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HYPERBOLIC MODELS IN GAS-SOLID CHROMATOGRAPHY

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Abstract

We present different models arising in chemical engineering and essentially related to isothermal gas chromatography. These models describe a fixed bed adsorption process of separation of a gaseous mixture: each compound can exist either in a mobile phase or a solid and static one, with a finite or infinite mass-exchange kinetics. Many authors, in the fields of chemical engineering and mathematics, have investigated these models under various assumptions, from a theoretical or numerical point of view. We explain first the relations between some of these approaches. Next, we present some results related to these models, some of them being new, particularly in the case of a monovariant system with one or two active compounds for the Cauchy problem. Lastly, we mention some open problems.

Key words: *gas chromatography, nonlinear chromatography, mass transfer kinetics, adsorption, systems of conservation laws*

1 Introduction

Chromatography is the collective term for a family of laboratory techniques for the separation of mixtures. It involves passing a mixture dissolved in a “mobile phase” (liquid or gaseous) through a stationary phase, which separates the analyte to be measured from other molecules in the mixture and allows it to be isolated (source: Wikipedia).

The principal methods are

Frontal Chromatography: a procedure in which the sample (liquid or gas) is fed continuously into the chromatographic bed. In frontal chromatography no additional mobile phase is used.

Displacement Chromatography: a procedure in which the mobile phase contains a compound (the Displacer) more strongly retained than the compounds of the sample under examination. The sample is fed into the system as a finite slug.

Elution Chromatography: a procedure in which the mobile phase is continuously passed through or along the chromatographic bed and the sample is fed into the system as a finite slug.

Chromatography may be preparative or analytical. Preparative chromatography seeks to separate the compounds of a mixture for further use (and is thus a form of purification). It is a process that has lately become of considerable interest in the pharmaceutical industry: only chromatography is sufficiently flexible and powerful to satisfy the practical requirements encountered in most difficult separations of pharmaceutical intermediates. Analytical chromatography normally operates with smaller amounts of material and seeks to measure the relative proportions of analytes in a mixture. The two are not mutually exclusive.

Another method of separating chemical substances is distillation, based on differences in their volatilities in a boiling liquid mixture. It is a process used for instance in petroleum industry. A common feature both to chromatography and distillation is that the separation follows from the interaction between two phases in motion one with respect to the other. A distillation column is heated at the bottom, thus separating the mixture in a gaseous phase moving upwards, and a liquid one moving downwards by gravity. In standard chromatography the mixture, in gaseous or liquid form, is injected in a column filled with some porous medium. The chemical compounds are partially retained by the pores, thus generating stationary phase in the column (fixed bed adsorption). In the modelling of such process, two types of phenomena are to be considered. On the one hand, the propagation of the mobile phase is ruled by the laws of fluid dynamics, gas dynamics, porous media,... On the other hand, the repartition of matter between the two phases relies on thermodynamics and the notion of diphasic equilibrium is involved.

There are many reference works in the field of Chromatography. G. Guiochon and B. Lin [17], for instance, describe the different mathematical models of chromatography, examine the assumptions on which they are based, consider their properties and discuss their solutions. In [18], one can find the fundamentals of thermodynamics, mass-transfer kinetics and flow through porous media that are relevant to chromatography. The authors present the models used in chromatography, the applications, describe the different processes used and the methods of optimization of the experimental conditions.

In this article we mainly consider the case of isothermal gas-solid chromatography, a procedure in which the temperature of the column is kept constant during the process. The mixture analyzed is vaporized at the entrance of a column that contains a solid substance (the adsorber) called the stationary phase and then is transported across it by a carrier gas. The carrier gas, or vector gas (usually nitrogen, sometimes hydrogen or helium), is the mobile

phase (see Fig. 1). In most cases it has to be inerted vis a vis the solutes and the stationary phase.

The paper is organized as follows. First, we examine and discuss some models arising in gas-solid chromatography (or closely related processes). Next we give some mathematical results which seem to us significant in that field. We emphasize in particular the case of the so-called Pressure Swing Adsorption process (PSA) in the case of two compounds, for which we give some new results by the authors. Lastly we mention some open problems.

We specify that we do not seek to be exhaustive, neither from the point of view of modelling, nor of that of the mathematical analysis. Our goal is to concentrate on some problems which appear more particularly interesting to us in terms of potential developments, pointing out various open problems.

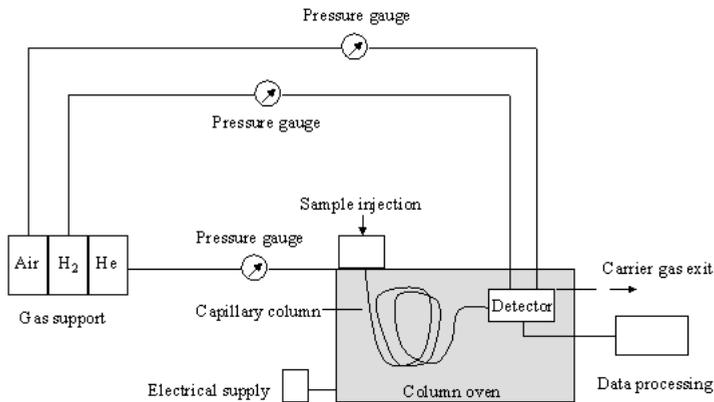


Figure 1: Construction scheme of a gas chromatograph. Source: home page of Zentrales Analytisches Labor, Brandenburgische Technische Universität Cottbus.

2 Some models in nonlinear chromatography

General references in this field are, for instance, [29, 17, 18]. One may consult [27] for a complete nomenclature for Chromatography.

In this section we choose to start with the model described by P. Rouchon and *al.* ([30]). The assumptions of the model are completely stated and some of them are used as a basis for a later discussion: finite exchange kinetics or not (Subsections 2.2 and 2.4), pressure law and sorption effect (Subsections 2.3 and

2.4). The mathematical results given in Section 3 are related to the models presented here. Some of them are new.

2.1 The model of Rouchon-Schonauer-Valentin-Guiochon

We recall the model described by P. Rouchon and *al.* ([30]) which accounts for the migration and transformation of the large concentration band of a single pure gaseous compound along a chromatography column. The main assumptions of this model are the following:

1. The column is supposed to be radially homogeneous and so is the input profile. Therefore the problem is monodimensional. The only variables are the abscissa x along the column and the time t .
2. Gases follow ideal gas laws for compressibility and mixing.
3. Darcy's law is valid in the range of flow velocity u investigated. The column permeability is constant independent of the abscissa.
4. The local pressure p is constant during an experiment, depends on the abscissa not on the time even during the passage of a large concentration band.
5. The carrier gas is not sorbed by the stationary phase.
6. Temperature T is constant during an experiment, independent of the position or the time.
7. Mass and heat energy exchanges between the mobile and the stationary phases are infinitely fast. The two phases are constantly at thermal and composition equilibrium.
8. Axial diffusion proceeds at negligible speed.

Notice that the assumption of isothermality 6 is easily justified provided that adequate time is allowed for exchange of energy with the surroundings and also for systems with little adsorption. Assumption 7 may be relaxed: it will be investigated in the next subsection. As pointed out in [30], combination of Assumptions 7 and 8 results in an infinite efficiency of the column. For a thorough discussion of the hypothesis, we refer to the book by Guiochon *et al.* [18] where a large amount of bibliography can also be found.

Let N_M^i and N_S^i , $1 \leq i \leq d$, be the number of moles of compound i per unit length of column at equilibrium, where the subscripts S and M stand for stationary and mobile phase respectively. We assume that the index d stands for the carrier gas, if present, thus $N_S^d = 0$. The equations for the conservation of mass are:

$$\partial_t(N_M^i + N_S^i) + \partial_x(uN_M^i) = 0, \quad 1 \leq i \leq d. \quad (1)$$

The quantities N_M^i and N_S^i are not independent, they are related by the so-called equilibrium isotherm k^i : $RT N_S^i = k^i(N_M^1, \dots, N_M^d)$ where T is the

temperature, R a positive constant. In particular we have $k^d = 0$ because the carrier gas is not sorbed.

Notice that the precise form of the isotherms is usually unknown but can be experimentally obtained. Simple examples of such a function are the linear isotherm $k^i = K_i N_M^i$, with $K_i \geq 0$, the Langmuir isotherm

$$k^i = \frac{Q_i K_i N_M^i}{1 + \sum_{j=1}^d K_j N_M^j}, \text{ with } K_i \geq 0, Q_i > 0 \text{ (see for instance [31]) and the}$$

BET isotherm defined by

$$k^1 = \frac{QKN_M^1}{(1 + KN_M^1 - (N_M^1/N_M^s))(1 - (N_M^1/N_M^s))}, Q > 0, K > 0, N_M^s > 0, k^2 = 0$$

for one adsorbable compound in an inert gas.

The unknowns are therefore the local mobile phase velocity u and the values of N_M^i for each compound i .

