

# Reactive Extraction Using Moving Liquid Membranes - Mathematical Model Calibration Through Experiments

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*A reactive extraction/back-extraction process was studied experimentally in a two-stage column. The mathematical model of the reactive extraction using a closed loop moving organic liquid membrane, based upon first principle equations, was derived as a set of Partial/Ordinary Differential Algebraic Equations (P/ODAE). The mathematical model, reduced through orthogonal collocation to a system of ODAE, was solved using a self-adaptive Runge-Kutta (RK)-type method. The mathematical model was calibrated using own batch experimental data and a modified genetic algorithm as optimizer.*

*Keywords: reactive extraction, liquid-liquid extraction, hydrocarboxylic acids, moving membrane column modeling*

Separation of many chemical compounds from aqueous waste streams (industrial effluents) to comply with the ecological discharge limits is essential from the pollution control's point of view; one particular class is represented by the organic acids [1-3]. Many separation processes aiming to recover the hydrocarboxylic acids from aqueous solutions have been investigated; their screening shows that liquid-liquid extraction is often the most suitable option [4-6] because other methods are expensive and environmentally unfriendly. One particular case of liquid-liquid extraction is represented by the liquid membrane (LM) processes, due to the significant specific interfacial areas (SIAs), which is one of the most important parameters of the dispersed liquid/liquid systems, satisfying the needs of process engineers [7] (between 1000 -3000 m<sup>2</sup>/m<sup>3</sup> of equipment volume), and a quasi-permanent membrane life due to the ease of formation and recovery. Since Li [8] made the first try to separate hydrocarbons by a liquid surfactant membrane (LSM), many efforts have been made to apply LMs to other separation processes like chemical species removal [9-11] or the control of water pollution and metal recovery [12-15]. Most of the research on the LM has been conducted in small batch or hollow fiber module membrane tests at laboratory scale [16-19] and significantly less research efforts for the continuous pilot scale tests have been made.

The LMs lump, according to their mobility, into two broad classes: *the mobile liquid surfactant membranes* (MLSMs) and *the supported liquid membranes* (SLMs). The MLSMs generally imply batch extraction column devices, with respect to the continuous phase, in which the dispersed membrane phase is strongly mixed with the donor phase – the SIA being directly related to the mixing intensity – and moves in and out the working volume. In the SLMs case, the membrane phase is immobilized in the pores of a solid wall (generally a hollow fiber type) and ensures the link between the donor and receiver phases, both having an independent circulation – in this case, the specific interfacial area depends only upon the porosity of the solid wall [20].

Since the extraction using the thermodynamic equilibrium between pure LMs and water (the most used donor liquid phase) was found economically unattractive, especially when the carried species have low concentrations, a new method, the reactive extraction

(RE), is developed in order to intensify separation throughout an active rather than passive mediated mass transfer [1]. This method represents a combination of chemical (solute and carrier reactions) and physical (diffusion and solubility of the system components) phenomena and requires a proper choice of extractants and diluents ensuring higher capacity and selectivity. Various aspects of RE, like the influence of the extractants, acid and carrier concentrations and type, nature of the acid and diluents, effect of extraction temperature, water co-extraction, were studied in literature [2]. At the same time, many chemical species were tested as reactive carrier confined into the membrane phase to recover the carboxylic acids from dilute solutions, i.e. organophosphorous compounds, tertiary and quaternary amines etc. The tertiary amines have proved to be the most successful reactive carrier species in the acid RE process with LMs [1].

The MLSM extraction is generally modeled using one of the following approaches: ordinary permeation, facilitated transport and molecular pumping. Recent works take into account undesirable intrinsic phenomena such as swelling and breakage of the drops, whose distribution have to be controlled during the RE process [21]. Few works present a complete mathematical model including all the processes implied by a reactive MLSM: the RE, the chemical processes within the moving liquid membrane (MLM) and the reactive back extraction.

The main objective of the present work is the modeling of the RE of the acetic acid from an aqueous dilute solution in a column device type using a moving liquid reactive membrane (MLRM) and the validation of the model using own experimental data. The experiments are developed in a two-stage column, whose active volumes are separated by a pseudo-stationary LM [22-25]. Several organic solvents (polar or non-polar) with or without trioctylamine (TOA) as reactive carrier were investigated as candidate MLRMs. The back-extraction (BE) process was conducted in the presence or absence of an alkaline solution (NaOH), in order to emphasize the role of the secondary RE on the column reactive separation yield. Thus, the model, based upon first principle equations, encapsulates the dynamic behavior of the RE/RBE column.

A complete set of factorial experiments were conducted, covering all possible combinations of plain or mediated extractions using MLMs: simple extraction/back-extraction

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in water, extraction followed by back-extraction in alkaline solution, extraction with carrier followed by plain back-extraction and finally reactive extraction with carrier/back-extraction in alkaline solution. This work will address the latter experiment; the corresponding data will be used to identify the parameters of the mathematical model of the reactive extraction using a closed loop MLRM, which represents a major extension of some previous works [22-24].

## Experimental part

### Materials, methods and equipment

#### Reagents and solutions

Distilled water (previously saturated with MLM) was used during the experimental part of this work. Acetic acid, the transported species, was supplied by Chimopar™ S.A. Bucharest, while the solvents (n-octanol, cyclohexanol, petroleum ether and paraffin oil), the alkali and TOA were purchased from Merck™ Co. The aqueous solutions were prepared by diluting acid solution with distilled water without pH adjustment, since this would have had as result a possible voluntary contamination of the mixture. The alkali solution was prepared using distilled water too. The organic solvent was saturated with water prior to be used.

The acid extraction from aqueous solution was performed in the experimental setup [23, 25] presented in figure 1.

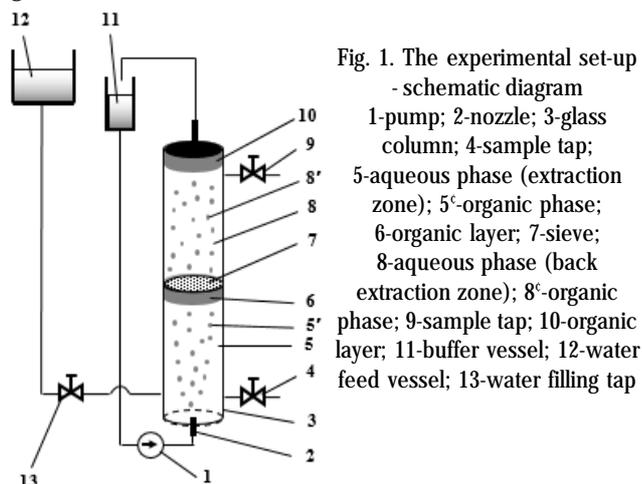


Fig. 1. The experimental set-up - schematic diagram  
1-pump; 2-nozzle; 3-glass column; 4-sample tap; 5-aqueous phase (extraction zone); 5'-organic phase; 6-organic layer; 7-sieve; 8-aqueous phase (back extraction zone); 8'-organic phase; 9-sample tap; 10-organic layer; 11-buffer vessel; 12-water feed vessel; 13-water filling tap

The glass column has 660 mm height and 40 mm inner diameter. The MLRM in this case is organic solvent in which the TOA is diluted; the MLRM is fed through the nozzle (2) into the extraction zone (5) by the pump (1). Dispersed in small droplets (5') the MLRM rise through the continuous aqueous phase due to the density difference and by coalescence under the sieve will form a continuous layer (6). This way, the aqueous phases (the extraction zone - 5 and the back-extraction zone - 8) are completely separated. When the MLRM enters the extraction zone, due to the incompressible nature of the liquids, new droplets of MLRM (8') are formed into the BE region, due to the sieve which acts like a nozzle. The droplets from the BE zone rise to the top of the column where they coalesce again into a bulk (10), preventing water from escaping the BE zone. From the top of the column, the MLRM is collected into a buffer vessel (11), from which the circuit is closed back by the pump (1). The MLRM acts as a carrier for the acetic acid. The acid removal has two components: the reactive one, TOA, which enhances the extraction process by chemically reacting (reversible process) with the acid to form a complex (Ac-TOA), and the passive one, the organic phase, in which TOA and Ac-TOA are confined; nonetheless, the organic phase participate, as well, to the extraction/back-extraction processes, since the acetic acid

has a significant solubility in the organic phase. Then the Ac-TOA is transported to the continuous layer under the sieve due to the MLRM ascending flow and from here into the BE region of the column. During this movement, the Ac-TOA formation process continues if the acid is in excess with respect to thermodynamic equilibrium, or, if the acid is in deficit, Ac-TOA decomposes into acid and TOA. In the BE zone, at the MLRM-water interface, the acetic acid gets consumed, into a very fast chemical process, by the alkali from the continuous phase to form a product (a salt of acetic acid) soluble in water only. The MLRM is recycled then and the process continues till the acid is completely removed from the bottom of the column. The concentration of the transported species (acetic acid) in the continuous phase of the extraction zone was determined by titration, removing small samples of liquid at several time-intervals, care being taken not to disturb the phases' circulation in the column.

