

## A New Approach for Chemical Transfer Reaction Models

Zakia Benjelloun-Dabaghi<sup>a</sup>, Renaud Cadours<sup>b</sup>, Sylvie Cauvin<sup>a</sup>, Pascal Mougin<sup>a</sup>

<sup>a</sup>*IFP- 1 & 4, avenue de Bois Préau - 92852 Rueil Malmaison, France*

<sup>b</sup>*IFP-Lyon, Rond Point de l'échangeur de Solaize, BP3, 69360 Vernaison, France*

### Abstract

Problem modelling transfer in the presence of reactions and chemical balances, mathematically results in a 1D differential algebraic, nonlinear equations with boundary and initial conditions. The solution of this system is very sensitive to the numerical method adopted and to the associated algorithm initialization.

The system is composed of three operators: species transfer, reactions and the term coupling the diffusion of the ionic species. The difficulty lies in the coupling term which is usually not taken into account and in the choice of the initialization method. In this work, the MODELICA language allows a simplified formal writing of the mathematical equations. A well adapted numerical method is proposed and validated by comparing the results with those given in Cadours and Bouallou (1998), on the case of CO<sub>2</sub> absorption by aqueous solutions of MDEA.

**Keywords:** Absorption, Algebraic, Differential, Dioxide of Carbon (CO<sub>2</sub>), Initialization, MethylDiEthanolAmine (MDEA), Modelica, Reaction, System1D, Transfer.

### 1. Introduction

Solving mathematical model to improve the understanding of physical phenomena, can be done today, thanks to suitable numerical methods and tools. Those problems are generally performed by solving a non linear differential-algebraic system that takes into account events, or deals with large complex equations.

The MODELICA ([www.Modelica.org](http://www.Modelica.org)) (Fritzson 2004) language allows the users to write the mathematical equations in a simple formal way and to express models in an causal way. To deal with modelling and simulation of very general 0D/1D dynamical systems, SCICOS Software ([www.scicos.org](http://www.scicos.org)) was extended to support the MODELICA language.

The hybrid-Implicit formalism in SCICOS allows users to model very general dynamic systems: Systems including continuous, discrete-time and event based behaviours which are generally referred to as hybrid systems. In Scicos, one can use implicit and explicit blocks. The advantage of implicit blocks relies in their facilities to model physical systems without worrying about writing down and simplifying the equations and making them explicit; it is done automatically by SCICOS. In implicit blocks, physical laws are expressed in terms of mathematical equations. The MODELICA compiler of SCICOS performs symbolic manipulations to simplify the model and generate an index-1 DAE (Campbell et al. 2005)

In our work, the problem of transfer in the presence of reactions and chemical balances is modelled in MODELICA. The resulting 1D differential algebraic, nonlinear system with boundary and initial equation is then simulated in SCICOS.

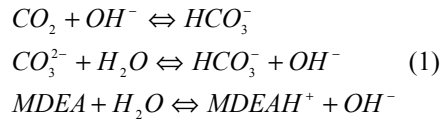
The writing in MODELICA language makes it possible to compare the solutions of the system with and without the coupling term of transfer, in order to evaluate its influence. We compare our results with those of the literature studies dealing with for example the absorption of acid gases in solutions of amines.

We validate this new formulation by comparing our results with those given in Glasscock and Rochelle (1989), Cadours and Bouallou (1998), on the case of the absorption of the carbon dioxide into aqueous mixtures of MDEA.

We show thanks to a simple example that the knowledge of the physical phenomena, and the use of a transformation of the system related to variable and boundaries conditions, makes it possible to overcome difficulties related to its numerical resolution if the system is stiff and ensure a fast convergence of the model.

## 2. The mathematical model

We briefly summarize the complete set of reactions that must be simulated in the mass-transfer model. For the absorption of  $CO_2$  in an aqueous solution of MDEA, the entire reaction scheme considered is shown below:



The resulting mathematical system is composed of three operators: species transfer, reactions and the term coupling the diffusion of the ionic species. The difficulty lies in the coupling term which is usually not taken into account ( $\phi$  in equation (2)).