Introducing the local pressure p and the mole fraction $X_i = \frac{N_M^i}{\sum_{k=1}^d N_M^k}$ of each

compound i , Rouchon and *al.* [30] write the equations (1) under the form:

$$\partial_x(upX_i) + \partial_t(pX_i + k^i(pX_1, \dots, pX_d)) = 0, \quad 1 \leq i \leq d. \quad (2)$$

Because $\sum_{i=1}^d X_i = 1$ and $k^d = 0$, the equation for the carrier gas may be replaced by the sum of all equations (1). This gives the total mass balance equation of the column:

$$\partial_x(up) + \partial_t(p + \sum_{i=1}^{d-1} k^i(pX_1, \dots, pX_d)) = 0. \quad (3)$$

The law of ideal gas writes:

$$pX_i \varepsilon^1 = N_M^i RT$$

where ε^1 , the porosity, and the temperature T are assumed here to be constant. Setting

$$F_i = \frac{up}{RT} X_i = \frac{uN_M^i}{\varepsilon^1}, \quad 1 \leq i \leq d, \quad F_0 = \frac{up}{RT}, \quad \varepsilon^2 = \sum_{i=1}^d N_M^i,$$

James ([19]) write these equations under the form:

$$\partial_x F_i + \partial_t \left(\frac{p}{RT} \frac{F_i}{F_0} + \frac{\varepsilon^2}{\varepsilon^1} h_i(F_1, \dots, F_d, F_0) \right) = 0, \quad 1 \leq i \leq d,$$

$$\partial_x F_0 + \partial_t \left(\frac{p}{RT} + \frac{\varepsilon^2}{\varepsilon^1} \sum_{i=1}^{d-1} h_i(F_1, \dots, F_d, F_0) \right) = 0,$$

thus keeping track of the temperature: this may be useful in case of experiments with prescribed temperature as a function of the time.

The functions $h_i(F_1, \dots, F_d, F_0) = \frac{\varepsilon^1 k_i}{\varepsilon^2 RT} = \frac{\varepsilon^1}{\varepsilon^2} N_S^i$ are the isotherms, written in the F -variables.

In the sequel we will make use of the concentrations c_i (moles/m³) of the i^{th} compound in the mobile phase as main unknowns (joined to u). The corresponding concentrations in the stationary phase are denoted q_i . At equilibrium they are given by $q_i = q_i^*(c_1, \dots, c_d)$ where q_i^* , $1 \leq i \leq d$ are the equilibrium isotherms corresponding to this new set of variables. Setting

$$\rho = \sum_{i=1}^d c_i, \text{ equations (2) and (3) read}$$

$$\partial_x(u c_i) + \partial_t(c_i + q_i^*(c_1, \dots, c_d)) = 0, \quad 1 \leq i \leq d, \quad (4)$$

$$\partial_x(u \rho) + \partial_t\left(\rho + \sum_{i=1}^d q_i^*(c_1, \dots, c_d)\right) = 0. \quad (5)$$

This is our reference model in the sequel.

2.2 A model with finite exchange kinetics

A question is that, given a certain amount of mixture, there exists a privileged repartition of the matter between the two phases (the so called stable equilibrium state): the equilibrium state can be reached in a short time with respect to the relative velocities of the phases (infinite mass-transfer kinetics: Assumption 7 above) or not. When the time needed to reach the equilibrium is not negligible with respect to the characteristic times induced by the velocity, we must give up Assumption 7 and take the deviation from equilibrium into account: the actual concentration q_i in the solid phase differs from $q_i^*(c_1, \dots, c_d)$. This phenomenon is known as a finite exchange kinetics. Finite exchange kinetics can be modelled by the following system of equations (with a suitable pressure law) for a column of length L :

$$\partial_t c_i + \partial_x(u c_i) = A_i (q_i - q_i^*(c_1, \dots, c_d)), \quad (6)$$

$$\partial_t q_i = -A_i (q_i - q_i^*(c_1, \dots, c_d)), \quad t \geq 0, \quad x \in (0, 1). \quad (7)$$

The right hand sides of the equations quantify the attraction of the system to the equilibrium state: it is a pulling back force proportional to the deviation from equilibrium. A compound with concentration c_i is said to be inert if $A_i = 0$ and $q_i^* = 0$.

When the coefficients A_i in (6)-(7) tend to infinity (instantaneous equilibrium),

say $A_i = 1/\varepsilon$ with $\varepsilon \rightarrow 0$ for instance, we get formally $q_i - q_i^* = -\frac{1}{A_i} \partial_t q_i \rightarrow 0$ and Eqs. (6)-(7) reduce to (4).

In Section 2.4 we present some theoretical results for a particular pressure law arising in the so-called ‘‘Pressure Swing Adsorption’’ process, dealing with a non constant velocity u .

In [21], James studied a system of semi linear transport equations, closely related to (6)-(7), modelling diphasic propagation arising in chemical engineering in which two phases are in motion with distinct **constant** speeds $u > 0$ and $v \leq 0$, covering the cases of liquid-solid chromatography and distillation. The model is the following:

$$\partial_t c_\varepsilon + \partial_x(uc_\varepsilon) = \frac{1}{\varepsilon}(q_\varepsilon - h(c_\varepsilon)), \quad (8)$$

$$\partial_t q_\varepsilon + \partial_x(vq_\varepsilon) = -\frac{1}{\varepsilon}(q_\varepsilon - h(c_\varepsilon)), \quad (9)$$

where $\varepsilon > 0$. The unknowns are the concentrations vectors $c_\varepsilon, q_\varepsilon \in \mathbb{R}^d$.

The right hand side, which has the same interpretation as in Eqs. (6)-(7), is written in an academic form, of course not standard in the chemical engineering literature. Note that this set of equations can be used at two levels: on the one hand, specific phenomena due to slow exchange kinetics are related to large values of ε , on the other hand, we can let ε go to zero as above.

2.3 Velocity and pressure law

In gas chromatography, velocity variations accompany changes in gas composition, especially in the case of high concentration solute: it is known as the sorption effect. To neglect this effect or not leads of course to models with very different mathematical properties. The sorption effect is of major importance in gas chromatography but often close to being insignificant in liquid-solid chromatography or distillation, which is the context of the model (8)-(9), for instance, where the velocities are kept constant.

2.3.1 Neglecting the sorption effect

According to Assumption 3 we write $u = -C \partial_x p$ where C is a constant depending on the porosity. Next, Assumption 4 gives $\partial_t p = 0$. Neglecting the sorption effect in first approximation, we assume that the total flow rate is constant i.e. $u p = \text{cste}$. Thus $p \partial_x p$ is a constant and we obtain immediately

$$p(x) = \sqrt{P_{in}^2 - \frac{x}{L}(P_{in}^2 - P_{out}^2)}.$$

In this expression P_{in} is the inlet pressure ratio, P_{out} is the outlet pressure ratio and L is the column length. For very small variations of pressure between inlet and outlet, we can therefore assume a constant velocity.

As pointed out by James ([21]), the assumption of constant total flow rate is not really physically relevant but the derivation of the pressure law may be viewed as an independent reasoning and others models are of course admissible.

2.3.2 Taking the sorption effect into account

Assume that the pressure is given by $p = k\rho^\gamma$, $k > 0$, $\gamma > 0$ (pressure law for a polytropic ideal gas) and that the speed follows Darcy's law: we have then

$$u = -K \partial_x \rho^\gamma, \text{ with } K > 0. \quad (10)$$

To our knowledge the problem (6)-(7)-(10) has never been investigated from a mathematical point of view. As a first approach we propose an existence result for two simplified models: see Theorem 5 and Remark 2 in Subsection 3.2.

Notice that setting $K = \frac{1}{\varepsilon}$ in (10) we get formally, when ε tends to zero, $\partial_x \rho^\gamma = 0$, that is $\rho = \rho(t)$. This means, in the isothermal case, that the total pressure is only time dependant (which dramatically differs from Assumption 4): the velocity $u(t, x)$ of the mixture has to be found in order to achieve a given pressure. This is exactly the context of the model developed in the next section.

2.4 Pressure Swing Adsorption (PSA)

2.4.1 Introduction

“Pressure Swing Adsorption (PSA) is a technology that is used to separate some species from a gas under pressure according to these species' molecular characteristics and affinity for an adsorbent material. It operates at near-ambient temperatures and so differs from cryogenic distillation techniques of gas separation. Special adsorptive materials (e.g., zeolites) are used as a molecular sieve, preferentially adsorbing the undesired gases at high pressure. The process then swings to low pressure to desorb the adsorbent material. Using two adsorbent vessels allows near-continuous production of the target gas. It also permits so-called pressure equalization, where the gas leaving the vessel being depressurized is used to partially pressurize the second vessel. This results in significant energy savings, and is common industrial practice.” (Wikipedia)

PSA is used extensively in the production and purification of oxygen, nitrogen and hydrogen for industrial uses. PSA can be used to separate a single gas from a mixture of gases. A typical PSA system involves a cyclic process where a number of connected vessels containing adsorbent material undergo successive pressurization and depressurization steps in order to produce a continuous stream of purified product gas (see Fig. 2).

