

## SIMULATION OF CHROMATOGRAPHIC PROFILES FOR MULTICOMPONENT MIXTURES OF AROMATIC COMPOUNDS

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**Abstract:** The aim of this work concerns the reconstruction of the elution profiles obtained in HPLC separation of aromatic compound mixtures. In particular, the proposed model represents the migration of tricomponent mixtures of alkylbenzenes (a class of compounds belonging to gasoil) in a chromatographic system. The obtained profiles are compared with experimental data and show the possibility to use the model as a tool for acquiring reliable and practical information on the peak identification in HPLC analysis.

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**Keywords:** gasoil, high performance liquid chromatography, mathematical modelling, elution profiles, competitive systems.

### 1. INTRODUCTION

The increasing demand for diesel fuel together with the tightening of environmental and technical specifications focused the attention of researchers on gasoil hydroprocessing. The main objectives of the recent studies deal with the production of new and more efficient catalysts, and the continuous optimization of the process operation. The latter goal can be achieved by using suitable mathematical models that should be detailed enough to allow a reliable prediction of the most critical specifications. Recently, a model based on a detailed experimental analysis carried out on a pilot plant was proposed to predict the hydrogenation of aromatic compounds (Melis *et al.*, 2004) and the hydrodesulfurization of the refractive compounds (Erby *et al.*, 2005) during the gas oil hydroprocessing. The implementation of the model required the characterization of the feed and the product of the reactor, in order to have the inlet and the output compound concentrations necessary for the model calibration. This is a quite demanding task, because of the overlapping peaks of compounds belonging to the same class. A solution was proposed in Sassu *et al.* (2003) through the development of a chromatographic based method (HPLC) to discriminate among aromatic subclasses. The proposed characterization method led to good results but it requires appropriate instruments and the

ability of an operator for the chromatogram deconvolution.

The lack of a simple and practical method to characterize the feed of a hydroprocessing unit can limit the use in the industry of reliable models for the prediction of the product characteristics for a given feedstock. On the other hand an automated procedure for the feedstock analysis can improve the routinely use of such models.

In this work a model is developed to evaluate the chromatographic profiles of multicomponent systems as a means to give useful insights in the peak identification of HPLC chromatograms obtained in the analysis of gasoil. The idea is to propose a model which is practical and easy to calibrate, hence the result will be a compromise between simplicity and reliability. In particular, the elution of alkylbenzenes, aromatic compounds belonging to the monoaromatic class (Melis *et al.*, 2004), is considered. The adsorption isotherms are identified by analyzing experimental data obtained by the elution of a single component, and then a relationship between the equilibrium constants and the molecular structure is defined in order to further reduce the model parameters. Finally, the differential equations governing the migration of the solutes for a tricomponent mixture are integrated and compared with experimental chromatograms.

## 2. EXPERIMENTAL STUDIES

HPLC analysis were conducted following the EN12916 method in a 25x0.4 cm stainless steel cartridge LiChroCART® packed with LiChrospher® 100 NH<sub>2</sub> (Merk, Germany), with a RI detector and a computerized data acquisition system. N-heptane was used as mobile phase and the injected sample volume was 10 µl.

The average particle size of the packing material was 5 µm. The total porosity  $\varepsilon_T$  was calculated by means of the following relationship (Guan and Guiochon, 1996):

$$\varepsilon_T = \varepsilon_{ext} + (1 - \varepsilon_{ext}) \cdot \varepsilon_p \quad (1a)$$

where  $\varepsilon_{ext}$  and  $\varepsilon_p$  are, respectively, the external and the internal porosity of the particle.  $\varepsilon_p$  for total porous materials, like that used in this work, is between 0.7 – 0.8 (as specified by the column producer: Merck, Germany), while  $\varepsilon_{ext}$  can be calculated for packed tubular systems by means of the relationship reported in Zou and Yu (1995). The obtained value for  $\varepsilon_{ext}$  is in the range 0.39 – 0.40. This leads to a total porosity of about 0.82 – 0.88.