### Modeling the process

#### Main hypothesis

The mathematical model, an extension of a former approach for plain physical extraction [23], was developed under the following simplifying assumptions (the schematic diagram in fig. 2):

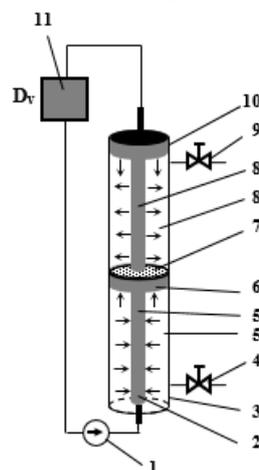


Fig. 2. The experimental set-up - the two phase circulation model  
1-pump; 2-nozzle; 3-glass column; 4-sample tap; 5-aqueous phase (extraction zone); 5'-organic phase; 6-organic layer; 7-sieve; 8-aqueous phase (back extraction zone); 8'-organic phase; 9-sample tap; 10-organic layer; 11-buffer vessel

-the dispersed organic phase (composite carrier - n-octanol and TOA) was lumped into two virtual cylinders, coaxial with and surrounded by the aqueous phase (fig. 2, 5 and 8), one for each of the halves of the column;

-the axial dispersion model was assumed for the organic phase rising through the virtual cylinders, to take into account the combined effect of the ascending drops coalescence - breaking phenomena (with a rather small frequency);

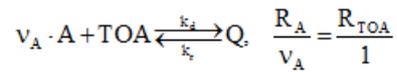
-both zones with acetic acid (bottom) and alkali (top) aqueous solutions were assumed perfectly mixed; if the circulating cells induced by the upward movement of the drops do not extend into the whole aqueous regions, a more suitable model could be used, such as a cascaded perfectly mixed cells with small interconnected flows;

-the organic layers under the sieve and on the top of the column together with the buffer vessel are considered perfectly mixed;

-the thermodynamic equilibrium is instantaneously established at the liquid-liquid interface for the transported species (acetic acid, in this case);

-the chemical reaction between the acid and the alkali solution (NaOH in large excess) in the BE zone is considered very fast, occurring at the organic-aqueous interface;

-the stoichiometry and kinetic of the chemical reaction between acetic acid and TOA has the form [26]:



$$R_A = k_d \cdot C_A^\alpha \cdot C_{\text{TOA}}^\beta - k_r \cdot C_Q^\gamma = k_d \cdot \left( C_A^\alpha \cdot C_{\text{TOA}}^\beta - \frac{C_Q^\gamma}{K_C} \right)$$

where  $\alpha=0.73$ ;  $\beta=1$  and  $\gamma=1$ ; from now on Ac-TOA will be denoted with Q; we considered this chemical reaction as fast with respect to the mass transfer since the species involved are two acid and base not so strong, while the mass transfer in the aqueous phase is rather high, due to the ascending motion of the drops.

- the volume of the pipes external to the column is negligible;
- the process is isothermal.

### Mathematical model

Taking into account the above mentioned hypotheses, the mathematical model is obtained as a system of partial and ordinary differential equations encoding the mass balances around the corresponding volumes for each zone of the column.

The extraction zone (bottom of the column)

The mathematical equations in dimensionless form (using the reference variables  $C_{A,ex}^{in}$ ,  $\bar{t}$ ,  $H_{ex}$ ,  $H_{bk}$ ) together with its two main novelties: a) every mass balance equation written for the composite organic carrier phase has a new term

accounting for the chemical process, i.e. in dimensionless form  $K_d \cdot \left( (\Gamma_{ex}^{A,o})^\alpha \cdot (\Gamma_{ex}^{\text{TOA}})^\beta - \frac{(\Gamma_{ex}^Q)^\gamma}{(C_{ex}^{A,in})^{\alpha+\beta-\gamma} \cdot K_C} \right)$ ; b) the overall mass

transfer coefficients are written considering the interplay between mass transfer and chemical process rates at the liquid - liquid interface are:

### The MLRM phase

For the acid:

$$\frac{\partial \Gamma_{ex}^{A,o}}{\partial \tau} + \frac{1}{\omega_{ex}} \cdot \frac{\partial \Gamma_{ex}^{A,o}}{\partial \xi_{-ex}} = \frac{D_{g_{ex}}^A}{\omega_{ex}} \cdot \frac{\partial^2 \Gamma_{ex}^{A,o}}{\partial \xi_{-ex}^2} + K_{ex}^o \cdot (\Gamma_{ex}^{A,a} - K_{eq} \cdot \Gamma_{ex}^{A,o}) - K_d \cdot \left( (\Gamma_{ex}^{A,o})^\alpha \cdot (\Gamma_{ex}^{\text{TOA}})^\beta - \frac{(\Gamma_{ex}^Q)^\gamma}{(C_{ex}^{A,in})^{\alpha+\beta-\gamma} \cdot K_C} \right) \quad (1)$$

Due to the fact that the chemical process between TOA and acetic acid may be seen as fast with respect to the mass transfer in both liquid phases, the overall mass transfer coefficient expression should had been derived accordingly [27]. The kinetic is non-linear with respect to reactants and none of them is in great excess, to be considered constant during the process; thus the reaction's order cannot be reduced to one and no analytical expression can be built. Taking into account that neither the partial mass transfer coefficients on both sides of the interface, nor the kinetic constant of the forward reaction are known, and should be regressed from experimental data once the mathematical model is built, we circumvent the aforementioned difficulty considering that only the mass transfer rates in both phases are rate limiting in

computing  $K_{ex}^o = \frac{1}{\frac{1}{k_{ex}^{A,a}} + \frac{K_{eq}}{k_{ex}^{A,o}}}$ . We are confident that the possible inferences between mass transfer and chemical process will appear, in fact, in the regressed values of  $k_{ex}^{A,a}$ ,  $k_{ex}^{A,o}$  and  $k_d$ .

For the TOA:

$$\frac{\partial \Gamma_{ex}^{\text{TOA}}}{\partial \tau} + \frac{1}{\omega_{ex}} \cdot \frac{\partial \Gamma_{ex}^{\text{TOA}}}{\partial \xi_{-ex}} = \frac{D_{g_{ex}}^{\text{TOA}}}{\omega_{ex}} \cdot \frac{\partial^2 \Gamma_{ex}^{\text{TOA}}}{\partial \xi_{-ex}^2} - \frac{K_d}{v_A} \cdot \left( (\Gamma_{ex}^{A,o})^\alpha \cdot (\Gamma_{ex}^{\text{TOA}})^\beta - \frac{(\Gamma_{ex}^Q)^\gamma}{(C_{ex}^{A,in})^{\alpha+\beta-\gamma} \cdot K_C} \right) \quad (2)$$

For the complex Q:

$$\frac{\partial \Gamma_{ex}^Q}{\partial \tau} + \frac{1}{\omega_{ex}} \cdot \frac{\partial \Gamma_{ex}^Q}{\partial \xi_{-ex}} = \frac{D_{g_{ex}}^Q}{\omega_{ex}} \cdot \frac{\partial^2 \Gamma_{ex}^Q}{\partial \xi_{-ex}^2} + \frac{K_d}{v_A} \cdot \left( (\Gamma_{ex}^{A,o})^\alpha \cdot (\Gamma_{ex}^{\text{TOA}})^\beta - \frac{(\Gamma_{ex}^Q)^\gamma}{(C_{ex}^{A,in})^{\alpha+\beta-\gamma} \cdot K_C} \right) \quad (3)$$

### The aqueous phase

For the acid:

$$\frac{d\Gamma_{\text{ex}}^{A,a}}{d\tau} = -K_{\text{ex}}^a \cdot \left( \frac{4 \cdot \delta_{\text{ex}}}{1 - \delta_{\text{ex}}^2} \cdot \int_0^1 (\Gamma_{\text{ex}}^{A,a} - K_{\text{eq}} \cdot \Gamma_{\text{ex}}^{A,o}) \cdot d\xi_{\text{ex}} + \frac{\Gamma_{\text{ex}}^{A,a} - K_{\text{eq}} \cdot \Gamma_{\text{ex}}^{A,o}}{S_{\text{ex}}} \right) \quad (4)$$