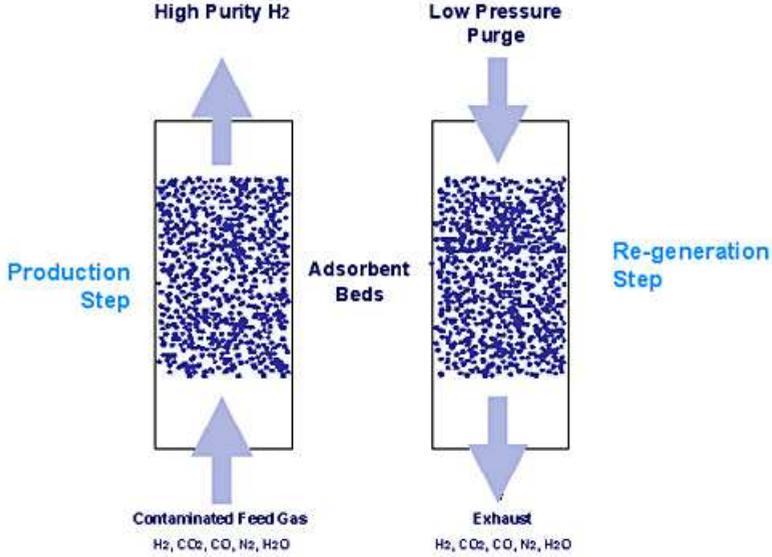


Figure 2: PSA process: production and regeneration steps. Source: questairinc.com

2.4.2 Modelling

Our purpose is to model a step of the cyclic process, restricted to isothermal behavior. As in general fixed bed chromatography, each of the d species ($d \geq 2$) simultaneously exists under two phases, a gaseous and movable one with concentration $c_i(t, x)$ or a solid (adsorbed) other with concentration $q_i(t, x)$, $1 \leq i \leq d$. The sorption effect is taken into account through a constraint on the pressure (see the end of 2.3.2). Following Ruthven (see [31]) we can describe the evolution of u , c_i , q_i according to the system (6)-(7) with suitable initial and boundary data:

$$c_i(0, x) = c_i^0(x), \quad q_i(0, x) = q_i^0(x) \text{ in }]0, 1[, \quad (11)$$

$$c_i(t, 0) = c_i^{in}(t), \quad u(t, 0) = u_0(t) > 0, \quad (12)$$

$$c_i(t, 1) = c_i^{out}(t) \text{ if } u(t, 1) < 0. \quad (13)$$

In (6)-(7) the velocity $u(t, x)$ of the mixture has to be found in order to achieve a given pressure (or density in this isothermal model):

$$\sum_{i=1}^d c_i = \rho(t), \quad (14)$$

where ρ represents the *given* total density of the mixture. The experimental device is realized so that it is a given function depending only upon time, which

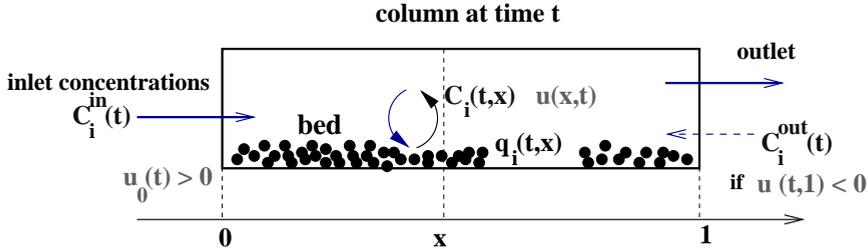


Figure 3: Unknown and boundary data in a step of the PSA process.

differs drastically from Assumption 4 (see Subsection 2.1). Adding (6) for $i = 1$ to d , we get, thanks to (14):

$$\partial_x u = -\frac{\partial_t \rho}{\rho} + \frac{1}{\rho} \sum_{i=1}^d A_i (q_i - q_i^*)(c_1, \dots, c_d), \quad (15)$$

which gives an integral dependency of u upon the concentrations.

3 Some mathematical results

In this section we investigate some of the preceding models from a theoretical or numerical point of view. We will focus in particular on the PSA system with finite or infinite exchange kinetics and give some recent results by the authors.

3.1 On a model with constant velocity

We present here some results due to James [21] for System (8)-(9). Some other results in a closely related case are given in Subsection 3.5.1 via the kinetic approach. In so far as the set of problems are connected (the case $v = 0$ corresponds to chromatography), it may be interesting to give an account of the main results in this direction.

First, as pointed out by James, the system admits a natural set of “diphasic entropies” under the form $\eta(c) = \eta_1(c) + \eta_2(h(c))$ where $\eta_1, \eta_2 : \mathbb{R}^d \rightarrow \mathbb{R}$ are two convex functions satisfying $\nabla_c \eta_1(c) = \nabla_c \eta_2(h(c))$ for all $c \in \mathbb{R}^d$.

Next, a quite natural set of boundary conditions is the following, as far as chromatography and distillation are concerned:

$$c_\varepsilon(0, t) = a(t) \in L^\infty(]0, +\infty[) \text{ (injection)}, \quad (16)$$

$$uc_\varepsilon(1, t) + vq_\varepsilon(1, t) = b(t) \in L^\infty(]0, +\infty[) \text{ (reflux) if } v < 0. \quad (17)$$

If $v = 0$ (case of chromatography), the reflux boundary condition simply disappears.

From the point of view of distillation, the boundary conditions are natural: the first one is a Dirichlet-like “injection” at one end of a column and only acts on the incoming variable ($u > 0$); the second one looks like a Neumann

condition on the other hand and imposes $v < 0$ (it is a simplified model of "reflux" in a distillation column).

It turns out that System (8)-(9) with (16)-(17) is well posed. Applying the fixed point theorem, there is an existence and uniqueness result for (8)-(9) in $L^\infty(]0, T[; L^1(]0, 1[)^{2d}$:

Theorem 1

For a given $T > 0$, assume that a and b are in $L^\infty(]0, T[)$, $c^0 \in L^\infty \cap L^1(]0, 1[)$ and that the function h is of class \mathcal{C}^1 . Then there exists a unique solution to (8)-(9) which lies in $L^\infty(]0, T[; L^1(]0, 1[))$.

When ε tends to zero we get formally a set of equations which express the conservation of matter:

$$\partial_t(c + h(c)) + \partial_x(uc + v h(c)) = 0. \tag{18}$$

However a difficulty arises if one lets ε go to 0 because the boundary conditions are not at equilibrium for $\varepsilon > 0$ so that boundary layers may appear.

James imposes the condition

$$f(c) = uc + v h(c) \leq \min_{t>0} b(t).$$

This condition implies some restrictions on the initial and boundary data, which lead to uniform L^∞ estimates for the solution to (8)-(9) for a broader class of fluxes.

In the scalar case and using compensated compactness, James proves that the solution of this system converges, as $\varepsilon \rightarrow 0$, to a solution of the preceding equation satisfying a set of entropy inequalities:

Theorem 2

Let be $T > 0$, $a, b \in L^\infty(]0, T[)$, $a \geq 0, b \leq 0, c^0 \in L^1(]0, 1[) \cap L^\infty(]0, 1[)$, $c^0 \geq 0$ and

$$c^* = \sup\{c \geq 0, \exists c' \leq c, f(c') \leq \min b(t)\} \geq \max[\|a\|_\infty, \|c^0\|_\infty].$$

Let $c_\varepsilon, q_\varepsilon$ be a solution of (8)-(9) with initial data at equilibrium:

$$c_\varepsilon(x, 0) = c^0(x) \in L^1(]0, 1[) \cap L^\infty(]0, 1[), \quad q_\varepsilon(x, 0) = h(c^0(x)).$$

Then there exists a subsequence of solutions which converges a.e. and strongly in $]0, 1[\times]0, +\infty[$ to $c \in L^\infty(]0, T[; L^1(]0, 1[)$ satisfying for any $\phi \in \mathcal{D}'_+(]0, 1[\times \mathbb{R}_+)$, $k \in \mathbb{R}$:

$$\begin{aligned} & \int_0^\infty \int_0^1 [(|c - k| + |h(c) - h(k)|) \partial_t \phi + (u|c - k| + v|h(c) - h(k)|) \partial_x \phi] dx dt \\ & \leq \int_0^\infty (u |a(t) - k| \phi(0, t) + |b(t) - f(k)| \phi(1, t)) dt - \\ & \quad \int_0^1 (|c^0(x) - k| + |h(c^0(x)) - h(k)|) \phi(x, 0) dx. \end{aligned}$$

This result is meaningful for $c^* > 0$, which occurs only if $f(c)$ becomes non positive for some c : notice that this excludes the case of the chromatography ($v = 0$).