The value of the total porosity was also experimentally calculated by considering the retention time of an inert (not polar compound). In particular, the total hold-up volume,  $V_0$ , was calculated by injecting a solution of cyclohexane in the HPLC apparatus, while the extra-column volume  $V_{ext}$ , was evaluated with another injection of the inert compound when the column had been bypassed with a connecting pipe of a known small volume. If  $V_{C0}$  is used to indicate the volume of the void column, the total porosity can be calculated with the following equation:

$$\varepsilon_T = \frac{V_0 - V_{ext}}{V_{C0}} \quad (1b)$$

Substituting the obtained values ( $V_0 = 3.0$  ml,  $V_{ext} = 0.233$  ml,  $V_{C0} = 3.142$  ml) the experimental total porosity is equal to 0.88, a value that is within the range predicted by Equation (1a).

The column holdup time is 3.75 min and the efficiency at a flow rate of 0.8 cm<sup>3</sup>/min is about  $N=12500$  theoretical plates (Chung and Weng, 1968).

The determination of the equilibrium isotherm was conducted by injecting solutions, at seven different concentrations, of the following alkyl benzenes compounds: nonadecylbenzene, octadecylbenzene, tridecylbenzene, dodecylbenzene, decylbenzene, octylbenzene, cyclohexylbenzene, butylbenzene. The concentration of every inlet sample is reported in Table 1.

The RI absorbance at the detector was recorded every 0.432 s and all experiments were conducted at ambient temperature. The comparison between experimental and calculated band profiles requires detector calibration in order to convert the detector signal (mV) into solute concentration (g/l). Calibration was performed by injecting different

solutions of the investigated compounds at known concentration. In this way, the calibration curve (linear in the concentration range used) was defined.

Table 1 Concentration of the injected samples for the isotherm identification.

Sample	Concentration (g/l)
1	0.5
2	2.5
3	4.0
4	10.0
5	20.0
6	30.0
7	40.0

## 3. THEORY

### 3.1 Chromatographic system – HPLC

The mathematical modeling of the chromatographic separation process has been extensively described in literature (Guiochon, 2002). In this work, we referred to the equilibrium dispersive model, where the mass transfer kinetics between the solute and the stationary phase is neglected. The equation describing the migration of the  $i$ -th compound in a chromatographic system is:

$$\begin{aligned} \varepsilon_T \cdot \frac{\partial C_i}{\partial t} + (1 - \varepsilon_T) \cdot \frac{\partial q_i}{\partial t} + \varepsilon_T \cdot u \cdot \frac{\partial C_i}{\partial x} = \\ = \varepsilon_T \cdot D_L \frac{\partial^2 C_i}{\partial x^2} \end{aligned} \quad (2a)$$

$$q_i = f(C_i), j = 1, \dots, N_C \quad (2b)$$

where  $C_i$  indicates the concentration in the mobile phase of the  $i$ -th compound,  $q_i$  is the solute concentration in the stationary phase, at equilibrium,  $\varepsilon_T$  is the total porosity,  $u$  is the interstitial velocity,  $D_L$  is the apparent dispersion coefficient,  $x$  and  $t$  are the abscissa along the column and the time, respectively, and  $N_C$  is the number of components in the mixture. Equation (2a) is valid when the efficiency of the column is high (Guiochon, 2002). In this case it is assumed that all the effects due to the mass transfer kinetics are limited, and they are taken into account by a single coefficient of apparent dispersion,  $D_L$ . The latter takes into account several contributions as axial diffusion, tortuosity and constriction of the channel between bed particles, eddy diffusion, external film mass transfer resistance and intraparticle or pore diffusion.  $D_L$  is related to the column HETP ( $H$ ) by means of the following equation

$$D_L = \frac{L \cdot u}{2 \cdot N} = \frac{H \cdot u}{2} \quad (3)$$

where  $L$  is the column length.