The separation zone between extraction and stripping

For the acid:

$$\begin{aligned} \frac{d\Gamma_{\text{ex-re}}^{A,o}}{d\tau} = & \frac{\Gamma_{\text{ex}}^{A,o} - \Gamma_{\text{ex-re}}^{A,o}}{\omega_{\text{ex-re}}} + K_{\text{ex-re}} \cdot (\Gamma_{\text{ex}}^{A,a} - K_{\text{eq}} \cdot \Gamma_{\text{ex-re}}^{A,o}) - \\ & - K_d \cdot \left( (\Gamma_{\text{ex-re}}^{A,o})^\alpha \cdot (\Gamma_{\text{ex-re}}^{\text{TOA}})^\beta - \frac{(\Gamma_{\text{ex-re}}^{\text{Q}})^{\gamma}}{(C_{\text{ex}}^{A,\text{in}})^{\alpha+\beta-\gamma} \cdot K_C} \right) \end{aligned} \quad (5)$$

For the TOA:

$$\frac{d\Gamma_{\text{ex-re}}^{\text{TOA}}}{d\tau} = \frac{\Gamma_{\text{ex}}^{\text{TOA}} - \Gamma_{\text{ex-re}}^{\text{TOA}}}{\omega_{\text{ex-re}}} - \frac{K_d}{V_A} \cdot \left( (\Gamma_{\text{ex-re}}^{A,o})^\alpha \cdot (\Gamma_{\text{ex-re}}^{\text{TOA}})^\beta - \frac{(\Gamma_{\text{ex-re}}^{\text{Q}})^{\gamma}}{(C_{\text{ex}}^{A,\text{in}})^{\alpha+\beta-\gamma} \cdot K_C} \right) \quad (6)$$

For the chemical complex:

$$\frac{d\Gamma_{\text{ex-re}}^{\text{Q}}}{d\tau} = \frac{\Gamma_{\text{ex}}^{\text{Q}} - \Gamma_{\text{ex-re}}^{\text{Q}}}{\omega_{\text{ex-re}}} + \frac{K_d}{V_A} \cdot \left( (\Gamma_{\text{ex-re}}^{A,o})^\alpha \cdot (\Gamma_{\text{ex-re}}^{\text{TOA}})^\beta - \frac{(\Gamma_{\text{ex-re}}^{\text{Q}})^{\gamma}}{(C_{\text{ex}}^{A,\text{in}})^{\alpha+\beta-\gamma} \cdot K_C} \right) \quad (7)$$

The stripping zone (top of the column)

The MLRM phase

For the acid:

$$\begin{aligned} \frac{\partial \Gamma_{\text{re}}^{A,o}}{\partial \tau} + \frac{1}{\omega_{\text{re}}} \cdot \frac{\partial \Gamma_{\text{re}}^{A,o}}{\partial \xi_{\text{re}}} = & \frac{Dg_{\text{re}}^A}{\omega_{\text{re}}} \cdot \frac{\partial^2 \Gamma_{\text{re}}^{A,o}}{\partial \xi_{\text{re}}^2} - K_{\text{re}}^o \cdot \Gamma_{\text{re}}^{A,o} \\ & - K_d \cdot \left( (\Gamma_{\text{ex-re}}^{A,o})^\alpha \cdot (\Gamma_{\text{ex-re}}^{\text{TOA}})^\beta - \frac{(\Gamma_{\text{ex-re}}^{\text{Q}})^{\gamma}}{(C_{\text{ex}}^{A,\text{in}})^{\alpha+\beta-\gamma} \cdot K_C} \right) \end{aligned} \quad (8)$$

Since the acid-base chemical reaction is considered very fast with respect to the mass transfer, the former takes place in a reaction front stabilized at the interface, so  $K_{\text{re}}^o$  is, in fact, the dimensionless partial mass transfer coefficient with respect to the organic phase.

For the TOA:

$$\frac{\partial \Gamma_{\text{re}}^{\text{TOA}}}{\partial \tau} + \frac{1}{\omega_{\text{re}}} \cdot \frac{\partial \Gamma_{\text{re}}^{\text{TOA}}}{\partial \xi_{\text{re}}} = \frac{Dg_{\text{re}}^{\text{TOA}}}{\omega_{\text{re}}} \cdot \frac{\partial^2 \Gamma_{\text{re}}^{\text{TOA}}}{\partial \xi_{\text{re}}^2} - \frac{K_d}{V_A} \cdot \left( (\Gamma_{\text{ex-re}}^{A,o})^\alpha \cdot (\Gamma_{\text{ex-re}}^{\text{TOA}})^\beta - \frac{(\Gamma_{\text{ex-re}}^{\text{Q}})^{\gamma}}{(C_{\text{ex}}^{A,\text{in}})^{\alpha+\beta-\gamma} \cdot K_C} \right) \quad (9)$$

For the chemical complex:

$$\frac{\partial \Gamma_{\text{re}}^{\text{Q}}}{\partial \tau} + \frac{1}{\omega_{\text{re}}} \cdot \frac{\partial \Gamma_{\text{re}}^{\text{Q}}}{\partial \xi_{\text{re}}} = \frac{Dg_{\text{re}}^{\text{Q}}}{\omega_{\text{re}}} \cdot \frac{\partial^2 \Gamma_{\text{re}}^{\text{Q}}}{\partial \xi_{\text{re}}^2} + \frac{K_d}{V_A} \cdot \left( (\Gamma_{\text{ex-re}}^{A,o})^\alpha \cdot (\Gamma_{\text{ex-re}}^{\text{TOA}})^\beta - \frac{(\Gamma_{\text{ex-re}}^{\text{Q}})^{\gamma}}{(C_{\text{ex}}^{A,\text{in}})^{\alpha+\beta-\gamma} \cdot K_C} \right) \quad (10)$$

The aqueous phase

For the base:

$$\frac{d\Gamma_{\text{re}}^{\text{B}}}{d\tau} = -K_{\text{re}}^a \cdot \left( \frac{4 \cdot \delta_{\text{re}}}{1 - \delta_{\text{re}}^2} \cdot \int_0^1 \Gamma_{\text{re}}^{A,o} \cdot d\xi_{\text{re}} + \frac{\Gamma_{\text{re}}^{A,o}}{S_{\text{re}}} \right) \quad (11)$$

All the acid from the organic carrier gets reacted with the base from the top column water, so the consumption rate of the base will be given by the molar flow of acid coming from the organic phase.

The continuous organic layer from the top of the column

For the acid:

$$\frac{d\Gamma_f^{A,o}}{dt} = \frac{\Gamma_{re}^{A,o} - \Gamma_f^{A,o}}{\omega_f} - K_f^o \cdot \Gamma_f^{A,o} - K_d \cdot \left( \left( \Gamma_{ex-re}^{A,o} \right)^\alpha \cdot \left( \Gamma_{ex-re}^{TOA} \right)^\beta - \frac{\left( \Gamma_{ex-re}^Q \right)^\gamma}{\left( C_{ex}^{A,in} \right)^{\alpha+\beta-\gamma} \cdot K_C} \right) \quad (12)$$

For the TOA:

$$\frac{d\Gamma_f^{TOA}}{dt} = \frac{\Gamma_{re}^{TOA} - \Gamma_f^{TOA}}{\omega_f} - \frac{K_d}{V_A} \cdot \left( \left( \Gamma_{ex-re}^{A,o} \right)^\alpha \cdot \left( \Gamma_{ex-re}^{TOA} \right)^\beta - \frac{\left( \Gamma_{ex-re}^Q \right)^\gamma}{\left( C_{ex}^{A,in} \right)^{\alpha+\beta-\gamma} \cdot K_C} \right) \quad (13)$$

For the chemical complex:

$$\frac{d\Gamma_f^Q}{dt} = \frac{\Gamma_{re}^Q - \Gamma_f^Q}{\omega_f} + \frac{K_d}{V_A} \cdot \left( \left( \Gamma_{ex-re}^{A,o} \right)^\alpha \cdot \left( \Gamma_{ex-re}^{TOA} \right)^\beta - \frac{\left( \Gamma_{ex-re}^Q \right)^\gamma}{\left( C_{ex}^{A,in} \right)^{\alpha+\beta-\gamma} \cdot K_C} \right) \quad (14)$$

The buffer vessel:

For the acid:

$$\frac{d\Gamma_v^{A,o}}{dt} = \frac{\Gamma_f^{A,o} - \Gamma_v^{A,o}}{\omega_v} - K_d \cdot \left( \left( \Gamma_{ex-re}^{A,o} \right)^\alpha \cdot \left( \Gamma_{ex-re}^{TOA} \right)^\beta - \frac{\left( \Gamma_{ex-re}^Q \right)^\gamma}{\left( C_{ex}^{A,in} \right)^{\alpha+\beta-\gamma} \cdot K_C} \right) \quad (15)$$

For the TOA:

$$\frac{d\Gamma_v^{TOA}}{dt} = \frac{\Gamma_f^{TOA} - \Gamma_v^{TOA}}{\omega_v} - \frac{K_d}{V_A} \cdot \left( \left( \Gamma_{ex-re}^{A,o} \right)^\alpha \cdot \left( \Gamma_{ex-re}^{TOA} \right)^\beta - \frac{\left( \Gamma_{ex-re}^Q \right)^\gamma}{\left( C_{ex}^{A,in} \right)^{\alpha+\beta-\gamma} \cdot K_C} \right) \quad (16)$$

For the chemical complex:

$$\frac{d\Gamma_v^Q}{dt} = \frac{\Gamma_f^Q - \Gamma_v^Q}{\omega_v} + \frac{K_d}{V_A} \cdot \left( \left( \Gamma_{ex-re}^{A,o} \right)^\alpha \cdot \left( \Gamma_{ex-re}^{TOA} \right)^\beta - \frac{\left( \Gamma_{ex-re}^Q \right)^\gamma}{\left( C_{ex}^{A,in} \right)^{\alpha+\beta-\gamma} \cdot K_C} \right) \quad (17)$$

The dimensionless initial and boundary conditions

Initial conditions:

$$\Gamma_f^{A,o} = \Gamma_f^Q = 0; \quad \Gamma_f^{TOA} = \frac{C_{ex}^{TOA,in}}{C_{ex}^{A,in}} \quad (18 f)$$

$$\tau = 0 \quad \xi_{ex} \geq 0 \quad (18)$$

$$\Gamma_{ex}^{A,a} = 1 \quad (18 a)$$

$$\Gamma_v^{A,o} = \Gamma_v^Q = 0; \quad \Gamma_v^{TOA} = \frac{C_{ex}^{TOA,in}}{C_{ex}^{A,in}} \quad (18 g)$$

$$\Gamma_{ex}^{A,o} = \Gamma_{ex}^Q = 0; \quad \Gamma_{ex}^{TOA} = \frac{C_{ex}^{TOA,in}}{C_{ex}^{A,in}} \quad (18 b)$$

Boundary conditions:

$$\tau > 0, \quad \xi_{ex} = 0 \quad (19)$$

$$\Gamma_{ex-re}^{A,o} = \Gamma_{ex-re}^Q = 0; \quad \Gamma_{ex-re}^{TOA} = \frac{C_{ex}^{TOA,in}}{C_{ex}^{A,in}} \quad (18 c)$$

$$\Gamma_{re}^{A,o} = \Gamma_{re}^Q = 0; \quad \Gamma_{re}^{TOA} = \frac{C_{ex}^{TOA,in}}{C_{ex}^{A,in}} \quad (18 d)$$

$$\Gamma_{re}^B = \frac{C_{re}^{B,in}}{C_{ex}^{A,in}} \quad (18 e)$$

$$\left\{ \begin{array}{l} \left. \frac{\partial \Gamma_{ex}^{A,o}}{\partial \xi_{ex}} \right|_{\xi_{ex}=0} = D_{G_{ex}^A} \cdot \left( \Gamma_{ex}^{A,o} - \Gamma_v^{A,o} \right) \\ \left. \frac{\partial \Gamma_{ex}^{TOA,o}}{\partial \xi_{ex}} \right|_{\xi_{ex}=0} = D_{G_{ex}^{TOA}} \cdot \left( \Gamma_{ex}^{TOA} - \Gamma_v^{TOA} \right) \\ \left. \frac{\partial \Gamma_{ex}^{Q,o}}{\partial \xi_{ex}} \right|_{\xi_{ex}=0} = D_{G_{ex}^Q} \cdot \left( \Gamma_{ex}^Q - \Gamma_v^Q \right) \end{array} \right. \quad (19 a)$$

$$\xi_{\text{ex}} = 1 \quad \frac{\partial \Gamma_{\text{ex}}^{\text{A.o}}}{\partial \xi_{\text{ex}}} = 0; \quad \frac{\partial \Gamma_{\text{ex}}^{\text{TOA}}}{\partial \xi_{\text{ex}}} = 0; \quad \frac{\partial \Gamma_{\text{ex}}^{\text{Q}}}{\partial \xi_{\text{ex}}} = 0 \quad (19 \text{ b})$$

$$\tau > 0, \quad \xi_{\text{re}} = 0 \quad (20)$$

$$\begin{cases} \Gamma_{\text{re}}^{\text{A.o}} = \Gamma_{\text{ex-re}}^{\text{A.o}} \\ \Gamma_{\text{re}}^{\text{TOA}} = \Gamma_{\text{ex-re}}^{\text{TOA}} \\ \Gamma_{\text{re}}^{\text{Q}} = \Gamma_{\text{ex-re}}^{\text{Q}} \end{cases} \quad (20 \text{ a})$$

$$\xi_{\text{re}} = 1 \quad \frac{\partial \Gamma_{\text{re}}^{\text{A.o}}}{\partial \xi_{\text{re}}} = 0; \quad \frac{\partial \Gamma_{\text{re}}^{\text{TOA}}}{\partial \xi_{\text{re}}} = 0; \quad \frac{\partial \Gamma_{\text{re}}^{\text{Q}}}{\partial \xi_{\text{re}}} = 0 \quad (20 \text{ b})$$

The initial conditions (18) to (18 g) state that there is only acetic acid in the water from the bottom of the column, while in the water from the top of the column there is only base (NaOH). Supplementary, in the MLRM, irrespective of its position, there is only TOA.

The boundary conditions (19 a) assert that what is brought at the entrance of the bottom column through convection, leaves this entrances through dispersion and convection, while (20 a) emphasize that at the entrance of the BE zone, the species concentrations in the MLRM are the same as in the MLRM under the sieve. At the same time, the boundary conditions (19 b) and (20 b) state that all species concentrations in the MLRM phase in the extraction and BE zones have a finite asymptotical variation.

#### Solving the mathematical model

The mathematical model described by the equations (1) ÷ (18) together with the initial and boundary conditions is a system of P/DAEs. To solve this system, each PDE was first transformed into an ODEs system through orthogonal collocation [28] – the spatial derivatives are replaced by the weighted sums of the dependent variables, thus transforming the PDE into a system of time dependent ODEs. The trial function was taken as a series of orthogonal polynomials whose roots are used as collocation points and the solution is sought at these collocation points. Afterwards, the complete ODE system was integrated with the self-adjustable RK-Fehdberg method. The calibration of the model against our own experimental data was done throughout regression analysis, using as objective function the mean square root of the norm of the residuals model – experiment, and an in-house Genetic Algorithm software optimizer [29], as detailed in [23].

#### Results and discussions

An extensive experimental work was done in laboratory to obtain the partition coefficients for all organic solvents used [22-24]. In the case of non polar solvents (paraffin oil or petroleum ether) the extraction efficiency was very small irrespective of the extraction type: a) simple extraction/back-extraction in water, b) extraction followed by back-extraction in alkaline solution, c) extraction with carrier followed by plain back-extraction and d) reactive extraction with carrier/back-extraction in alkaline solution. Better results were obtained using cyclohexanol as organic phase, but this solvent has the inconvenient of being soluble in water, contaminating the water itself during the back-extraction process.

The high partition coefficient under thermodynamic equilibrium is responsible for the sequestration of a large

quantity of acid inside the MLRM, in the case of passive discontinuous extraction/back-extraction in/to water. It is worth mentioning that, for equal volumes of water ( $V^a$ ) in the extraction/back-extraction zones (the volume of organic phase,  $V^o$  being the same), the final concentration of transported acid in the latter zone, starting from  $C_{\text{ex}}^{\text{A.in}}$  in the former, is:

$$C_{\text{re}}^{\text{A.a}} = C_{\text{ex}}^{\text{A.in}} \frac{K_{\text{eq}} \cdot V^o \cdot V^a}{(K_{\text{eq}} \cdot V^a + V^o)^2} \quad (21)$$

In the case of passive extraction followed by reactive back-extraction in alkaline solution of NaOH, the process efficiency increases but the best results are obtained using a reactive carrier in the MLRM.