In [23], James and *al.* study numerically the same model to take in account the finite exchange kinetics. The resulting hyperbolic system with a non linear relaxation term is then formally treated with a Chapman-Enskog type expansion. A first order correction to the classical quasilinear hyperbolic model is derived which consists in a nonlinear diffusion term. Numerical schemes for both models, relaxed and parabolic, are then tested and compared for different initial and boundary values.

Lastly, in [22], the authors describe and validate a numerical solution of the inverse problem of nonlinear chromatography using the model given by Eq. (18). The method allows the determination of best numerical estimates of the coefficients of an isotherm model from the individual elution profiles of the two compounds of a binary mixture. In two cases, when the isotherm model is satisfactory, the authors observed a very good agreement between the equilibrium isotherm equations obtained by this new method and those determined by the classical combination of elution by characteristic points and binary frontal analysis. Practically, this method would significantly reduce the amounts of products required to determine a set of competitive binary isotherms.

3.2 On a model with Darcy's velocity

As a first approach to a study of the complete model (6)-(7)-(10) we propose an existence result for the following simplified one:

$$\partial_t c_i + \partial_x(u c_i) = 0, \quad \text{in } (0, T) \times \mathbb{R}, \quad (19)$$

$$u = -\partial_x \rho^\gamma, \quad \gamma > 0, \quad \rho = \sum_{i=1}^d c_i, \quad (20)$$

$$c_i(0, x) = c_i^0(x), \quad x \in \mathbb{R}. \quad (21)$$

Notice that we work on \mathbb{R} in order to focus on the main difficulties, but we assume that the initial data c_i^0 are compactly supported. Furthermore we assume $A_i = 0$ to avoid some problems related to the nonlinearities q_i^* . Adding (19) for $i = 1$ to d we get, thanks to (10), $\partial_t \rho - \partial_x(\rho \partial_x \rho^\gamma) = 0$, that we write under the form:

$$\partial_t \rho - \frac{\gamma}{\gamma + 1} \Delta \rho^{\gamma+1} = 0$$

which is a porous medium equation. There exists a large amount of works on this subject. The first results are due to Oleinik, Kalashnikov and Chzhou [28]. For regularity results on ρ consult for instance Aronson [1, 2, 3], Aronson-Benilan [4], Caffarelli-Friedmann [5], Dibenedetto [14]. Concerning the domain of dependency $\mathcal{P}[\rho] = \{\rho > 0\}$ in one dimension we know, under suitable

assumptions, that if the initial data ρ^0 is supported in a bounded interval, then ρ is compactly supported for all time and $\mathcal{P}[\rho]$ is enclosed between two monotonic and lipschitz continuous curves $x = \xi_i(t)$ (see [24, 34] for instance). More precisely we will use explicitly the following results:

consider the problem

$$\partial_t \rho = \Delta \rho^m \quad \text{in } S = (0, T] \times \mathbb{R}, \quad \rho(0, x) = \rho^0(x), \quad x \in \mathbb{R} \quad (22)$$

where $m > 1$. Following [1] we say that a function $\rho(t, x)$ is a weak solution of (22) if

- ρ^0 is non negative, continuous, bounded in \bar{S} ,
- $\partial_x \rho^m \in L^\infty$,
- ρ satisfies:

$$\forall \phi \in \mathcal{D}([0, T] \times \mathbb{R}) \quad \int_S (\partial_x \rho^m \partial_x \phi - \rho \partial_t \phi) \, dx \, dt = \int_{\mathbb{R}} \rho^0(x) \phi(0, x) \, dx.$$

Proposition 3 *If $(\rho^0)^m$ is lipschitz continuous, the problem (22) has a unique weak solution ρ . Moreover ρ is a classical solution on $\mathcal{P}[\rho] = \{\rho > 0\}$.*

Remark 1 *The L^∞ bound for $\partial_x \rho^m$ depends only upon the lipschitz constant of $(\rho^0)^m$.*

Proposition 4 *Assume that $(\rho^0)^m$ is lipschitz continuous and let ρ be the weak solution of (22). For all $\tau > 0$ there exists a positive constant $C = C(m, \tau, \|\rho^0\|_\infty)$ such that*

$$\forall (t, x), (t, x') \in [\tau, T] \times \mathbb{R}, \quad |\rho^{m-1}(t, x) - \rho^{m-1}(t, x')| \leq C |x - x'|.$$

If $(\rho^0)^{m-1}$ is lipschitz continuous the same conclusion holds for all $(t, x), (t, x') \in [0, T] \times \mathbb{R}$ and C depends on the lipschitz constant of $(\rho^0)^{m-1}$ instead of τ .

We are looking *a priori* for a weak solution with $c_i \in L^\infty$ and we will get, depending on the assumption on ρ^0 , $u \in L^\infty((\tau, T) \times \mathbb{R})$ for all $\tau > 0$ or $u \in L^\infty((0, T) \times \mathbb{R})$ which does not allow to pass to the limit in a sequence of smooth approximate solutions in the weak formulation of (19). However, if ρ is smooth, we have $u c_i = -\frac{\gamma}{\gamma+1} \frac{c_i}{\rho} \partial_x \rho^{\gamma+1}$ with $\frac{c_i}{\rho} \in L^\infty$ and we will get $\partial_x \rho^{\gamma+1} \in L^\infty$ and a BV estimate for $\frac{c_i}{\rho}$. Thus we choose to formulate the problem as follows:

$$\partial_t c_i - \frac{\gamma}{\gamma+1} \partial_x \left(\frac{c_i}{\rho} \partial_x \rho^{\gamma+1} \right) = 0 \quad \text{in } (0, T) \times \mathbb{R}, \quad 1 \leq i \leq d, \quad (23)$$

$$\text{with } \gamma > 0, \quad \rho = \sum_{i=1}^d c_i. \quad (24)$$

For mere technical reasons, the initial data $c_i^0(x)$ are written under the form $c_i^0(x) = \rho^0(x) a_i(x)$ where the functions a_i are defined on \mathbb{R} , non negative, and satisfy $\sum_{i=1}^d a_i = 1$. We make the following assumptions:

$$\forall i \in \{1, \dots, d\} \quad a_i \text{ has bounded variation on } \mathbb{R}, \quad (25)$$

$$\rho^0 \text{ is lipschitz continuous, non negative and compactly supported}, \quad (26)$$

$$\exists C > 0, \quad \forall \eta > 0 \quad \int_{\mathbb{R}} \left| \partial_x \left(\frac{1}{\rho^0 + \eta} \right) \right| \leq C/\eta. \quad (27)$$

The technical assumption (27) is related to the the behavior of ρ^0 near the point where this function vanishes. It is satisfied for instance if ρ^0 is lipschitz continuous, supported in some interval $[a, b]$, positive in $]a, b[$, monotone in the neighborhood of a and b .

We state now our main result:

Theorem 5 *Under the assumptions (25)-(26)-(27), Problem (23)-(24) has at least a solution (c_1, \dots, c_d) with $c_i \in L^\infty$, $c_i \geq 0$, $\rho = \sum_{i=1}^d c_i$ continuous on $\mathbb{R}^+ \times \mathbb{R}$ and such that:*

$$\forall T > 0, \quad \partial_x \rho^{\gamma+1} \in L^\infty((0, T) \times \mathbb{R}), \quad \frac{c_i}{\rho} \in L^\infty((0, T); BV(\mathbb{R})),$$

$$\forall T > 0, \forall \tau > 0, u = -\partial_x \rho^\gamma \in L^\infty((\tau, T) \times \mathbb{R}).$$

Moreover, if $(\rho^0)^\gamma$ is lipschitz continuous then $u \in L^\infty((0, T) \times \mathbb{R})$.

Outlines of the proof- The estimates on u are straightforward consequences of the general properties of the solution of the porous medium equation: consult for instance Aronson [1].

Assume the initial data in $\mathcal{C}^2(\mathbb{R})$ (thanks to a regularization step that we skip), let be $\eta > 0$, $c_{i,\eta}^0 = c_i^0 + \eta/d$, $1 \leq i \leq d$ and $\rho_\eta^0 = \rho^0 + \eta = \sum_{1 \leq i \leq d} c_{i,\eta}^0$. Let ρ_η be

the unique solution of the following problem (\mathcal{P}_η) :

$$\partial_t \rho_\eta - \frac{\gamma}{\gamma+1} \Delta \rho_\eta^{\gamma+1} = 0, \quad (28)$$

$$\rho_\eta(0, x) = \rho_\eta^0. \quad (29)$$

Notice that ρ_η satisfies:

$$\partial_t \rho_\eta + \partial_x (u_\eta \rho_\eta) = 0, \quad (30)$$

with $u_\eta = -\partial_x (\rho_\eta^\gamma)$ which is Lipschitz continuous on \mathbb{R} , uniformly with respect to $t \in [0, T]$. Let $c_{i,\eta}$, $1 \leq i \leq d$, be the solution of the advection equation

$$\partial_t c_{i,\eta} + \partial_x(u_\eta c_{i,\eta}) = 0 \quad (31)$$

$$c_{i,\eta}(0, x) = c_{i,\eta}^0, \quad (32)$$

then we have clearly $\rho_\eta = \sum_{1 \leq i \leq d} c_{i,\eta}$.