The solution of Equation (2) requires the specification of the initial condition

$$C_i(0, x) = 0 \quad (4a)$$

and boundary conditions

$$C_i(t, x = 0) = \begin{cases} C_i^0 & \text{at } t \leq t_p \\ 0 & \text{at } t > t_p \end{cases} \quad (4b)$$

$$\left. \frac{\partial C_i}{\partial x} \right|_{x=L} = 0 \quad (4c)$$

Because the concentration of the solute in the solid is a function of  $C_i$  (2b), it follows that the elution profile of a multicomponent mixture is obtained by integrating the following system of partial differential equations:

$$\frac{\partial C_i}{\partial t} + F \sum_{j=1}^{N_c} \frac{\partial q_j}{\partial C_j} \frac{\partial C_j}{\partial t} + u \cdot \frac{\partial C_i}{\partial x} = D_L \frac{\partial^2 C_i}{\partial x^2} \quad (5)$$

$$i = 1, \dots, N_c$$

where  $F = \frac{(1 - \varepsilon_T)}{\varepsilon_T}$ .

### 3.2 Equilibrium model identification and parameter estimation

The most important aspect in chromatographic processes is the mechanism of adsorption, which determines the partitioning of components injected between the liquid and the solid phase. The phenomenon of adsorption depends on the affinity of a species for the stationary phase and it is related to the molecular structure of the considered compounds.

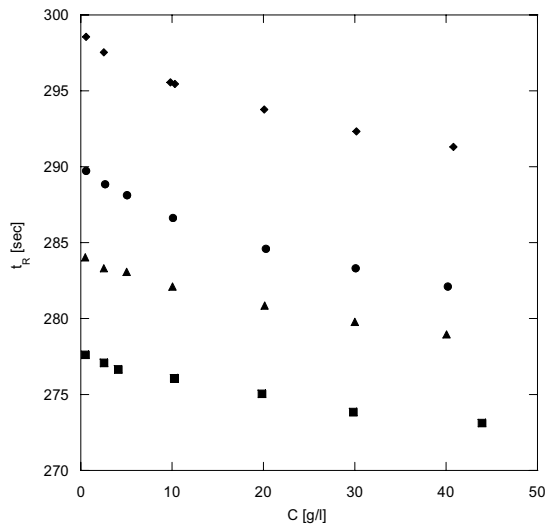


Fig. 1. Experimental retention time of some investigated compounds with respect to the injected concentration: butylbenzene (♦), decylbenzene (●), nonadecylbenzene (▲), tridecylbenzene (■).

The first step of the development of the chromatographic model is therefore the identification of the function  $q(C)$ , which describes the adsorption phenomenon inside the column. This task was

accomplished by simply considering the experimental data obtained in absence of competition, that is by analyzing the behavior of the experimental retention time with respect to the concentration, when a solution containing one compound is injected. Experimental data are shown in Figure 1 for some of the investigated compounds. In all the analysed cases, the curvature resembles the behavior of a Langmuir equilibrium model (Guiochon *at al.*, 1988), hence the following equation is assumed to describe the equilibrium between the two phases:

$$q_i = \frac{k_i q_0 C_i}{1 + k_i C_i} \quad (6)$$

This simple model is suitable for our case, because for practical purposes, the least number of parameter allowing a reliable representation of the chromatographic system is preferred.

Now that the equation governing the adsorption is specified, the next step is to estimate the equilibrium model parameters. There are several methods to accomplish this task, generally referred as static and dynamic experimental methods (Seidel-Morgenstern, 2004). In this case, because of the high efficiency of the used chromatographic column (cf. Section 2), the calibration of the equilibrium model was carried out by means of the peak-maxima method (Seidel-Morgenstern, 2004). In this method the ideal model of chromatography is used, that is equivalent to assume that the column efficiency is infinite. The equation used to estimate the equilibrium parameters is then the following:

$$\frac{\partial C_i}{\partial t} + F \cdot \frac{\partial q_i}{\partial t} + u \cdot \frac{\partial C_i}{\partial x} = 0 \quad (7)$$