The experiments involving RE/RBE were done for the system n-octanol as passive and TOA as reactive carriers, taking into account their very small miscibility with water and high values of acid partition coefficient for the system n-octanol/water. Two flow rates of MLRM were used, in order to emphasize the influence of the flow conditions and drop formation at the bottom of the column and at sieve, upon the overall performance of this compact RE column: 0.45 cm<sup>3</sup>/s and 0.9 cm<sup>3</sup>/s. The residence times for each zone of the experimental column (fig. 2 for the zones considered in the physical and mathematical model) are presented in table 1, for each of the two aforementioned flows.

It is worth mentioning that the MLRM has an external recycle period of 85.3 seconds, in the case of 0.45 cm<sup>3</sup>/s flow, and 34.2 seconds, in the case of 0.9 cm<sup>3</sup>/s flow, respectively.

The parameters of the mathematical model were split in two: those who can be taken/computed from the available literature correlations and design data (table 1), and those specific to the system at hand, which should be found through regression using our own experimental data. The overall partition coefficient for the acetic acid in the system water/n-octanol was experimentally found and the geometry-related mathematical model parameters were computed using the experimental set-up geometry or the operating conditions. The unknown parameters, for which a regression analysis was necessary are: the specific partial mass transfer coefficients  $k_{\text{ex}}^{\text{A.a}} \cdot A_{\text{ex}}$ ,  $k_{\text{ex}}^{\text{A.o}} \cdot A_{\text{ex}}$  and

$k_{\text{re}}^{\text{A.o}} \cdot A_{\text{re}}$ , the dispersion groups for both axial dispersion zones,  $Dg_{\text{ex}}$ ,  $Dg_{\text{re}}$  and the direct  $k_d$  and reverse  $k_r$  kinetic constants of the chemical reaction between acetic acid and TOA. It must be emphasized that in order to simplify the regression analysis and due to some hard experimental evidences we assumed that all dispersion groups for the species in the extraction and back-extraction zones have the same value,  $Dg_{\text{ex}}$  for the former, and  $Dg_{\text{re}}$  for the latter.

The model correlates well the experimental data (see fig. 3) – the mean residual between experiment and model was 4.7e-03 for 0.45 cm<sup>3</sup>/s flow case and 5.4e-03 for 0.9 cm<sup>3</sup>/s case – showing that, after a rather long time, the acid consumes completely even from the organic phase, rendering the process attractive for indirect contaminants removal, for example.

The values obtained through regression for the parameters specific to the back-extraction zone (the dispersion group  $Dg_{\text{re}}$  and the specific partial mass transfer coefficient  $k_{\text{re}}^{\text{A.o}} \cdot A_{\text{re}}$ ) are surprisingly close, indicating that the corresponding two-phase circulation is only slightly affected by the MLRM flow (table 2).

Nomenclature	Value		um
Organic phase flow rate	0.45	0.9	cm <sup>3</sup> /s
Residence time of extraction zone	14.7	5.2	s
Residence time of organic under the sieve zone	21.7	8.7	s
Residence time of the back-extraction zone	8.9	4.4	s
Residence time of the top column organic zone	21.1	8.9	s
Residence time of the buffer vessel	18.9	7.0	s
Volume of extraction zone (aqueous)	4.566E-06		m <sup>3</sup>
Volume of extraction-back-extraction zone (organic):	7.76E-06		m <sup>3</sup>
Volume of final zone (organic)	8E-06		m <sup>3</sup>
Volume of buffer tank (organic)	6.3E-06		m <sup>3</sup>
Diameter of the column	4E-02		m
Partition coefficient extraction zone	1.72		dimensionless
Equivalent diameter extraction zone	3.7E-03		m
Equivalent diameter back-extraction zone	3.7E-03		m
Initial concentration of species in the extraction (acetic acid in aqueous):	2.041		g/L
Stoichiometric coefficient of the acid	1		mol
Initial concentration of TOA in the organic (t=0)	17,68		g/L
	0.05		M
Initial concentration of NaOH in the back-extraction zone (t=0)	4		g/L

**Table 1**  
THE MAIN PARAMETERS VALUE  
OF THE MATHEMATICAL MODEL

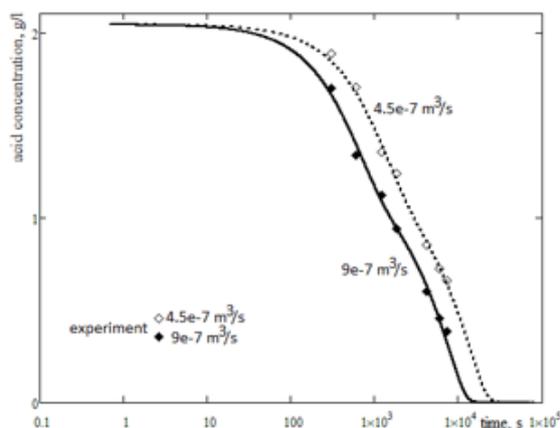


Fig. 3. Time concentration profiles of the acetic acid in the extraction zone of the column; mathematical model vs. experiments for both MLRM flows of 0.45 cm<sup>3</sup>/s and 0.9 cm<sup>3</sup>/s.

Due to the sieve acting as sparger, the number of drops is rather constant, irrespective of the organic flow, the latter influencing though their volume, which will affect slightly their ascending movement. On the contrary, the values obtained through regression for the parameters specific to the extraction zone are rather different, indicating a clear dependency of the induced two-phase circulation upon the MLRM flow. A lower MLRM flow favors the

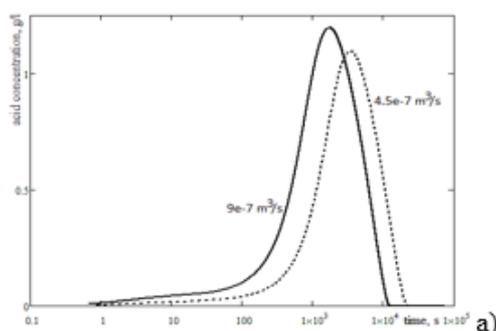
coalescence-breaking of the drops in the vicinity of the sparger and, as such, a higher value for the dispersion group, whilst when the MLRM flow is higher, the drops are ejected as jet, decreasing the probability of coalescence-breaking phenomena but increasing the turbulence level in the continuous phase. Accordingly, the dispersion group has a lower value (each drop rises individually), while the specific partial mass transfer coefficient  $k_{ex}^{A,a} \cdot A_{ex}$  has a higher value (table 2). Quite remarkably, the direct and reverse kinetic constants are rather close for both MLRM flows.

After a very short period, the acetic acid concentration in the donor phase (water from the bottom of the column) drops with a decreasing rate, due to the decrease of the driving force of the mass transfer from water to organic phase. This is confirmed by the acetic acid profiles in the organic phase for both flows (fig. 4), which has a maximum, after which there is a faster decrease till the complete vanish from the MLRM phase.

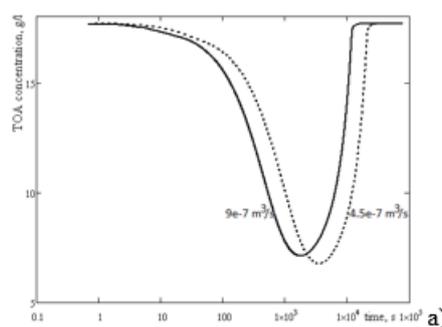
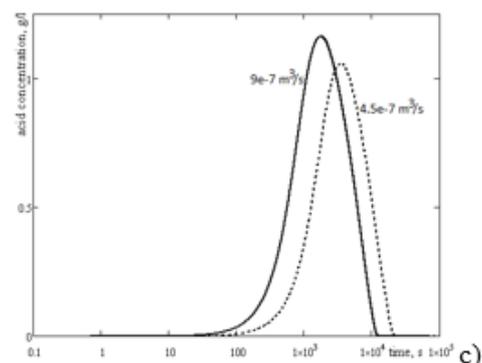
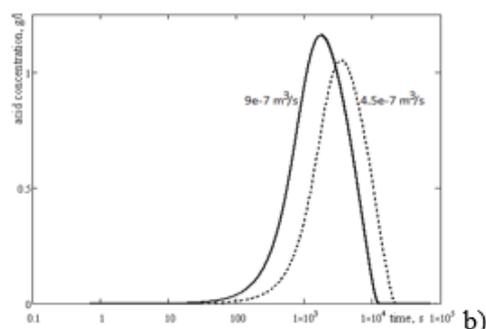
The acid profile concentration in MLRM is influenced by the partition coefficient, the mass transfer coefficients, the chemical reaction rate, the unreacted acid quantities, the chemical complex presence due to the organic recycling in the column and by the flow rate too. The accumulation of the acetic acid in the MLRM phase, which is the result of the dichotomy between the mass transfer and the chemical reaction rates, is also a clear sign that the mass transfer and the chemical reaction between TOA and acid