Notice that by comparison principle we have

$$\eta \leq \rho_\eta \leq \|\rho^0\|_\infty + \eta \quad \text{in } [0, T] \times \mathbb{R}$$

and also

$$0 < \eta_1 \leq \eta_2 \implies \rho_{\eta_1} \leq \rho_{\eta_2} \quad \text{in } [0, T] \times \mathbb{R}.$$

Thanks to standard arguments we can then assume that (up to a subsequence):

$$\rho_\eta \rightarrow \rho \text{ in } L^p_{loc} \quad \forall p \geq 1, \quad u_\eta \rightarrow u = -\partial_x \rho^\gamma \text{ in } \mathcal{D}', \quad c_{i,\eta} \rightarrow c_i \text{ in } L^\infty \text{ weak*} \quad (33)$$

but it is not enough to pass to the limit in the weak formulation of (\mathcal{P}_η) . More precisely, according to (23), we have to show that for all $\phi \in \mathcal{D}'([0, T] \times \mathbb{R})$:

$$\int_0^T \int_{\mathbb{R}} u_\eta c_{i,\eta} \partial_x \phi \xrightarrow{\eta \rightarrow 0} \int_0^T \int_{\mathbb{R}} -\frac{\gamma}{\gamma+1} \frac{c_i}{\rho} \partial_x \rho^{\gamma+1} \partial_x \phi. \quad (34)$$

Let be $\alpha > 0$ fixed. The left hand side of (34) is written as:

$$\int_0^T \int_{\mathbb{R}} u_\eta c_{i,\eta} \partial_x \phi = I_\eta + J_\eta$$

$$\text{with } I_\eta = \int_0^T \int_{\{\rho < \alpha\}} u_\eta c_{i,\eta} \partial_x \phi \text{ and } J_\eta = \int_0^T \int_{\{\rho \geq \alpha\}} u_\eta c_{i,\eta} \partial_x \phi.$$

The integral I_η : we have $u_\eta c_{i,\eta} = -(\partial_x \rho_\eta^{\gamma+1}) c_{i,\eta} = -\frac{\gamma}{\gamma + \frac{1}{2}} \rho_\eta^{\frac{1}{2}} \partial_x (\rho_\eta)^{\gamma + \frac{1}{2}} \frac{c_{i,\eta}}{\rho_\eta}$

and thus

$$\left| u_\eta c_{i,\eta} \right| \leq \rho_\eta^{\frac{1}{2}} \left| \partial_x (\rho_\eta)^{\gamma + \frac{1}{2}} \right|. \quad (35)$$

Using Assumption (26) and Eq. (28) multiplied by ρ_η^γ , we get the following lemma:

Lemma 6

$$\exists C > 0, \quad \forall \eta > 0, \quad \forall (a, b) \in \mathbb{R}^2, \quad a \geq b, \quad \forall T > 0 \quad \int_0^T \int_a^b \left| \partial_x (\rho_\eta)^{\gamma + \frac{1}{2}} \right|^2 dx dt \leq C.$$

Notice that we use here that there exists a uniform L^∞ bound for $\partial_x (\rho_\eta)^{\gamma+1}$ as a solution of (28): see the remark following Prop. 3. Using (35), this last lemma and the Hölder inequality, we finally get

$$\exists C > 0, \quad \limsup I_\eta \leq C \sqrt{\alpha} \quad (36)$$

The integral J_η : we write $u_\eta c_{i,\eta} = -\frac{\gamma}{\gamma+1} \partial_x (\rho_\eta)^{\gamma+1} \frac{c_{i,\eta}}{\rho_\eta}$. Thanks to the uniform L^∞ bound for $\partial_x (\rho_\eta)^{\gamma+1}$ and (33) we can assume that

$$\partial_x (\rho_\eta)^{\gamma+1} \rightharpoonup \partial_x \rho^{\gamma+1} \text{ weak*}$$

and it remains to study the sequence $\left(\frac{c_{i,\eta}}{\rho_\eta} \right)_{\eta>0}$. From (30)-(31) we deduce that

$$\partial_t \left(\frac{c_{i,\eta}}{\rho_\eta} \right) + u_\eta \partial_x \left(\frac{c_{i,\eta}}{\rho_\eta} \right) = 0 \quad (37)$$

and we get classically (recall that $c_{i,\eta}/\rho_\eta$ is compactly supported):

$$\partial_t \int_{\mathbb{R}} \left| \partial_x \left(\frac{c_{i,\eta}}{\rho_\eta} \right) \right| dx = 0.$$

Next, we have:

$$\partial_x \left(\frac{c_i^0 + \eta/d}{\rho^0 + \eta} \right) = (\partial_x a_i) \left(\frac{\rho^0}{\rho^0 + \eta} \right)^2 + \frac{\eta \rho^0}{(\rho^0 + \eta)^2} \partial_x a_i + (a_i - \frac{1}{d}) \frac{\eta}{(\rho^0 + \eta)^2} \partial_x \rho^0$$

and thus, thanks to Assumptions (25)-(26)-(27), we get the uniform bound:

$$\int_0^T \int_{\mathbb{R}} \left| \partial_x \left(\frac{c_{i,\eta}}{\rho_\eta} \right) \right| dx \leq C \quad (38)$$

for some positive constant C . Recall that u_η is uniformly bounded in $L^\infty((\tau, T) \times \mathbb{R})$ for all $\tau > 0$. Thus, from (37) and (38) we deduce

$$\int_{\{\rho \geq \alpha\} \cap \{\tau \leq t \leq T\}} \left| \partial_t \left(\frac{c_{i,\eta}}{\rho_\eta} \right) \right| \leq C(\tau, \alpha). \quad (39)$$

From (38) and (39) we deduce that the sequence $\left(\frac{c_{i,\eta}}{\rho_\eta} \right)_{\eta>0}$ is uniformly bounded with respect to η in $BV(\{\rho \geq \alpha\} \cap \{\tau \leq t \leq T\})$, and the following lemma holds:

Lemma 7 *The sequence $\left(\frac{c_{i,\eta}}{\rho_\eta} \right)_{\eta>0}$ is relatively compact in $L^p_{loc}(\{\rho \geq \alpha\} \times \{t \geq \beta\})$ for all $p \geq 1$, $\alpha > 0$ and $\beta \in]0, T[$.*

Then, using lemma 7 and a diagonal extraction process we deduce that there exists a sequence $(\alpha_n, \tau_n) \in \mathbb{R}_+ \times \mathbb{R}_+$ such that $\alpha_n, \tau_n \rightarrow 0$ and

$$\limsup J_\eta = -\frac{\gamma}{\gamma+1} \int_{\{\rho \geq \alpha_n\} \cap \{t > \tau_n\}} \frac{c_i}{\rho} \partial_x \rho^{\gamma+1} \partial_x \phi + R_n \quad (40)$$

with $|R_n| \leq C \tau_n$.

Thanks to (36) and (40) we get easily (34), and thus Theorem 5 holds. \square

Notice that the method used for the proof of Lemma 7 is no longer valid in more than one dimension.

Remark 2 *Dealing with a single compound and working in \mathbb{R}^n , the problem (6)-(7) with u given by (10) writes :*

$$\begin{aligned}\partial_t \rho - \frac{\gamma}{\gamma+1} \Delta \rho^{\gamma+1} &= A(q - q^*(\rho)), \\ \partial_t q &= -A(q - q^*(\rho)),\end{aligned}$$

with initial data ρ_0, q_0 . For this problem, Bourdarias ([7]) obtained an existence result with continuous bounded solutions. The solution is easily obtained via a monotonicity argument. The method cannot be extended to the case of many compounds, which is an open problem.

3.3 PSA with finite exchange kinetics

In [6], both BV and L^∞ theory are developed for the isothermal model (6)-(7)-(14) and the main results are summarized below. Let us point out that one of the mathematical interests of the model is its analogies and differences compared to various other classical equations of physics or chemistry. First, this model shares a similar structure with conservation laws under the form

$$\partial_t \rho + \partial_x(\rho u(\rho)) = 0, \quad \partial_x u(\rho) = F(\rho)$$

where $u(\rho)$ has an integral dependency upon ρ , while in scalar conservation laws u depends upon ρ . It is underlined that, due to this particular dependency, oscillations can propagate thus differing from Burger's example (see Lions-Perthame-Tadmor[25]), but we will not insist on this aspect.

3.3.1 Theoretical results in BV or L^∞ framework

As a first result, we give an existence result for a solution with concentrations having bounded variation and a lipschitz continuous velocity.

