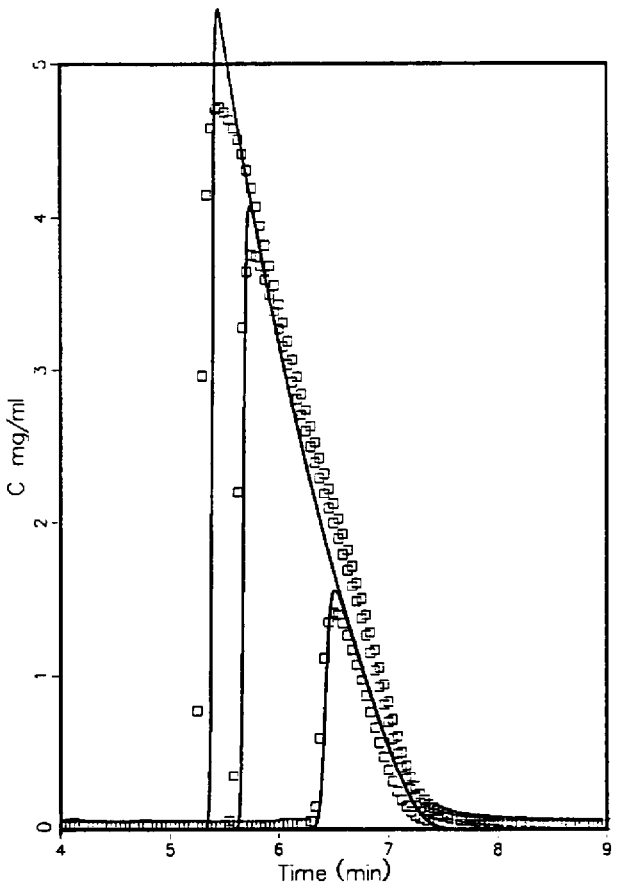

Fig. 4. Overloaded elution band profiles of samples of 3-phenylpropanol on C_{18}-bonded silica. Symbols, experimental; solid lines, theoretical. 0.9 mg = 1.3% of CSC; 3.7 mg = 5.3% of CSC; 5.5 mg = 7.8% of CSC.

Comparison of experimental data with the Craig and Rouchon et al. [15] models. The Craig (dashed line) and Rouchon *et al.* (solid lines) algorithms were used to calculate the band profiles. A comparison with experimental data is shown in Fig. 7. The measured injection profile was employed as the inlet boundary condition for this series of comparisons. Therefore, the solid line in Fig. 6 is the same as that line in Fig. 7.

In general, the Craig model gives sharper taller peaks than the Rouchon *et al.* model. This is a result of the differences in the calculation procedure for these two models. In both models, the HETP or the amount of band spreading is specified for one component for a known value of k'. As discussed under Theory, this approach leads to an artificial relationship between the amount of band spreading and k'. For the Rouchon *et al.* model, when k' is near zero there is more band spreading than at the specified reference k' value. For the Craig model, in the limit as k' goes to zero, the amount of band broadening goes to zero. Hence the amount of band spreading is less