$D_v$ [cm <sup>3</sup> /s]	$k_{ex}^{A,a} \cdot A_{ex}$ [m <sup>3</sup> /s]	$k_{ex}^{A,o} \cdot A_{ex}$ [m <sup>3</sup> /s]	$k_{re}^{A,o} \cdot A_{re}$ [m <sup>3</sup> /s]	$Dg_{ex}$ [m <sup>2</sup> /s]	$Dg_{re}$ [m <sup>2</sup> /s]	$k_d$ [ $\frac{(L/mol)^{0.73}}{min}$ ]	$k_r$ [min <sup>-1</sup> ]
0.45	3.68e-05	1.27e-04	3.79e-06	1.11	0.218	0.56	0.0186
0.9	1.03e-04	8.61e-05	5.18e-06	0.61	0.25	0.65	0.0251

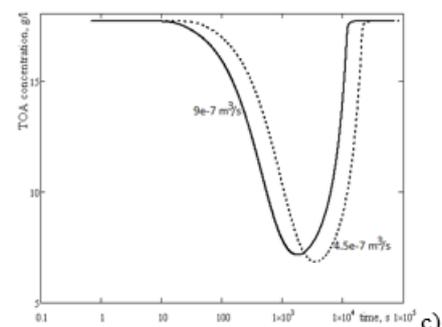
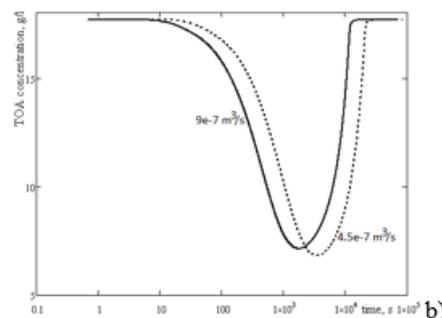
**Table 2**  
THE MODEL  
REGRESSED  
PARAMETERS AGAINST  
OUR OWN  
EXPERIMENTAL DATA



**Fig. 4.**  
Concentration profiles of acetic acid in the MLRM phase for both MLRM flows of 0.45 cm<sup>3</sup>/s and 0.9 cm<sup>3</sup>/s:  
a) under the sieve; b) column top; c) buffer vessel



**Fig. 5.**  
Concentration profile of TOA in the MLRM phase for both MLRM flows of 0.45 cm<sup>3</sup>/s and 0.9 cm<sup>3</sup>/s:  
a) under the sieve; b) column top; c) buffer vessel



half of the column and of the MLRM on the top of the column, respectively.

More, the peaks have decreasing values for the three aforementioned zones since the mass transfer from the organic phase to the water, in the upper half of the column, lowers the acid concentration in the MLRM on the top of the column zone. The chemical process between acid and TOA takes place in the MLRM phase irrespective of the zone; this diminishes further the acid concentration of the buffer vessel against the MLRM on the top of the column. It should be mentioned that the peak values for the acid concentration are lower and time delayed for the 0.45 cm<sup>3</sup>/s flow case because the mass transfer from the donor phase to the MLRM is closer to the mass transfer from the MLRM to the alkali solution, contrary to the 0.9 cm<sup>3</sup>/s flow case (table 2 for exact values). At the same time, the mass transfer from the MLRM to the alkali solution in the latter case is higher than in the former, which, combined with the higher residence times, give the chemical process

are of the same order of magnitude. More, the values of the specific partial mass transfer coefficient  $k_{re}^{A,o} \cdot A_{re}$  indicate that, due to the phase-circulation in the back-extraction zone, the consumption of the acid through reaction with NaOH is slower than the carrying of the acid through mass transfer in the extraction zone. It should be mentioned that the latter is continuously decreasing, following the acid concentration depletion, while the former increases, according to the raise of acid concentration in the MLRM phase. After the peak, the consumption prevails, the mass transfer driving force in the extraction zone being too small to compensate it.

A closer look at figure 4 reveals that there is a time delay of peak locations for the three perfectly mixed zones of MLRM phases – under the sieve (fig. 4a), top of the column (fig. 4b) and buffer vessel (fig. 4c), respectively – due to residence times of the axial dispersion zone in the upper

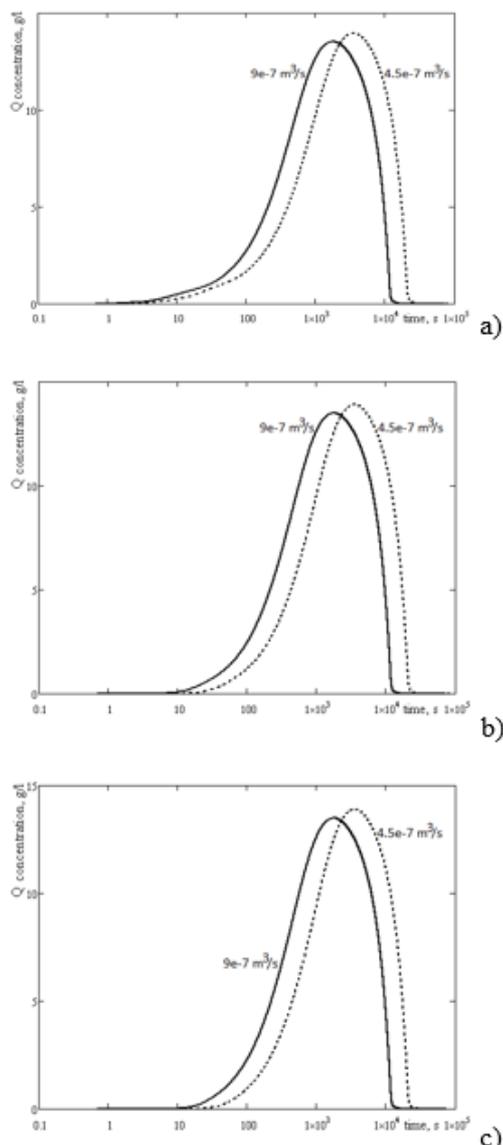


Fig. 6. Concentration profile of the Ac-TOA complex in the MLRM phase for both MLRM flows of 0.45 cm<sup>3</sup>/s and

0.9 cm<sup>3</sup>/s: a) under the sieve; b) column top; c) buffer vessel between the acid and TOA more time to advance towards equilibrium; thus, the chemical complex concentrations are higher and TOA dips are lower for the 0.45 cm<sup>3</sup>/s flow case against the 0.9 cm<sup>3</sup>/s flow case (figs. 5 and 6).

The previous research with the same system but without RE [22-24] showed that after a sufficiently long time, the phases reached equilibrium in the column. This means that the extracted species cannot be totally removed from the donor phase. Due to the chemical reaction with the alkali from the receiver phase, the RE process became irreversible and the acid could be removed from the donor phase, eventually, which is an important improvement concerning the extraction efficiency.

The same behavior is observed for the other two participants to the chemical process, namely TOA (fig. 5) and the chemical complex (fig. 6). There is a close relationship between the acid peaks, the TOA dips and the chemical complex peaks, since the chemical process in MLRM is reversible. As long as the acid concentration increases, the chemical equilibrium is displaced towards the chemical complex, which could be seen as supplemental storage for the acid extracted from the donor phase. Once the acid goes over the peak, the chemical complex releases the acid, which will be consumed in the irreversible chemical reaction with NaOH.

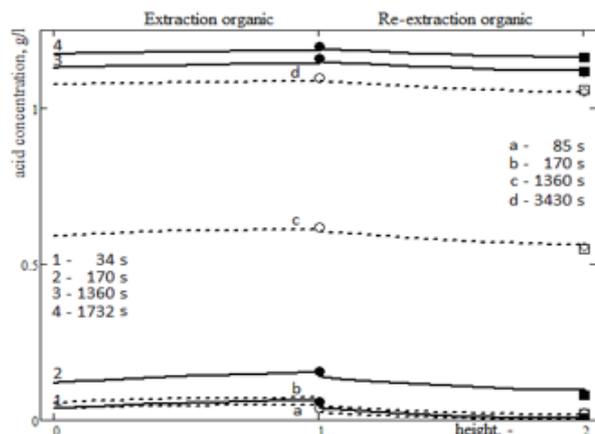


Fig. 7. Axial profiles of the acetic acid concentration for different operating times – the buffer volume has lowest concentration

A general image of the acid concentration profile in the MLRM along the column is given in figure 7.

