SIMULATION OF COUPLED EFFECTS
IN LIQUID-LIQUID EXTRACTION COLUMN

J. Toutain, J.M. Le Lann, C. Gourdon, X. Joulia[1]
Institut National Polytechnique de Toulouse (I.N.P.T.)
Ecole Nationale Supérieure d'Ingénieurs de Génie Chimique (E.N.S.I.G.C.)
Laboratoire de Génie Chimique (L.G.C., U.M.R. C.N.R.S 5503)
18 Chemin de la loge 31078 TOULOUSE Cedex, FRANCE
Tél. : (+33) 5 62 25 23 00 ; Fax. : (+33) 5 62 25 23 18
E-mail : Xavier.Joulia@ensigct.fr

Scientific Topic : II.1.c

Abstract : A simulation tool incorporating a Maxwell-Stefan approach coupled with a drop population model for the dynamic simulation of liquid-liquid extraction pulsed column has been developed. Fundamental mechanisms like transport, axial back-mixing and forward-mixing, drop breakage and interdrop coalescence, including the Marangoni effect, are described in a detail way.

Keywords : Dynamic ; Extraction ; Maxwell-Stefan approach ; Drop population model ; Marangoni effect.

---

[1] Correspondence concerning this article should be addressed to this author

INTRODUCTION

Although distillation and absorption are the most commonly applied unit operations for separating fluid mixtures consisting of two or more components, there is a broad and growing range of situations in which liquid-liquid extraction is the appropriate method. There are basically two ways of simulating the differential continuous contact equipments such as the extraction column :

1.The first one is focused on the description of hydrodynamics. In a first approximation, the dispersed phase may be considered as a pseudo-continuous phase and the hydrodynamics described by means of a plug-flow model. Furthermore, an axial dispersion term, representing axial back-mixing, may be introduced. It can be satisfactorily used for the description of the continuous phase but with less accuracy for the dispersed phase. A second general approach considers the dispersed phase as a polydispersed drop population. Some authors developed models which account with the drop size distribution. An important feature of these models is the fact that they are able to describe axial forward-mixing, due to the different rising velocities of the drops of different sizes, which sometimes considerably reduce the efficiency of the contactor. The application of these models failed because they provided satisfactory results only for constant or nearly constant hold-up profiles. This is not always guaranteed under industrial operating conditions. An alternative model allows explicitly for the fundamental mechanisms of drop transport, drop breakage and interdrop coalescence.

2. The second way pays more attention to the description of mass transfer between the phases than to hydrodynamics. Mass transfer in multicomponent mixtures is more complicated than for a binary mixture because of a possible coupling between the individual concentrations. These phenomena are especially pronounced for non-ideal mixtures, separated at extreme operating conditions. The use of Stefan-Maxwell equations of multicomponent diffusion, applied to a film model, is now widespread and is able to predict the actual performance of a separation unit, provided that the right correlations are available, especially for the prediction of the interfacial area [1].

The simulation tool proposed in this work deals with a detailed description of the column hydrodynamics coupled to the Maxwell-Stefan approach in order to express more accurately mass transfer between every drop class of the dispersed phase and the continuous phase. The continuous contact equipment is represented by a sequence of non-equilibrium stages, including the settling parts at the top and bottom of the column. Mass balances relative to the continuous phase and each drop class lead, with the transfer rate equations, to a DAE system which are solved by Gear's method.

The coupling effects between hydrodynamics and mass transfer are emphasised : unlike in the simplified model proposed by Zimmermann and al. [2], Marangoni effect is here explicitly taken into account [3]. Therefore, concentration profiles, as well as hydrodynamic characteristics such as hold-up and drop size distribution, are calculated more confidently, according to the two interphase transfer directions. The following part present some significant results.

VALIDATION OF THE MODEL

1. Framework

The model presented here is applicable to any kind of countercurrent extraction process. It can be used to simulate sieve tray columns as well as discs and rings, pulsed columns...etc. A pilot pulsed column, whose technological and geometrical characteristics are listed in Table 1, was used as the experimental reference. The measurements correspond to steady state profiles. These have been obtained for the operating conditions listed in Table 2 [4].

Table 1 - Column Specifications

Internal column diameter	72 mm
External column diameter	80 mm
Settling parts height	0.38 m
Active part height	4.30 m
Distance between the sieves	0.10 m
Tray type	sieve tray

Table 2 - Operating conditions

Case name	Agitation intensity, clearance	Mass transfer direction	Sum of phase velocities (cm/s)	Phase ratio dispersed/ continuous	Acetone feed mass fraction in the continuous phase	Acetone feed mass fraction in the dispersed phase
A	1.5 cm/s, 23%	$C \rightarrow D$	0.87	1.45	5.62 %	0 %
B	2.0 cm/s, 23%	$C \rightarrow D$	0.74	1.46	5.58 %	0 %
C	1.5 cm/s, 23%	$C \rightarrow D$	0.93	1.52	5.55 %	2.33 %
D	1.5 cm/s, 23%	$D \rightarrow C$	0.96	1.68	0 %	5.74 %
E	2.0 cm/s, 39%	No transfer	1.22	1.00	0 %	0 %

2. Phases properties

The involved ternary system is toluene-water-acetone, whose physico-chemical and thermodynamical properties are well known (see Table 3). As mentionned above, our model accounts for the coupling effects between hydrodynamics and mass transfer. Without going into detail, the model of Chester and al. [3] allows to estimate the interdrop coalescence probability when mass transfers occurs in order to take into account Marangoni effect. It depends very strongly on the interfacial tension gradient and explicitly on the transfer potential.