Theorem 8 *Assume that the initial and boundary data are at equilibrium, that the initial data have bounded variation in $(0,1)$ and that the boundary data, the isotherms and the total density are lipschitz continuous. Then the problem (6)-(7)-(14) has an unique solution $((c_i), (q_i), u)$ such that $c_i \geq 0, q_i \geq 0$ and*

$$\begin{aligned}\forall T > 0, c_i, q_i &\in L^\infty((0, T) \times (0, 1)) \cap L^\infty(0, T; BV(0, 1)), \\ \partial_x u &\in L^\infty((0, T) \times (0, 1)) \cap L^1(0, T; BV(0, 1)).\end{aligned}$$

Outlines of the proof- the proof is performed in two steps. First, for a fixed velocity u uniformly Lipschitz continuous in $(0,1)$ we get a solution $((c_i), (q_i))$ of (6)-(7) via a fixed point procedure in $L^1((0, T) \times (0, 1))^{2d}$. This solution satisfies some L^∞ estimates. Moreover, the fundamental BV estimate holds:

$$\forall T > 0, \exists C > 0, \forall t \leq T, \forall i, \quad TV(c_i(t, \cdot)) + TV(q_i(t, \cdot)) \leq C \left(1 + \int_0^t \int_0^1 |\partial_{xx}^2 u|\right), \quad (41)$$

where the constant C depends on T , the L^∞ norms of c_i , q_i , u , $\partial_x u$ and the boundary data, and on the total variation of the initial data. Next, thanks to (41) and the L^∞ estimates we can build a fixed point procedure to define the velocity u . \square

In the L^∞ framework, which is the more natural for this problem, there is an existence result but uniqueness is still an open problem:

Theorem 9

Assume that the initial and boundary data are at equilibrium, that initial data are in L^∞ , that the boundary data have Lipschitz regularity and $\partial_{tt}^2 \rho \in L^\infty(0, T)$. Then the problem (6)-(7)-(14) has at least a solution $c_i, q_i \in L_{t,x}^\infty$, $u \in L_t^\infty(W_x^{1,\infty})$ for all $T > 0$.

Outlines of the proof- the initial data are approximated in L^1 by a sequence of data in $BV(0, 1)$, bounded in L^∞ . Thanks to a compactness property in L^1 and some regularization lemma due to DiPerna-Lions ([15]) it can be shown that the corresponding solutions (given by Theorem 8) converge in L^1 towards a solution of the problem (see [6] for details). \square

Remark 3 *It is possible to deal without the assumption of equilibrium for the initial and boundary data. This is illustrated in Fig. 4 where the initial data are zero for the solid phases, and in Fig. 5 where the boundary data \tilde{c}_i^{in} are not at equilibrium: in this last case, a boundary layer occurs. It may be shown, using a classical analysis, that the limits of the solutions $c_i(t, x)$ when x goes to zero are $\tilde{c}_i^{in}(t) = \frac{\rho c_i^{in}(t)}{\sum_i c_i^{in}(t)}$ and this is observed at the numerical level, via the numerical scheme presented below.*

3.3.2 Numerical approximation

A numerical analysis of this problem was performed in [8]. For the time discretization, using an operator splitting, an intermediate spatial regularization step is introduced in order to obtain some BV estimates for the approximate solutions (with BV initial data). With respect to the fully discrete finite volume scheme, it appears that it is possible to get such estimates without any regularization step because of the dissipative effect of the upwind scheme used to treat the transport part of the equations. The scheme is built as follows: we use a uniform spatial mesh $m_j =]x_{j-1/2}, x_{j+1/2}[$, $j = 1, \dots, N$, with center x_j and size Δx and a time step Δt . The initial data are assumed to be piecewise constant over cells m_j . Assume that the discrete unknown $(c_i)_j^n$ and $(q_i)_j^n$ corresponding to the meshes m_j at a given time $t_n = n \Delta t$ are already computed, then:

First step: adsorption. We solve on a time step $[t_n = n, t_{n+1}]$ the system of ODEs

$$\partial_t c_i = A_i (q_i - q_i^*(c_1, \dots, c_d)), \quad (42)$$

$$\partial_t q_i = -A_i (q_i - q_i^*(c_1, \dots, c_d)), \quad t_n \leq t \leq t_{n+1}, \quad (43)$$

for $x = x_j$, $j = 1, \dots, N$, with $(c_i)_j^n$ and $(q_i)_j^n$ as initial data. We get the updated values $(q_i)_j^{n+1}$, intermediate values $(c_i)_j^{n+1/2}$ and we set $\rho_j^{n+1} = \sum_j (c_i)_j^{n+1/2}$. We assume that we proceed with an arbitrary accuracy, in such

a way that $(c_i)_j^{n+1/2}, (q_i)_j^{n+1/2} \geq 0$ and $0 < \alpha \leq \rho_j^{n+1} \leq \beta$ where α and β depend only upon the data of the problem (following the properties of the exact solution).

Second step: transport. The transport part is discretized with a classical upwind finite volume scheme as

$$(c_i)_j^{n+1} = (c_i)_j^{n+1/2} - \lambda \left(u_{j+1/2}^n (c_i)_{j+1/2}^{n+1/2} - u_{j-1/2}^n (c_i)_{j-1/2}^{n+1/2} \right) \quad (44)$$

with $\lambda = \Delta t / \Delta x$ and

$$(c_i)_{j+1/2}^{n+1/2} = \begin{cases} (c_i)_j^{n+1/2} & \text{if } u_{j+1/2}^n \geq 0, \\ u_{j+1/2}^n & \text{if } u_{j+1/2}^n < 0, \end{cases}$$

where $u_{j+1/2}^n$ has to be defined in such a way that the constraint (14) holds. It is easy to show that this is realized through the formula

$$u_{j+1/2}^n = \frac{\rho_j^{n+1} - \rho(t_n) + \lambda u_{j-1/2}^n \sum_j (c_i)_{j-1/2}^{n+1/2}}{\lambda \sum_j (c_i)_{j+1/2}^{n+1/2}}$$

which allows to compute all the discrete velocities used in (44), starting from the given velocity $u_{-1/2}^n = u_0(t_n)$. The positivity of the updated concentrations $(c_i)_j^{n+1}$ is ensured thanks to the CFL condition $\Delta t \leq \Delta x / \|u\|_\infty$.

This scheme is convergent and an $O(\Delta t)^{1/2}$ convergent rate is obtained. Notice that it may be extended to second order, adapting Van-Leer's method. As a conclusion we present two numerical experiments illustrating Remark 3. The results have been obtained with Langmuir isotherms. We do not precise the values of all the parameters involved, because we just emphasize the qualitative aspect.

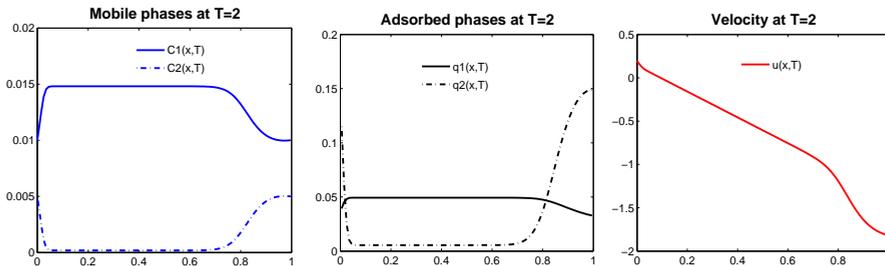


Figure 4: A case of outlet reflux due to a rapid adsorption of one compound. The initial values are not at equilibrium because $c_1^0 = 0.01$, $c_2^0 = 0.005$ whereas $q_1^0 = q_2^0 = 0$ (the bed is supposed to be purged) and the mass-transfer kinetics is greater for the second compound ($A_2 \gg A_1$). This case shows the relevance of the outlet boundary condition (13): it may actually occur that the velocity changes its sign.

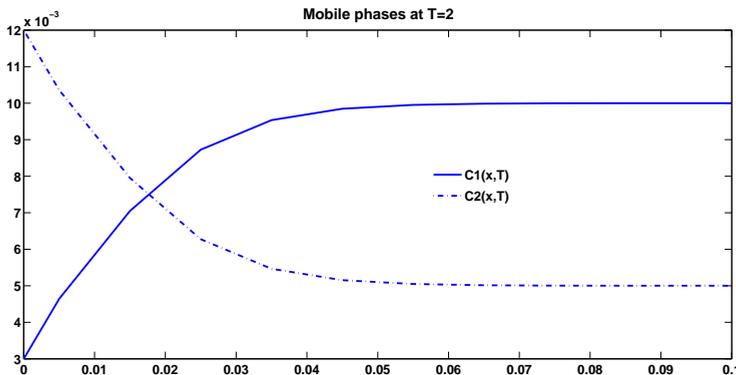


Figure 5: Boundary layer phenomenon: the boundary data are not at equilibrium (here $c_1^{in} = 0.001$, $c_2^{in} = 0.004$, $\rho = 0.015$) and the computed solutions take near $x = 0$ the theoretical values given in Rem. 3, that is here $\widetilde{c}_1^{in} = 0.003$ and $\widetilde{c}_2^{in} = 0.012$.