According to the theory given in Glasscock and Rochelle (1989), Cadours and Bouallou (1998) the Nernst-Planck equation is written for each component involved in the previous chemical reactions (1)

$$\frac{\partial C_i(x,t)}{\partial t} = D_i \frac{\partial^2 C_i(x,t)}{\partial x^2} - z_i D_i \frac{F}{RT} \frac{\partial(\phi(x,t) \times C_i(x,t))}{\partial x} + R_i(x,t) \quad (2)$$

$\phi(x,t)$  is the electrostatic potential gradient, it can be defined according the ion concentration and their diffusivity, in following:

$$\phi(x,t) = \frac{RT}{F} \frac{\sum_{i=1}^{NC} z_i D_i \frac{\partial C_i(x,t)}{\partial x}}{\sum_{i=1}^{NC} z_i^2 D_i C_i} \quad (3)$$

$R_i(x,t)$ , is the species production rate.  $D_i$  diffusivity coefficient for species  $i$ .  $F$  is the Faraday constant,  $R$  the constant of perfect gas and  $T$  the temperature. The composition of all the species is obtained by the material balance equations (1), and the charge

balance given by:  $\sum_{i=1}^{NC} z_i C_i(x,t) = 0$  (4) In order to obtain a well posed problem

(number of unknown equal to a number of equations in the system), we replace, any equation related to a specie  $i$  in (2) by the equation (4). Thus, we obtain an algebraic-

differential non linear system composed of six unknowns:  $CO_2$ ,  $MDEA$ ,  $MDEA^+$ ,  $HCO_3^-$ ,  $CO_3^{2-}$  and  $OH^-$ . According to the film theory used in Glasscock and Rochelle (1989), Cadours and Bouallou (1998), we consider a film of width  $\delta$ .

**Initial conditions**  $1 \leq i \leq NC$

For gas specie ( $CO_2$ ), a linear profile is adopted

$$C_i(x,0) = \left(1 - \frac{x}{\delta}\right) \frac{P_i}{H_i} + C_{i,zm} \frac{x}{\delta} \quad x \geq 0 \quad (5)$$

$$\text{For non gas species : } C_i(x,0) = C_{i,zm} \quad x \geq 0 \quad (6)$$

**Boundary conditions**

At the gas-liquid interface,  $x = 0$

$$\text{For gas specie ( } CO_2 \text{ ) : } C_i(0,t) = \frac{P_i}{H_i} \quad \forall t > 0 \quad (7)$$

$P_i$  And  $H_i$  depend on temperature and initial amine composition. They are given by thermodynamic equilibrium.

$$\text{For non gas species; the transferred species flow is null } \left. \frac{\partial C_i}{\partial x} \right|_{x=0} = 0 \quad (8)$$

In the bulk,  $x = \delta$ , we consider the chemical equilibrium between all species in MDEA solution:  $C_i(\delta,t) = C_{i,zm} \quad \forall i \quad (9)$

**Model parameters**

The values of the different parameters used to simulate the model are the same, in Glasscock-Rochelle (1989) and Cadours-Bouallou (1998). For this model, the orders of magnitude of the kinetic coefficients are very different. It makes the system very stiff, and numerically difficult to solve though it is not large.

**Numerical approximation**

After the modelling step detailed in the previous section, adimensioning of the equations is necessary to simplify the numerical resolution of the stiff system, and to make the physical and chemical interpretation of the phenomena easier. Then, according to the knowledge of the mathematical aspects of the numerical scheme associated to each type of equation, here a parabolic one, a finite approximation using an order 1 and 2 centred is used for space discretisation of Planck's equation.

For the discretisation in time, DASSL integrator has been used in all the publications on the subject until today. It's a **Backward Differentiation Formulae**, and it is well adapted to a stiff system. In this work, DASKR (Najafi 2008) a **BDF** implicit and stiff differential-algebraic system solver, with root finding, and direct, preconditioned Krylov linear solvers is used.