In the extraction zone, the MLRM enriches asymptotically in acid, despite its consumption in the chemical process with the carrier. Still, the concentration of the acid at the exit of the MLRM extraction zone is lower than the acid concentration in the MLRM under the sieve, due to the supplemental mass transfer of the acid from the donor phase to this MLRM phase through the annular surface between these zones. In the back-extraction zone, the MLRM phase loses acid irreversible, due to its consumption in the chemical process with NaOH, and reversible, because it reacts with the carrier. Due to the same two processes, the concentration of the acid in the MLRM from the top of the column is even lower. As the acid concentration in the MLRM phase increases, the gradient in both extraction and back-extraction zones gets lower (fig. 7, profiles 1 vs. 4, and profiles a vs. d). Figure 7 shows neatly how faster the overall process rate is for the 0.9 cm<sup>3</sup>/s flow case with respect to the 0.45 cm<sup>3</sup>/s flow case (the full and dotted lines for 170 and 1360 s), due to the better contact between the donor and MLRM phases in the bottom half of the column.

## Conclusions

The physical and mathematical models for the RE/RBE process using MLRM and taking place in compartmented column are written and solved. In order to validate the mathematical model, an improved procedure based upon GA, was used to match the computed and experimental concentration profiles, regressing some of the parameters against own experimental data. To eliminate the difficulties associated with the computation of the correct values for the interfacial area between the rising droplets and the stagnant liquid phase, the real adjustable parameters were the specific partial mass transfer coefficients:  $k_{ex}^{A,a} \cdot A_{ex}$ ,  $k_{ex}^{A,o} \cdot A_{ex}$  and  $k_{re}^{A,o} \cdot A_{re}$ . The other adjustable parameters were the dispersion groups for MLRM in the bottom and top halves of the column and the kinetic constants of the reversible chemical reaction between the acid and the carrier (TOA). The mathematical model was solved using the orthogonal collocation method, which transforms the partial derivatives with respect to space into algebraic terms, thus changing the PDEs into ODEs with respect to time.

The model accurately describes the RE process that runs into the experimental column. The model offers the possibility to simulate different situations and to develop further strategies necessary for effective running the extraction at its maximum capability.

## Nomenclature

$A_{\text{ex}}$  mass transfer area from which organic drops extract the species (the lateral virtual cylinder area formed by the organic phase, which rise in aqueous phase in the extraction zone),  $\text{m}^2$

$A_{\text{re}}$  mass transfer area from which organic drops extract the species (the lateral virtual cylinder area formed by the organic phase, which rise in aqueous phase in the stripping zone),  $\text{m}^2$

$C_{\text{A}}$  acid concentration,  $\text{mol/L}$

$C_{\text{TOA}}$  TOA concentration,  $\text{mol/L}$

$C_{\text{Q}}$  chemical complex concentration,  $\text{mol/L}$

$C_{\text{ex}}^{\text{A,o}}$  concentration of transported acid in the organic phase from extraction zone,  $\text{g/L}$

$C_{\text{ex}}^{\text{A,o}*}$  equilibrium concentration of transported acid in the organic phase from extraction zone,  $\text{g/L}$

$C_{\text{ex}}^{\text{TOA}}$  concentration of TOA in the organic phase from extraction zone,  $\text{g/L}$

$C_{\text{ex}}^{\text{Q}}$  concentration of chemical complex in the organic phase from extraction zone,  $\text{g/L}$

$C_{\text{ex}}^{\text{A,a}}$  concentration of the acid in the aqueous phase from extraction zone,  $\text{g/L}$

$C_{\text{ex}}^{\text{A,a}*}$  equilibrium concentration of the acid in the aqueous phase from extraction zone,  $\text{g/L}$

$C_{\text{ex-re}}^{\text{A,o}}$  concentration of the acid in the organic layer formed below the sieve,  $\text{g/L}$

$C_{\text{ex-re}}^{\text{Q}}$  concentration of the chemical complex in the organic layer formed below the sieve,  $\text{g/L}$

$C_{\text{ex-re}}^{\text{TOA}}$  concentration of TOA in the organic layer formed below the sieve,  $\text{g/L}$

$C_{\text{re}}^{\text{A,o}}$  concentration of the unreacted acid in the organic phase from stripping zone,  $\text{g/L}$

$C_{\text{re}}^{\text{Q}}$  concentration of the chemical complex in the organic phase from stripping zone,  $\text{g/L}$

$C_{\text{re}}^{\text{TOA}}$  concentration of TOA in the organic phase from stripping zone,  $\text{g/L}$

$C_{\text{re}}^{\text{B}}$  concentration of the alkali in aqueous phase from stripping zone,  $\text{g/L}$

$C_{\text{re}}^{\text{B,in}}$  initial concentration of the alkali in aqueous phase from stripping zone,  $\text{g/L}$

$C_{\text{f}}^{\text{A,o}}$  concentration of the acid in organic layer formed on the top of the column,  $\text{g/L}$

$C_{\text{f}}^{\text{Q}}$  concentration of the chemical complex in organic layer formed on the top of the column,  $\text{g/L}$

$C_{\text{f}}^{\text{TOA}}$  concentration of the TOA in organic layer formed on the top of the column,  $\text{g/L}$

$C_{\text{v}}^{\text{A,o}}$  acid concentration in the buffer vessel,  $\text{g/L}$

$C_{\text{v}}^{\text{Q}}$  chemical complex concentration in the buffer vessel,  $\text{g/L}$

$C_{\text{v}}^{\text{TOA}}$  TOA concentration in buffer vessel,  $\text{g/L}$

$C^{\text{TOA,in}}$  initial value of TOA concentration,  $\text{g/L}$

$C_{\text{ex}}^{\text{A,in}}$  initial value of the acid concentration in aqueous phase from extraction zone,  $\text{g/L}$

$D_{\text{c}}$  diameter of the column,  $\text{m}$

$D_{\text{ech,ex}}^{\text{o}}$  equivalent diameter of the organic phase in the extraction zone,  $\text{m}$

$D_{\text{ech, re}}^{\text{o}}$  equivalent diameter of the organic phase in the stripping zone, m

$D_{\text{L, ex}}^{\text{A}}$  axial dispersion coefficient of the acid in organic in the extraction zone,  $\text{m}^2/\text{s}$

$D_{\text{L, ex}}^{\text{TOA}}$  axial dispersion coefficient of the TOA in organic in the extraction zone,  $\text{m}^2/\text{s}$

$D_{\text{L, ex}}^{\text{Q}}$  axial dispersion coefficient of the chemical complex in organic in the extraction zone,  $\text{m}^2/\text{s}$

$D_{\text{L, re}}^{\text{A}}$  axial dispersion coefficient of the acid in organic in the back-extraction zone,  $\text{m}^2/\text{s}$

$D_{\text{L, re}}^{\text{TOA}}$  axial dispersion coefficient of the TOA in organic in the back-extraction zone,  $\text{m}^2/\text{s}$

$D_{\text{L, re}}^{\text{Q}}$  axial dispersion coefficient of the chemical complex in organic in the back-extraction zone,  $\text{m}^2/\text{s}$

$D_v$  volumetric flow rate of the organic phase,  $\text{cm}^3/\text{s}$

$Dg_{\text{ex}}^{\text{A}}$  dimensionless group given by  $\frac{D_{\text{L, ex}}^{\text{A}}}{H_{\text{ex}} \cdot u_{\text{ex}}}$  ratio

$Dg_{\text{ex}}^{\text{TOA}}$  dimensionless group given by  $\frac{D_{\text{L, ex}}^{\text{TOA}}}{H_{\text{ex}} \cdot u_{\text{ex}}}$  ratio

$Dg_{\text{ex}}^{\text{Q}}$  Dimensionless group given by  $\frac{D_{\text{L, ex}}^{\text{Q}}}{H_{\text{ex}} \cdot u_{\text{ex}}}$  ratio

$Dg_{\text{re}}^{\text{A}}$  dimensionless group given by  $\frac{D_{\text{L, re}}^{\text{A}}}{H_{\text{re}} \cdot u_{\text{re}}}$  ratio

$Dg_{\text{re}}^{\text{TOA}}$  dimensionless group given by  $\frac{D_{\text{L, re}}^{\text{TOA}}}{H_{\text{re}} \cdot u_{\text{re}}}$  ratio

$Dg_{\text{re}}^{\text{Q}}$  dimensionless group given by  $\frac{D_{\text{L, re}}^{\text{Q}}}{H_{\text{re}} \cdot u_{\text{re}}}$  ratio