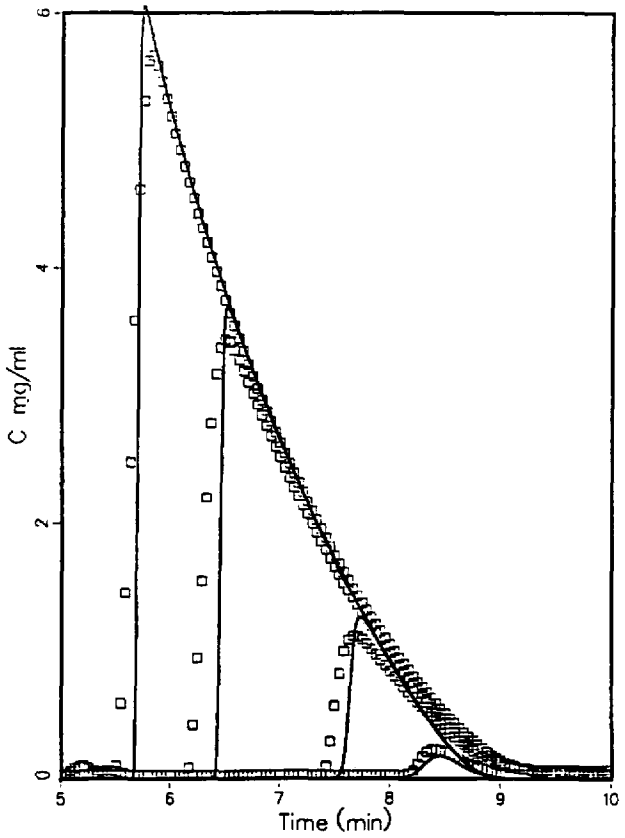

Fig. 5. Overloaded elution band profiles of samples of 2,6-dimethylphenol on C_{18}-bonded silica. Symbols, experimental, solid lines, theoretical. 0.08 mg = 0.1% of CSC; 0.8 mg = 1% of CSC; 3.9 mg = 4.9% of CSC; 7.8 mg = 9.7% of CSC.

than at the reference k' value. Because in these experiments the injection was made at high concentration, the velocity of the molecules associated with a given concentration is large so the local k' is near zero over a certain length of the column. Hence this leads to the Craig model giving sharper taller peaks than the Rouchon *et al.* model.

TABLE II

SUMMARY OF THE SAMPLE SIZES FOR THE BINARY DATA

Mixture	Total amount (mg)	2-Phenylethanol (mg)	3-Phenylpropanol (mg)	L_f [a] (%)	
				2-Phenylethanol	3-Phenylpropanol
1:1	20	10	10	7	7
1:3	28	7	21	5	15
3:1	40	30	10	21	7

[a] Defined by eqn. 16.

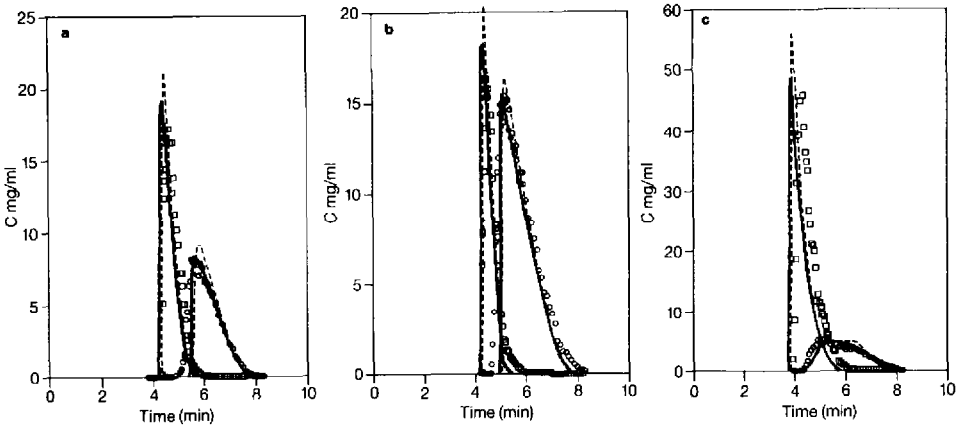

Fig. 6. Comparison of experimental data and predicted profiles using the Rouchon *et al.* [15] model with a rectangular injection function and the measured injection profile. Solid line, Rouchon *et al.* [15] with measured injection profile; dashed line, rectangular injection function. (□) 2-phenylethanol; (○) 3-phenylpropanol experimental data. (a) 1:1 mixture; (b) 1:3 mixture; (c) 3:1 mixture.

Comparison of the Craig and control diffusion model. In contrast with the Craig model, the control diffusion model allows independent specification of the diffusion coefficients of each solute [12]. Hence a more accurate prediction is obtained. Fig. 8 compares the predictions obtained by the Craig model and the controlled diffusion model for 1:1 and 3:1 mixtures. The profile for the early eluting component is the same for both models, but for the second component there are slight deviations. In Fig. 8a (1:1 mixture), the retention time of the front is slightly less and the concentration at the peak maximum slightly lower. In Fig. 8b (3:1 mixture), the front of the second component is only slightly more diffuse. For the 1:3 mixture, the control diffusion model and the Craig model give identical results.