Equation (7) is solved by using the initial and boundary conditions reported in Equations (4a) and (4b), respectively. In this case, because the injection pulse is rectangular, there are two discontinuities which propagate along the column and it is necessary to resort to the shock-wave theory to describe the phenomenon (Golshan-Shirazi and Guiochon, 1988). In particular, for the experimental conditions reported in Section 2, it was verified that the retention time is given by:

$$t_{Ri} = t_{ext} + t_p + t_0 + \left[ (F \cdot k_i \cdot q_0 \cdot t_0)^{0.5} - (t_p \cdot k_i \cdot C_i^0)^{0.5} \right]^2 \quad (8)$$

where  $t_0$  and  $t_{ext}$  are, respectively, the column and the extra-column hold up time. The optimization was then carried on by comparing the experimental retention time determined at different inlet concentrations with the value calculated with Equation (8). The following objective function was used for the parameter estimation

$$OF = \sum_{j=1}^{N_c} \sum_{i=1}^p (t_{R(i,j)}^{(calc)} - t_{R(i,j)}^{(exp)})^2 \quad (9)$$

where  $N_C$  and  $P$  are the number, respectively, of the components and the experimental points. It was assumed that  $q_0$  is the same for all the components. The isotherm parameters were changed to minimize the objective function, using a modified Levenberg-Marquardt algorithm.

## 4. RESULTS AND DISCUSSION

### 4.1 Adsorption isotherm model

The identification of the isotherm model by means of the analysis of the retention time of the alkyl compounds with respect to the concentration, led to the assumption that the equilibrium between mobile and stationary phase could be described by a Langmuir model. This equation was indeed able to reproduce quite accurately the experimental retention time for the elution of a single component. All the investigated compounds belong to the same class (alkylbenzenes), therefore it could be useful to find out a rule that relates the adsorption parameters to the structure of the molecule of the eluted species. At this regards, the adsorption constants  $k_i$  calculated for the components listed in Section 2 are reported in Figure 2 with respect to the number of carbon atoms that form the alkyl chain. It is evident that  $k_i$  parameter is a linear function of the length of the alkyl chain. This result suggests the possibility to reduce the number of parameters necessary to describe the chromatographic process for the considered class of compounds. The value of  $q_0$  is the same for all the components and is equal to 1.461.

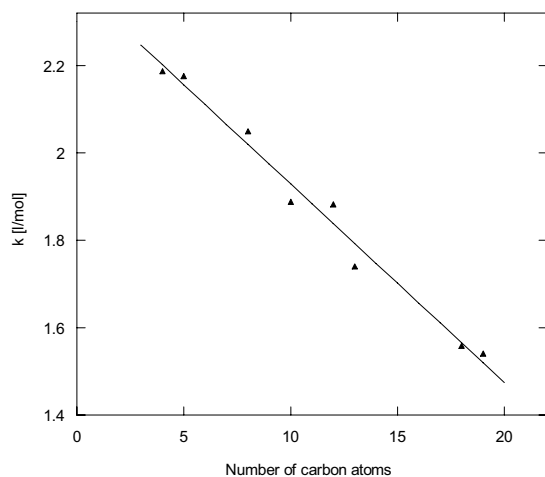


Fig. 2. Adsorption constants  $k_i$  calculated for the investigated components with respect to the number of carbon atoms of the alkyl chain.

In order to verify the reliability of dependence of  $k_i$  from the alkyl chain length, the elution profile of the nonylbenzene was simulated by predicting its isotherm parameters from the linear regression. It is worth noting that no experimental data of nonylbenzene were used during the equilibrium parameter estimation. The elution profile was obtained by integrating Equation (2), with the conditions (4), to evaluate the concentration along

the column, coupled with a simple CSTR model, with a volume of 45  $\mu\text{l}$ , that describes the dynamic of the solute in the cell of the detector. Furthermore a delay of 0.235 min were added to the retention time, because it takes into account the time necessary for the sample to flow along the connection pipes of the chromatographic system. Equation (2) was integrated using the orthogonal collocation on finite element method (OCFE, Ma and Guiochon, 1991), that show a much higher accuracy and robustness with respect to the finite difference methods, but it requires higher computation efforts. A comparison between the calculated profile and the experimental one is shown in Figure 3, for a concentration of nonylbenzene equal to 2.51 g/l. The agreement between the profiles was found to be very good, validating both the fluidynamical and thermodynamical model.