The simulation is performed by MODELICA / SCICOS. The model (equations, parameters, boundary conditions and initial conditions) are simply and formally written under an implicit SCICOS block diagram which contains a computation code. Then the performed integrator DASKR to solve the stiff system in time is performed.

**Adimensioned system:**  $\bar{x} = \frac{x}{\delta}$ , where  $\delta$  is the film width  $\bar{t} = \frac{t D_{CO_2}}{\delta^2}$ ,  $D_i = \frac{D_i}{D_{CO_2}}$ ,

$$\bar{\phi} = \frac{\phi F \delta}{RT}$$

**The differents approximations used:** Let be  $x_0 = 0, x_1, \dots, x_{N+1} = \delta$  one subdivision of the interval  $[0, \delta]$  such as  $x_{j+1} - x_j = h$ ,  $j = 1, \dots, N$   $h = \frac{\delta}{N}$  Set  $C_j^i$  the concentration of the species  $i$  defined  $C^i(x_j, t) = C_j^i$ , The differente approximation are done:

- At the interface  $x=0$ :  $\frac{\partial C_j^i}{\partial x} = \frac{C_j^i - C_{j+1}^i}{\Delta x}$  (10),

- In the film,  $0 < x < \delta$ ,

$$\frac{\partial C_j^i}{\partial x} = \frac{C_{j+1}^i - C_{j-1}^i}{2\Delta x} \quad (11) \quad \frac{\partial^2 C_j^i}{\partial x^2} = \frac{C_{j+1}^i - 2C_j^i + C_{j-1}^i}{(\Delta x)^2} \quad (12)$$

- In the bulk  $x = \delta$ :  $\frac{\partial C_j^i}{\partial x} = \frac{C_{j-1}^i - C_j^i}{2\Delta x}$  (13)

The term of the electrostatic potential gradient will approximate as follows:

$$\phi_j = \frac{RT}{F} \frac{\sum_{i=1}^{NC} z_i D_i \frac{\partial C_j^i}{\partial x}}{\sum_{i=1}^{NC} z_i^2 D_i C_j^i} \approx \frac{RT}{F} \frac{\sum_{i=1}^{NC} z_i D_i \left( \frac{C_{j+1}^i - C_{j-1}^i}{2\Delta x} \right)}{\sum_{i=1}^{NC} z_i^2 D_i C_j^i} \quad (14)$$

- At the interface  $x=0$ :  $\frac{\partial \phi_j}{\partial x} = \frac{\phi_j - \phi_{j+1}}{\Delta x}$  (15)

- In the film,  $0 < x < \delta$ :  $\frac{\partial \phi_j}{\partial x} = \frac{\phi_{j+1} - \phi_{j-1}}{2\Delta x}$  (16)

- In the bulk  $x = \delta$ :  $\frac{\partial \phi_j}{\partial x} = \frac{\phi_{j-1} - \phi_j}{\Delta x}$  (17)

### System initialization

Often, to solve a non linear algebro-differential or purely algebraic system, mathematicians are confronted to the initialization problem. An important advantage of MODELICA lies in the symbolic manipulation of models.

If the initial condition is unknown, solving algebraic system or algebro-differential system can be generally done in two steps. First, by symbolic manipulation, we reduce the model. Physical considerations or chemical ones (steady state, ideal solution, equilibrium) allows us to initialize the reduced system, and then to obtain a solution which is considered as the initialization of the complete system.

### 3. Results

First, we simulate the system considering the diffusion operator. Then, to evaluate the influence of the reaction term, simulations are done with the two operators diffusion and reaction. Then, the influence of the gradient term is studied both on the diffusion operator and on the coupled operator diffusion/reaction. Comparison with Glasscock-Rochelle (1989) system coupling potential gradient with the reaction does not converge so the results are not compared. In the other cases, the same results are obtained in Glasscock-Rochelle (1989) and in Cadours-Bouallou (1998). In Cadours-Bouallou (1998), only transfer and reaction phenomena are considered.