$H_{\text{ex}}$  length of the extraction zone, m

$H_{\text{re}}$  length of the stripping zone, m

$H_{\text{ex-re}}^{\text{o}}$  under the sieve organic layer thickness, m

$H_{\text{f}}^{\text{o}}$  top of the column organic layer thickness, m

$K_{\text{eq}}$  overall reverse partition coefficient (defined like the ratio between concentration of the acid in aqueous and organic phases)

$$K_{\text{eq}} = \frac{C_{\text{ex}}^{\text{A, a*}}}{C_{\text{ex}}^{\text{A, o*}}} = \frac{C_{\text{ex}}^{\text{A, a*}}}{C_{\text{ex}}^{\text{A, o}}}$$

$K_{\text{d}}$  group defined by the  $k_{\text{d}} \cdot \bar{t} \cdot (C_{\text{ex}}^{\text{A, in}})^{\alpha+\beta-1}$  relation

$K_{\text{C}}$   $\frac{k_{\text{d}}}{k_{\text{r}}}$  ratio

$K_{\text{ex}}^{\text{o}}$  group defined by the  $\frac{k_{\text{ex}}^{\text{A, o}} \cdot \bar{t}}{D_{\text{ech, ex}}^{\text{o}}}$  relation

$K_{\text{ex}}^{\text{a}}$  group defined by the  $\frac{\bar{t} \cdot k_{\text{ex}}^{\text{A, a}}}{D_{\text{c}}}$  relation

$K_{\text{ex-re}}$	group defined by the $K_{\text{LA}} \cdot \bar{t} \cdot \frac{(1-\delta_{\text{ex}}^2)}{H_{\text{o,ex-re}}}$ relation
$K_{\text{re}}^{\text{o}}$	group defined by the $\frac{k_{\text{re}}^{\text{A,o}} \cdot \bar{t}}{D_{\text{ech, re}}^{\text{o}}}$ relation
$K_{\text{re}}^{\text{a}}$	group defined by the $\frac{k_{\text{re}}^{\text{A,a}} \cdot \bar{t}}{D_{\text{c}}}$ relation
$K_{\text{f}}^{\text{o}}$	group defined by the $\frac{k_{\text{re}}^{\text{A,o}} \cdot \bar{t} \cdot (1-\delta_{\text{re}}^2)}{H_{\text{f}}^{\text{o}}}$ ratio (relation)
$k_{\text{d}}$	direct kinetic constant of the chemical reaction between acetic acid and TOA, $(\text{L/mol})^{0.73}/\text{min}$
$k_{\text{r}}$	reverse kinetic constant of the chemical reaction between acetic acid and TOA, $\text{min}^{-1}$
$k_{\text{ex}}^{\text{A,o}}$	mass transfer coefficient of the acid in organic phase in extraction zone, m/s
$k_{\text{ex}}^{\text{A,a}}$	mass transfer coefficient of the acid in aqueous phase in extraction zone, m/s
$k_{\text{re}}^{\text{A,o}}$	mass transfer coefficient of the acid in organic phase in stripping zone, m/s
$u_{\text{ex}}$	organic phase velocity in the extraction zone, m/s
$u_{\text{re}}$	organic phase velocity in the stripping zone, m/s
$R_{\text{A}}$	chemical complex generation rate, $\text{mol}/(\text{L} \cdot \text{min})$
$S_{\text{ex}}$	dimensionless group given by $\frac{H_{\text{ex}}}{D_{\text{c}}}$ ratio
$S_{\text{re}}$	dimensionless group given by $\frac{H_{\text{re}}}{D_{\text{c}}}$ ratio
$t$	current time, s
$\bar{t}$	organic phase residence time given by the ratio $\frac{V_{\text{tot}}^{\text{o}}}{D_{\text{v}}}$
$V_{\text{ex}}^{\text{a}}$	volume of the aqueous phase in the extraction zone, $\text{m}^3$
$V_{\text{re}}^{\text{a}}$	volume of the aqueous phase in the back-extraction zone, $\text{m}^3$
$V_{\text{ex-re}}^{\text{o}}$	volume of the organic solvent under the sieve, $\text{m}^3$
$V_{\text{ex}}^{\text{o}}$	volume of the organic phase in the extraction zone, $\text{m}^3$
$V_{\text{re}}^{\text{o}}$	volume of the organic phase in the stripping zone, $\text{m}^3$
$V_{\text{f}}^{\text{o}}$	volume of the organic phase on the top of the column, $\text{m}^3$
$V_{\text{buffer}}^{\text{o}}$	buffer vessel volume, $\text{m}^3$
$V_{\text{tot}}^{\text{o}}$	total organic phase volume, $\text{m}^3$
$z$	current coordination of the column height, m
$\Gamma_{\text{ex}}^{\text{A,a}}$	dimensionless acid concentration in the aqueous (extraction zone) given by the $\frac{C_{\text{ex}}^{\text{A,a}}}{C_{\text{ex}}^{\text{A,in}}}$ ratio
$\Gamma_{\text{f}}^{\text{Q}}$	dimensionless chemical complex concentration in organic given by the $\frac{C_{\text{f}}^{\text{Q}}}{C_{\text{ex}}^{\text{A,in}}}$ ratio

$\Gamma_v^{A,o}$	dimensionless acid concentration in organic given by the $\frac{C_v^{A,o}}{C_{ex}^{A,in}}$ ratio
$\Gamma_v^{TOA}$	dimensionless TOA concentration in organic given by the $\frac{C_v^{TOA}}{C_{ex}^{A,in}}$ ratio
$\Gamma_v^Q$	dimensionless chemical complex concentration in organic given by the $\frac{C_v^Q}{C_{ex}^{A,in}}$ ratio
$\delta_{ex}$	dimensionless diameter given by the ratio
$\delta_{re}$	dimensionless diameter given by the ratio
$v_A$	stoichiometric coefficient of the acid
$\tau$	dimensionless time given by the ratio
$\xi_{ex}$	dimensionless coordination given by the ratio
$\xi_{re}$	dimensionless coordination given by the ratio
$\Omega_{ex}$	dimensionless volume given by the ratio
$\Omega_{ex-re}$	dimensionless volume given by the ratio
$\Omega_{re}$	dimensionless volume given by the ratio
$\Omega_f$	dimensionless volume given by the ratio
$\Omega_v$	dimensionless volume given by the ratio
$\Gamma_{ex}^{TOA}$	dimensionless TOA concentration in organic (extraction zone) given by the $\frac{C_{ex}^{TOA}}{C_{ex}^{A,in}}$ ratio
$\Gamma_{ex}^Q$	dimensionless chemical complex concentration (extraction zone) given by the $\frac{C_{ex}^Q}{C_{ex}^{A,in}}$ ratio
$\Gamma_{ex}^{A,o}$	dimensionless acid concentration in the organic (extraction zone) given by the $\frac{C_{ex}^{A,o}}{C_{ex}^{A,in}}$ ratio
$\Gamma_{ex-re}^{A,o}$	dimensionless acid concentration in organic (organic under sieve) given by the $\frac{C_{ex-re}^{A,o}}{C_{ex}^{A,in}}$ ratio
$\Gamma_{ex-re}^{TOA}$	dimensionless TOA concentration in organic (organic under sieve) given by the $\frac{C_{ex-re}^{TOA}}{C_{ex}^{A,in}}$ ratio

- $\Gamma_{ex-re}^Q$  dimensionless chemical complex concentration in organic (organic under sieve) given by  $\frac{C_{ex-re}^Q}{C_{ex}^{A,in}}$  ratio
- $\Gamma_{re}^{A,o}$  dimensionless acid concentration in aqueous (back-extraction zone) given by the  $\frac{C_{re}^{A,o}}{C_{ex}^{A,in}}$  ratio
- $\Gamma_{re}^B$  dimensionless alkali concentration in aqueous (back-extraction zone) given by the  $\frac{C_{re}^B}{C_{ex}^{A,in}}$  ratio
- $\Gamma_{re}^{TOA}$  dimensionless TOA concentration in organic (back-extraction zone) given by the  $\frac{C_{re}^{TOA}}{C_{ex}^{A,in}}$  ratio
- $\Gamma_{re}^Q$  dimensionless chemical complex concentration in organic (back-extraction zone) given by the  $\frac{C_{re}^Q}{C_{ex}^{A,in}}$  ratio
- $\Gamma_f^{A,o}$  dimensionless acid concentration in organic given by the  $\frac{C_f^{A,o}}{C_{ex}^{A,in}}$  ratio
- $\Gamma_f^{TOA}$  dimensionless TOA concentration in organic given by the  $\frac{C_f^{TOA}}{C_{ex}^{A,in}}$  ratio

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