3.4 Some results on the PSA system with infinite exchange kinetics

When the coefficients A_i in (6)-(7) tend to infinity (instantaneous equilibrium), say $A_i = 1/\varepsilon$ with $\varepsilon \rightarrow 0$ for instance, we get formally, as in the model studied by James (see Subsection 3.1)

$$q_i - q_i^* = -\frac{1}{A_i} \partial_t q_i \rightarrow 0$$

and Equations (6)-(7) reduce to

$$\partial_t(c_i + q_i^*(c_1, \dots, c_d)) + \partial_x(u c_i) = 0, \quad 1 \leq i \leq d, \quad (45)$$

with the constraint (14), thus dealing with a non constant speed. This equation is similar to (18) but here $v = 0$ and u is not constant.

Recently ([9]) the authors focused on the problem (45)-(14) with two compounds and a constant total density $\rho \equiv 1$, assuming an isobaric behavior (which is not really restrictive from a theoretical point of view). The system is:

$$\partial_t(c_1 + q_1^*(c_1, c_2)) + \partial_x(uc_1) = 0, \quad (46)$$

$$\partial_t(c_2 + q_2^*(c_1, c_2)) + \partial_x(uc_2) = 0, \quad (47)$$

$$c_1 + c_2 = \rho = 1. \quad (48)$$

Douglas and *al.* ([16]) developed a general criterion for determining the transitions type for this monovariant system and gave several examples (see also [33]). A first attempt, in the simpler case where one of the compounds is inert, led the authors to an existence and uniqueness result (see [9]) summarized in the next subsection. Rouchon and *al.* ([30]) discussed this model and performed a numerical simulation in the case of one inert compound. The general case, presented in Subsection 3.4.2, is now better understood ([10]) from a mathematical point of view.

3.4.1 Case of an inert carrier gas

In this subsection, we assume that one of the compounds is inert with concentration c_2 and that the spatial domain is \mathbb{R}_+ for the sake of simplicity. We set $c = c_2$ and $h(c) = -q_1^*(c_1, c_2) = -q_1^*(1 - c, c)$, thus, using (15), the system (46)-(47)-(48) may be written under the form:

$$\begin{cases} \partial_t c + \partial_x(uc) = 0, \\ \partial_t h(c) - \partial_x u = 0, \end{cases} \quad (49)$$

supplemented by initial and boundary data:

$$\begin{cases} c(0, x) = c_0(x) \in [0, 1], & x > 0, \\ c(t, 0) = c_b(t) \in [0, 1], & t > 0, \\ u(t, 0) = u_b(t), & t > 0. \end{cases} \quad (50)$$

We assume in (50) an influx boundary condition, i.e. $\forall t > 0, u_b(t) > 0$ and, in this first simplified approach

$$H'(c) \geq 0, \quad h'(c) > 0, \quad (51)$$

where $H(c) = 1 + ch'(c)$. The reference for the results described in this subsection is [9].

First we obtain an existence result for smooth solutions using a classical characteristic method. The interest of this result is mainly to suggest us an entropy condition for shockwaves:

$$(EC) \quad \text{“}c \text{ increases through a shock”}.$$

For smooth solutions, the active gas desorbs and u increases to evacuate gases. Next, we obtain a global existence theorem for a weak solution of System (49)-(50):

Theorem 10 (Global large weak solution)

Let be $X > 0$, $T > 0$. Assume (51) and that $c_0 \in BV(0, X)$, $c_b \in BV(0, T)$, $u_b \in L^\infty(0, T)$, satisfying $0 \leq c_0, c_b \leq 1$ and $\inf_{0 < t < T} u_b(t) > 0$. Then the system (49)-(50) admits a weak solution given by an adapted Godunov scheme. Furthermore, c and u satisfy:

$$\begin{aligned} c &\in L^\infty((0, T) \times (0, X)) \cap L^\infty((0, T); BV(0, X)), \\ c &\in Lip(0, T; L^1(0, X)), \quad c \in BV((0, T) \times (0, X)), \\ u &\in L^\infty((0, T) \times (0, X)) \cap L^\infty((0, T); BV(0, X)), \end{aligned}$$

with bounds on c and u and these functions satisfy initial boundary conditions (50) strongly.

The proof relies on a precise study of the solutions to the Riemann problem satisfying the entropy condition (EC). We use a Godunov scheme to construct an approximate weak solution of Problem (49)-(50) and we give some L^∞ and BV bounds. Lastly, we show that a sequence of approximate solutions converges in some sense towards a global weak entropy solution.

The uniqueness problem for weak entropy solutions was solved in some class of piecewise smooth functions. Nevertheless, this case is relevant in most practical cases and involve global solutions with shock waves and contact discontinuities. Notice that the assumptions in (51) are not really physically relevant because they hold for particular isotherm only. This restriction is avoided in the general approach below (but we no longer have an uniqueness result).

As an illustration for this particular problem we consider the case of an increasing smooth initial concentration of inert gas: a shock develops and then propagates (Fig. 6). Dealing with a finite exchange kinetics, the same case is investigated using the numerical method described in Section 3.3.2 with some increasing values of the coefficient A governing the kinetics for the active gas. The numerical experiments suggest that the model (6)-(7)-(14) could converge in some sense towards the model (45)-(14), but this is still an open problem.

3.4.2 General case

In [10], the authors deal with the case of two compounds which may be active or not, with physically relevant assumptions. Following Rouchon and *al.* ([30]) the problem is analyzed as an hyperbolic system with respect to the (x, t) variables, that is with x as the evolution variable. It appears to be really the key for the mathematical analysis of the problem.

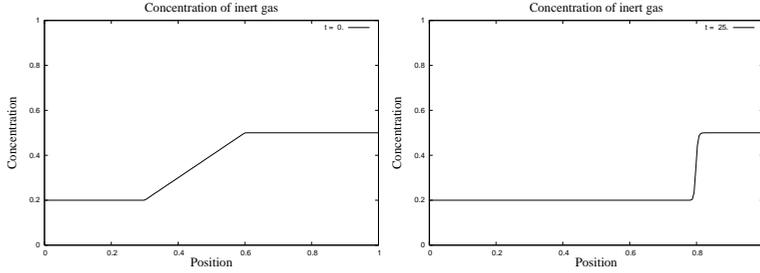


Figure 6: Development of a shock (right side). The initial concentration (left side) is continuous and nondecreasing.

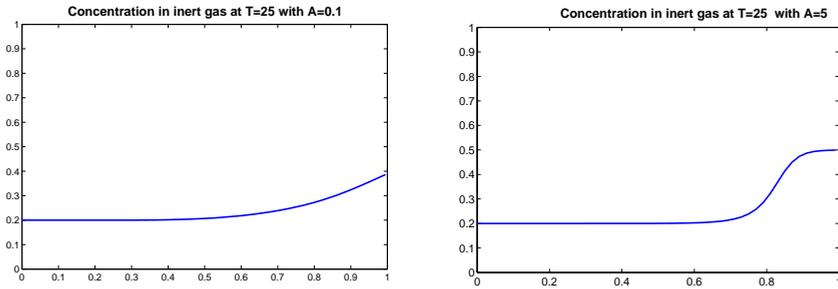


Figure 7: Evolution of an increasing smooth initial concentration of inert gas with a finite exchange kinetics and two different "drawback" coefficients A for the active gas: $A = 0.1$ (left) and $A = 5$ (right). The initial and boundary data are the same as in Fig. 6

We set $c = c_1$ (as in [16], instead of c_2 in [9]), $m = uc$ (flow rate of the first species) and

$$\begin{aligned} q_i(c) &= q_i^*(c, 1 - c), \quad i = 1, 2, \\ h(c) &= q_1(c) + q_2(c), \\ I(c) &= c + q_1(c), \end{aligned}$$

(notice the change of sign in h with respect to [9]). The problem (46)-(47)-(48) is then written under the form

$$\begin{cases} \partial_t I(c) + \partial_x(uc) = 0, \\ \partial_t h(c) + \partial_x u = 0, \end{cases} \quad (52)$$

or equivalently

$$\partial_x U + \partial_t \Phi(U) = 0 \text{ with } U = \begin{pmatrix} u \\ m \end{pmatrix} \text{ and } \Phi(U) = \begin{pmatrix} h(m/u) \\ I(m/u) \end{pmatrix} \quad (53)$$

supplemented by initial and boundary data.

We assume that $q'_1 \geq 0$ and $q'_2 \leq 0$ (general property of all isotherms, see [16]).

This system (53) is hyperbolic, with eigenvalues 0 and $\lambda = \frac{u}{H(c)}$. Introducing the function $f = q_1 c_2 - q_2 c_1$ defined by Douglas and *al.* in [16], written here under the form $f(c) = q_1(c) - c h(c)$, it appears that λ is genuinely nonlinear in each domain where $f'' \neq 0$.