Scenario simulations for  $CO_2$ , comparison Modelica /Scicos and Cadours /Bouallou  
( $CO_2$ ) initial = 0.1mol/m<sup>3</sup>

$\delta$	Diffusion (1)	Cadours & Bouallou (2)	Diffusion and reaction (3)	Difference Abs((3)-(2))	Diffusion, reaction and potential (4)	Difference : Abs ((4)-(3))	Difference : Abs ((4)-(2))
0	0.1	0.1	0.1	0.0000000	0.1	0.0000000	0.0000000
0.1	0.0889	0.0168	0.01751	0.0007100	0.01766	0.0001500	0.0008600
0.2	0.0779	0.00323	0.0035	0.0002700	0.00372	0.0002200	0.0004900
0.3	0.0668	0.00104	0.00109	0.0000500	0.00131	0.0002200	0.0002700
0.4	0.0557	0.000669	0.00066	0.0000090	0.00084	0.0001800	0.0001710
0.5	0.0447	0.000585	0.00056	0.0000250	0.00071	0.0001500	0.0001250
0.6	0.0336	0.000543	0.00051	0.0000330	0.00063	0.0001200	0.0000870
0.7	0.0225	0.000507	0.00048	0.0000270	0.00055	0.0000700	0.0000430
0.8	0.0115	0.000471	0.00044	0.0000310	0.00048	0.0000400	0.0000090
0.9	0.0004	0.000435	0.0004	0.0000350	0.0004	0.0000000	0.0000350

As expected, the reaction term have a considerable effect on mass transfer. The potential gradient influence can be neglected, taking into account the uncertainties on the diffusion coefficient, especially for ionic species. These results confirm the usual assumption of many works in the literature concerning the potential gradient.

All those results are obtained immediately on a standard Windows Machine.

### 4. Conclusion

Modelling using an implicit causal approach has the major advantage of maintaining the similarity between the model and the chemical/physical system. Unlike other approaches in which a small change in the system may lead to big changes in the model, writing the equations in MODELICA in an implicit form allows the users to implement and to modify the system very easily.

Symbolic manipulation of models lies in giving several possibilities such as index reduction and generation of the analytical Jacobian which speeds up the simulation.

This work shows, that with the Modelica / Scicos formulation, it can be easier to study compare and explain influences of different phenomena which happen in the absorption of  $CO_2$  in an aqueous solution of MDEA for example.

In SimPA2-C6E2 RNTL project (Najafi 2005), this approach was validated in drilling oil, to deal with a large complex 1D implicit system, and in automotive industry to test the abilities of this approach to solve the switch in the same bloc's equations, known as commutated models, and to solve corresponding 0D hybrid system.

Our aim, in the future is to test this approach in a large non linear system related to the simulation of absorption into alkanolamines mixture.

## References

1. Brenan K.E., Campbell S.L., Petzold L.R. : Numerical solution of Initial – Value Problems Differential – Algebraic Equations. "Classics in Applied Mathematics", Siam eds.(1996).
2. Cadours R., Bouallou C. : Rigorous simulation of gas absorption into aqueous solutions. Ind. Eng. Chem. Res. 1998, 37, 1063.
3. Campbell S.L.; Chancelier J.P.; and Nikoukhah R., 2005. Modeling and simulation Scilab/Scicos. Springer Verlag, 1st ed.
4. Fritzson P., 2004. Principles of Object-Oriented Modeling and Simulation with Modelica 2.1. Wiley-IEEE Press, 1st ed. ISBN 0-471-47163-1.
5. Glasscock D.A., Rochelle G.T. : Numerical simulation of theories for gas absorption with chemical reaction. AIChE J. 1989, 35, 1271.
6. Najafi Massoud, Benjelloun - Dabaghi Zakia: Modeling complex systems with Modelica in Scicos, Application to mean value spark engine, and drilling well. Journal of Oil and Gas Technologies (to appear)
7. Najafi M., 2005. The Numerical Solver for the Simulation of the hybrid Dynamical Systems. Doctor of science thesis, Paris XII University.