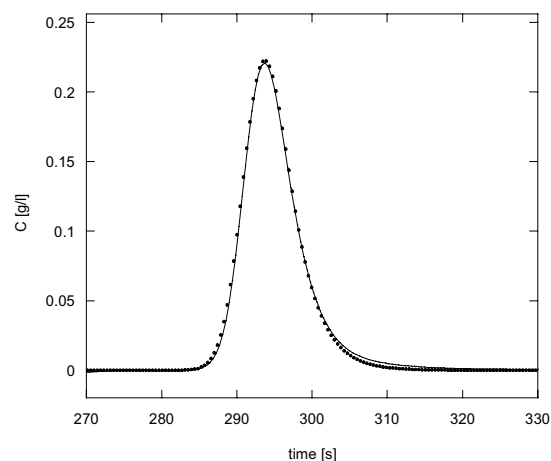


Fig. 3. Elution profile of nonylbenzene: experimental data (dotted line), simulated data (solid line).

### 4.2 Study of chromatographic profiles for a multicomponent mixture

The isotherm parameters obtained in the previous Section were then used to calculate the elution profiles for a mixture containing three compounds. In particular, because of the competition among the species, the Langmuir's isotherm of Equation (6) becomes:

$$q_i = \frac{k_i q_0 C_i}{1 + \sum_{j=1}^3 k_j C_j} \quad (10)$$

where the value of  $k_j$  are that obtained by the linear regression described above.

Table 2 Concentration of the tricomponent mixtures.

Mixture	Nonylbenzene (g/l)	Tridecylbenzene (g/l)	Octadecylbenzene (g/l)
A	0.72	2.63	2.51
B	2.55	2.52	0.48

The results for the elution of a tricomponent mixture were obtained by integrating the system of partial

differential equation (5), with the conditions (4), to evaluate the concentration along the column. All the obtained profiles were corrected for the contribution of detector cell and extra-column volume as described in the previous section. Equations (5) were integrated using, again, the orthogonal collocation on finite element method (OCFE, Ma and Guiochon, 1991).

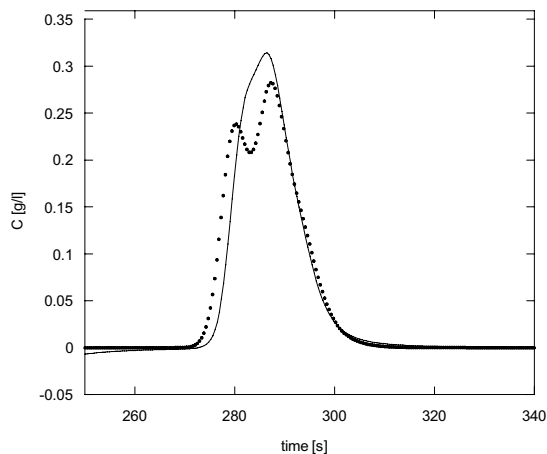


Fig. 4a. Elution profile of mixture A: experimental data (dotted line), simulated data (solid line).

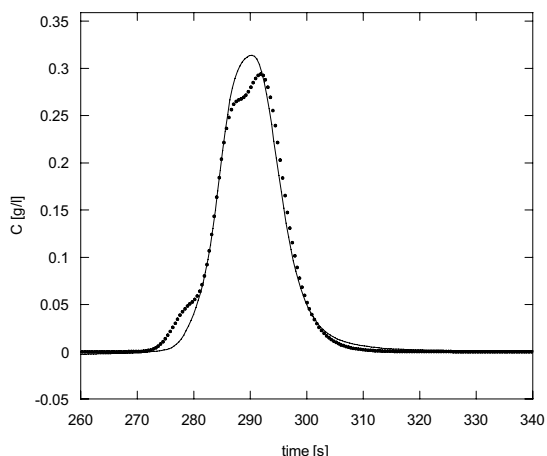


Fig. 4b. Elution profile of mixture B: experimental data (dotted line), simulated data (solid line).