Next, the system admits the two Riemann invariants: c and $w = \ln u + g(c)$,

where g satisfies $g'(c) = \frac{-h'(c)}{H(c)}$ and the smooth entropy families

$$S(c, u) = \phi(w) + u \psi(c) \quad (54)$$

where ϕ and ψ are any smooth real functions.

Let be $G = e^g$: if the sign of G'' changes then the system does not admit any convex smooth entropy but for each convex or degenerate convex smooth function ψ (i.e. $\psi'' \geq 0$) the corresponding entropy $S = u \psi(c)$ is degenerate convex. Introducing a suitable notion of entropy solution, the authors in [10] show the existence of at least such a solution.

The mathematical definition of weak entropy solution is the following: let be $T > 0$, $X > 0$, $u \in L^\infty((0, T) \times (0, X), \mathbb{R}^+)$, $0 \leq c(t, x) \leq 1$ for almost $(t, x) \in (0, T) \times (0, X)$. Then (c, u) is a weak entropy solution if for all convex (or degenerate convex) ψ

$$\frac{\partial}{\partial x}(u\psi(c)) + \frac{\partial}{\partial t}Q(c) \leq 0,$$

in the distribution sense, where $Q' = H\psi' + h'\psi$.

In addition, if $G'' \geq 0$ on $[0, 1]$, (c, u) has to satisfy $\frac{\partial}{\partial x}(uG(c)) \leq 0$.

The main result, relying on the resolution of the Riemann problem and on the Godunov scheme, is the following:

Theorem 11

Let be $T > 0$, $X > 0$, $c_0 \in BV(0, X)$, $c_b \in BV(0, T)$, satisfying $0 \leq c_0, c_b \leq 1$ and $\inf_{0 < t < T} u_b(t) > 0$. Then the system admits a weak entropy solution.

A natural framework for this problem, as in the case of the PSA system with finite exchange kinetics, would be the L^∞ one. Some tracks are presently explored but it is still an open problem.

3.5 Kinetic approaches

The theory of kinetic formulation of hyperbolic systems, introduced by P.-L. Lions, B. Perthame and E. Tadmor [25], consists in representing a whole family of entropy inequalities by a single equation, using a supplementary variable, for the fundamental solution of the wave equation for entropies. It often leads to numerical schemes enjoying interesting properties and easy to implement.

We give first a result due to James, Peng and Perthame ([20]) concerning the

system of electrophoresis. Next, using the results stated in 3.4.2, we present a similar approach for the PSA system, currently developed by the authors.

3.5.1 Kinetic formulation for Electrophoresis

Electrophoresis is a process of separation for compounds in a aqueous solution with an electric field. The corresponding model is close to the chromatography system with Langmuir isotherm ([13, 32]). F. James, Y.-J. Peng and B. Perthame ([20]) have complemented on the system of electrophoresis the theory of kinetic formulation of hyperbolic systems. They gave several applications of this kinetic formulation: a maximum principle and a stability result in L^∞ using compensated compactness. Even though this system is rather related to liquid-solid chromatography (the sorption effect is neglected) we mention these results because the method is powerful and may be extended in other contexts.

The system of electrophoresis is

$$\partial_t c_i + \partial_x \frac{\alpha_i c_i}{D} = 0, \quad t \geq 0, \quad 1 \leq i \leq d, \quad (55)$$

where c_1, \dots, c_d are the positive unknowns, $D = 1 + c_1 + \dots + c_d$ and the α_i are given numbers satisfying $0 < \alpha_1 < \dots < \alpha_d$.

This system admits d eigenvalues $0 < \lambda_1(c) \leq \dots \leq \lambda_d(c)$ and $w_i = \lambda_i D$ is a i -Riemann invariant.

The first step consists in building $d + 1$ families of nonlinear entropies: it is summarized in the following proposition.

Proposition 12

For $0 \leq i \leq d$, the function

$$\chi_i(\xi; w_1, \dots, w_d) = \prod_{j=1}^d \left| 1 - \frac{\xi}{w_j} \right| \mathbb{1}_{]w_i, w_{i+1}[}(\xi)$$

is an entropy of System (55), convex in c , with the entropy flux

$$\phi_i(\xi; w_1, \dots, w_d) = \frac{\xi}{D} \chi_i(\xi; w_1, \dots, w_d).$$

An entropy solution of (55) is a solution satisfying in the distribution sense the inequality

$$\partial_t E + \partial_x F \leq 0$$

for any convex entropy of the form

$$E(c) = \int_{\mathbb{R}_+} g(\xi) \chi_i(\xi; w_1, \dots, w_d) d\xi$$

for some $i, 1 \leq i \leq d, g \in L^1(\mathbb{R}_+)$. Then the authors in [20] derive the following kinetic formulation of (55): there are $d + 1$ non-positive measures $m_i(x, \xi, t)$ such that

$$\partial_t \chi_i(\xi, c(x, t)) + \partial_x \left(\frac{\xi}{D} \chi_i(\xi, c(x, t)) \right) = m_i \quad \text{in } \mathcal{D}'(\mathbb{R}_x \times \mathbb{R}_{+\xi} \times \mathbb{R}_{+t}).$$

Two applications are given in [20]: the maximum and minimum principle on the Riemann invariants and a compactness result. They are recalled in the following two theorems.

Theorem 13

Let c be an entropy solution satisfying $c \in L^\infty(0, T; L^1_{loc}(\mathbb{R}))$, $c_i \geq 0$, $1 \leq i \leq d$. Then

$$\alpha_{i-1} \leq \inf_{y \in \mathbb{R}} w_i(y, 0) \leq w_i(x, t) \leq \sup_{y \in \mathbb{R}} w_i(y, 0) \leq \alpha_i$$

and for some constant $L > 0$

$$L \inf_{y \in \mathbb{R}} c_i^0(y) \leq c_i(x, t) \leq \frac{1}{L} \sup_{y \in \mathbb{R}} c_i^0(y), \quad 1 \leq i \leq d.$$

Theorem 14

Consider an uniformly bounded family $(c_{i,n}(x, t))_{n \geq 0}$ of entropy solutions to the electrophoresis who satisfy that the initial data are uniformly bounded and

$$c_{i,n}(x, t) \rightharpoonup c_i(x, t) \in L^\infty((0, T) \times \mathbb{R}), \quad 1 \leq i \leq d$$

weak* for all $T \in (0, \infty)$ as n tends to $+\infty$. Then $(c_{i,n})_n$ converges pointwise to c_i an entropy solution.

3.5.2 A kinetic approach for the PSA system

A kinetic formulation built on the entropies (54) given in Section 3.4.2 as well as several applications were investigated and will be presented in a forthcoming paper ([11]). More precisely, using the entropy family $u \psi(c)$ where $\psi'' \geq 0$ we first state:

Theorem 15

If (u, c) is a weak entropy solution of System (52), then there exists a nonnegative measure $m(t, x, \xi)$ such that:

$$\partial_x(u \chi(c, \cdot)) + (H(\xi) - a(\xi)) \partial_t \chi(c, \cdot) + \partial_t (h(c) \chi(c, \cdot)) = \partial_\xi m.$$

where

$$\chi(c, \xi) = \begin{cases} 1 & \text{if } 0 < \xi < c \\ 0 & \text{else} \end{cases} \quad \text{and} \quad a(\xi) = 1 + f'(\xi) = H(\xi) - h(\xi).$$

Conversely, if there exists a positive function u such that $\ln u \in L^\infty$, a function $f \in L^1_\xi$ such that $0 \leq f \leq 1$ and a nonnegative measure m such that

$$\partial_x(u f(t, x, \xi)) + a(\xi) \partial_t f(t, x, \xi) + \partial_t (h(c) f(t, x, \xi)) = \partial_\xi m$$

then (u, c) is an entropy solution of (52) with $c(t, x) = \int_0^1 f(t, x, \xi) d\xi$.

Notice that this formulation is not purely kinetic, as in the case of the isentropic gas dynamics system (see [26]).

With this kinetic formulation, the authors in [11] derive a kinetic numerical scheme. This first order explicit scheme satisfies in-cell entropy inequalities, the maximum principle on the concentrations, some BV bounds and is much more simple to implement than Godunov's scheme.

4 Open problems

There are a lot of open problems related to the system (46)-(47)-(48). First, the rigorous derivation of this system from (6)-(7)-(14) considered as a relaxation problem, as in James ([21]), with a small parameter $\varepsilon = 1/A_i$ is *a priori* quite more difficult than for the system (8)-(9). In particular, all the BV estimates stated in [7] blow up. Notice however that numerical experiments, as in Section 3.4.1, show a good behavior in physically relevant context.

The study of oscillating solutions is currently performed by the authors ([12]). A rigorous and general link between the problem with the velocity given by Darcy's law and the constraint (14) has still to be carried out.

There exists some variants of the model taking the axial diffusion or the temperature into account. In particular, the temperature plays a role which may be non negligible. Up to our knowledge, the corresponding problems have never been mathematically studied.

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