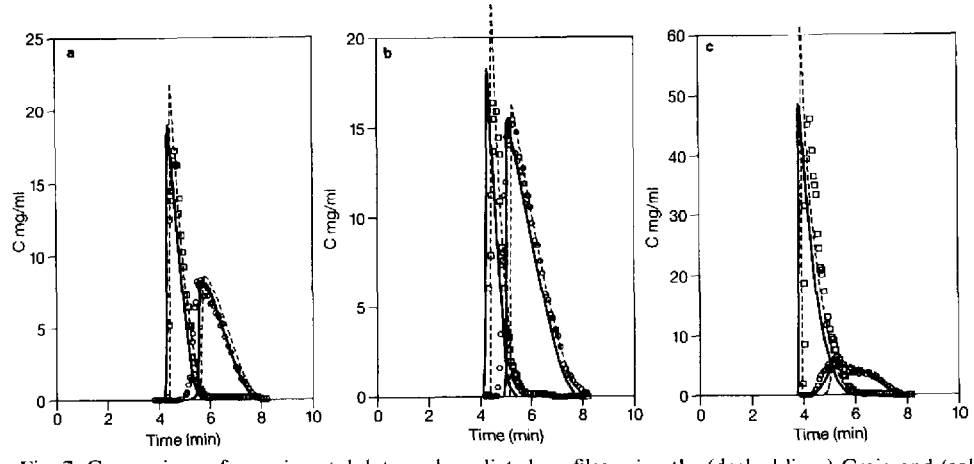

Fig. 7. Comparison of experimental data and predicted profiles using the (dashed lines) Craig and (solid lines) Rouchon *et al.* [15] semi-ideal models. (□) 2-Phenylethanol; (○) 3-phenylpropanol experimental data. (a) 1:1 mixture; (b) 1:3 mixture; (c) 3:1 mixture.

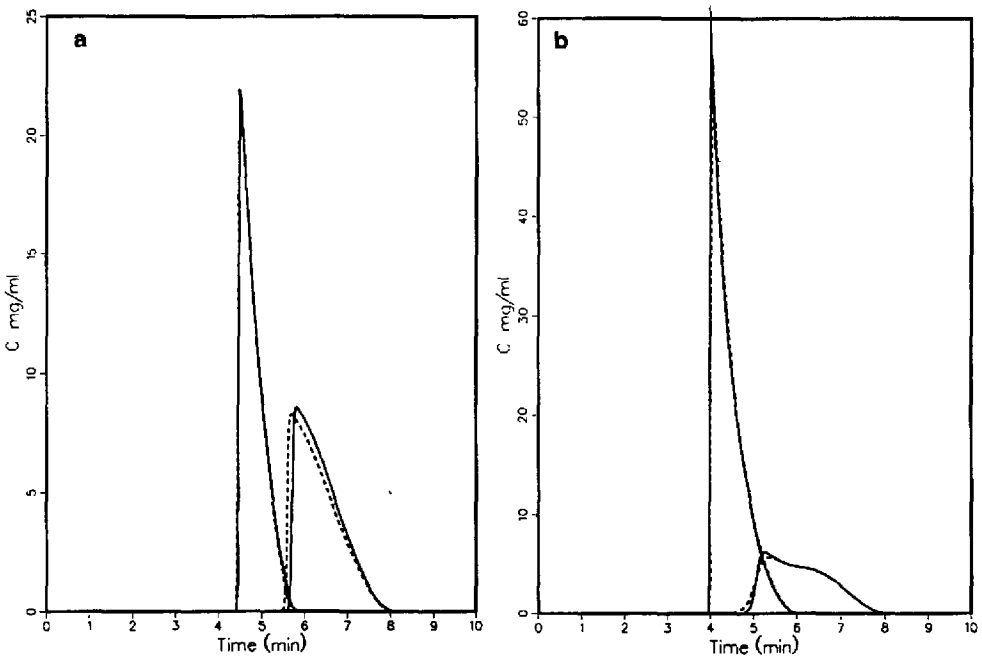

Fig. 8. Comparison of the (solid lines) Craig and (dashed lines) control diffusion models. (a) 1:1 Mixture; (b) 3:1 mixture.

CONCLUSIONS

Differences are observed between individual band profiles calculated using the Rouchon *et al.* [15], Craig and control diffusion procedures. These models correspond to slightly different ways of writing the finite difference equations. None of these calculation procedures gives profiles which are consistently in excellent agreement with all the experimental data, but all the models give good agreement with the experimental data. The present problem seems to be in finding an accurate model to predict competitive equilibrium isotherms from single-component data. Until more refined methods of determining competitive isotherms are developed and better models to fit the data are proposed, the differences between these theoretical profiles are not significant.

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