In Figures 4 the elution profiles calculated for the ternary mixtures described in Table 2 are compared with the experimental chromatograms; in particular Figure 4a represents the results of elution of mixture A and Figure 4b that for mixture B. Results show a satisfactory agreement between the experimental data and the calculated ones, even if the match is not perfect.

The disagreement is principally due to the behavior of the octadecylbenzene, which shows a predicted elution time shorter than the experimental one.

Anyway, it is worth noting that the aim of the present study was to find a simple and practical tool to support characterization of refinery feedstock through HPLC. For this reason, some assumptions were made in order to minimize the effort necessary for the calibration and integration of the model. First, the chromatographic model was developed describing the equilibrium phenomena by means of the simplest adsorption model, that is the Langmuir

isotherm. This choice was made in order to decrease as much as possible the number of parameters used, though reducing the model efficiency. All the parameters of the competitive isotherm were evaluated by means of the experimental retention time obtained for the single, pure compounds. Furthermore, since the Langmuir isotherm is known to be thermodynamically inconsistent unless the saturation concentrations of all the species are identical (Broughton 1948), the parameter  $q_0$  was assumed to be the same for all the compounds. However, it is worth noting that this is rarely verified in practice (Golshan-Shirazi and Guiochon, 1989) especially if the adsorption of species with very different geometrical structures is described (Katti *et al.*, 1992). The second important aspect to be considered is that the fluidynamical parameters were straightforwardly obtained by considering the information on the system reported by the instrument producer and conducting simple experiment to calculate the system hold-up and detector cell volume.

It is worth noting that one of the components of the mixture (nonylbenzene) was not included in the procedure of the equilibrium parameter estimation. It means that no experimental data were available for the characterisation of this single component elution; hence its  $k_i$  is predicted by the linear function obtained with data shown in Figure 2. This indicates that it is not necessary to conduct experiment for the calibration of the isotherm model of each compound, but its parameters can be predicted by the information obtained from a limit number of selected species belonging to the same class.

All the considerations above show that it is possible to easily obtain a reasonable practical prediction of the behavior of tricomponent mixtures, minimizing the efforts for the calibration model. These results could be then applied to improve peak separation procedures in the characterization of aromatic feedstock through chromatographic analysis.

#### 4. CONCLUSIONS

In this work the model of a chromatographic system was developed, in order to reconstruct the elution profile of multicomponent mixture. The objective was to develop an instrument that can support the characterization of refinery feedstock through HPLC, giving information on the separation of the aromatic groups. In particular, the attention was focused on alkylbenzenes compounds, which is one of the aromatic classes present in gasoil. This choice was due to the main interest for this petroleum fraction, driven by the increasing demands in line with the environmental specifications. Results show that it is possible to reproduce with a satisfactory agreement the chromatogram profile of a tricomponent system, using a simple Langmuir model for the absorption mechanism. In particular it is important to underline that the calibration of the adsorption model was obtained by considering the experimental retention time of a single solute, evaluated at different solute concentrations. The analysis of the isotherm parameters showed the existence of a linear

dependence between the length of the alkyl chain and the affinity of the compounds for the stationary phase, giving a tool for the prediction of equilibrium parameters from the molecular structure, and allowing the reduction of the number of experiments necessary for the calibration step.

The equilibrium isotherm was then used to calculate the elution profile of a tricomponent mixture by integrating the equilibrium dispersive model, where the competition among the three compounds was simply taken into account by using the form of the Langmuir equation for multicomponent systems, using the equilibrium parameters that had been calculated in absence of competition. The calculated profile showed a satisfactory agreement when compared with the experimental chromatograms, indicating that the proposed model can give useful information for the interpretation and deconvolution of HPLC chromatograms of aromatic mixtures.

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