Therefore, interdrop coalescence is enhanced when the solute (acetone) transfers from dispersed phase to continuous phase ($D \rightarrow C$). On the opposite, when acetone transfers from the continuous to the dispersed phase ($C \rightarrow D$), coalescence is strongly reduced. As a consequence, the average size of the drops, defined by the Sauter diameter (d_{32}), is expected to be grower in the case $D \rightarrow C$ than for $C \rightarrow D$. Such a case corresponds

to those usually observed for ternary systems. In the framework of our simulation, the Marangoni effect can be neglected. In the following parts, the predicted profile, accounting (or not) for Marangoni effect, are compared to experimental ones, when available.

Table 3 - Physico-chemical and thermodynamical properties

Thermodynamical model	Uniquac (DECHEMA)				

i	j	$(\lambda_{ji}-\lambda_{ii})$	$(\lambda_{ij}-\lambda_{ii})$	
1	2	987.42	172.79	component 1 : toluene
1	3	269.90	-138.80	component 2 : water
3	2	390.94	-86.302	component 3 : acetone

Infinite dilution diffusion coefficient

$D_{i,j}^{\infty}$	i = 1	i = 2	i = 3
j = 1		$4.45\cdot10^{-5}$ cm^2/s	$2.93\cdot10^{-5}$ cm^2/s
j = 2	$0.85\cdot10^{-5}$ cm^2/s		$1.16\cdot10^{-5}$ cm^2/s
j = 3	$3.43\cdot10^{-5}$ cm^2/s	$6.19\cdot10^{-5}$ cm^2/s	

[5, 6, 7]

Mutual diffusion coefficient

$$D_{i,j}=\left[\left(D_{i,j}^{\infty}\right)^{x_j}\cdot\left(D_{j,i}^{\infty}\right)^{x_i}\right]$$

[8]

Mass transfer coefficient

Organic phase

$$Sh = 0.818\cdot Ga^{0.434}\cdot P^{0.011}\cdot\left(\frac{\mu_C}{\mu_D}\right)$$

[9]

Aqueous phase

$$Sh = 2.18\cdot Ga^{0.174}\cdot Sc^{\frac{1}{3}}\quad\left(3\cdot10^4 < Ga < 23.43\cdot10^4\right)$$

$$Sh = 0.072\cdot Ga^{0.451}\cdot Sc^{\frac{1}{3}}\quad\left(23.43\cdot10^4 < Ga < 50\cdot10^4\right)$$

[10]

Interfacial tension

$$\sigma = \frac{135.405\cdot\left(Y_3^I - 0.6367\right)^2 + 79.72012\cdot\left(Y_3^I - 0.6367\right)^3}{1+5\cdot Y_3^I}$$

[11]

3. Results

Figures 1 and 2 present the acetone concentration profiles throughout the column. In all cases, predicted values and experimental values are in very good agreement, whenever Marangoni effect neglected. Especially, concentration steps due to axial backmixing on the feed levels of each phase are well represented. Nevertheless, the simulations accounting for the Marangoni effect provide concentrations profiles closer the experimental ones, except for the case C, where the predicted profiles are quite identical. In this case, mass transfer between the phases is more limited, since both phases contain acetone in the feed. Correspondingly, the Marangoni effect is here reduced and does not affect concentrations profiles.
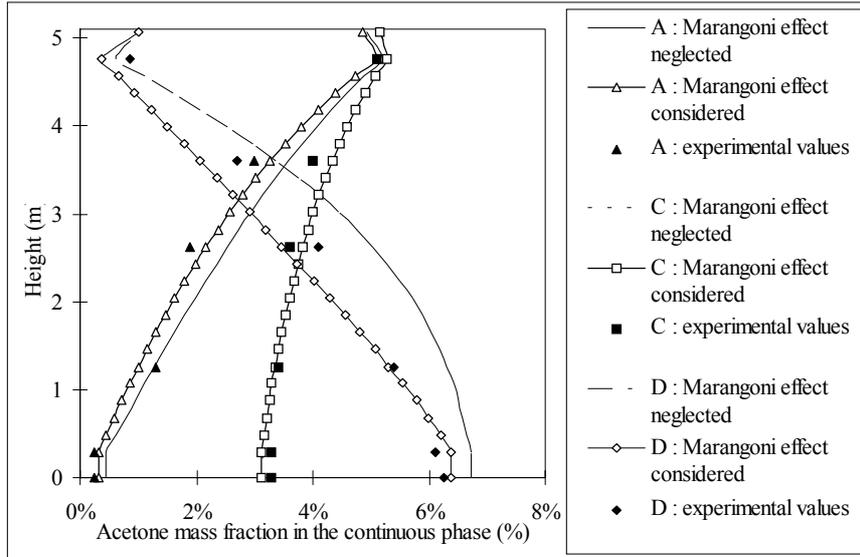
Figure 1 - Predicted and experimental Acetone

mass fraction profiles in the continuous phase
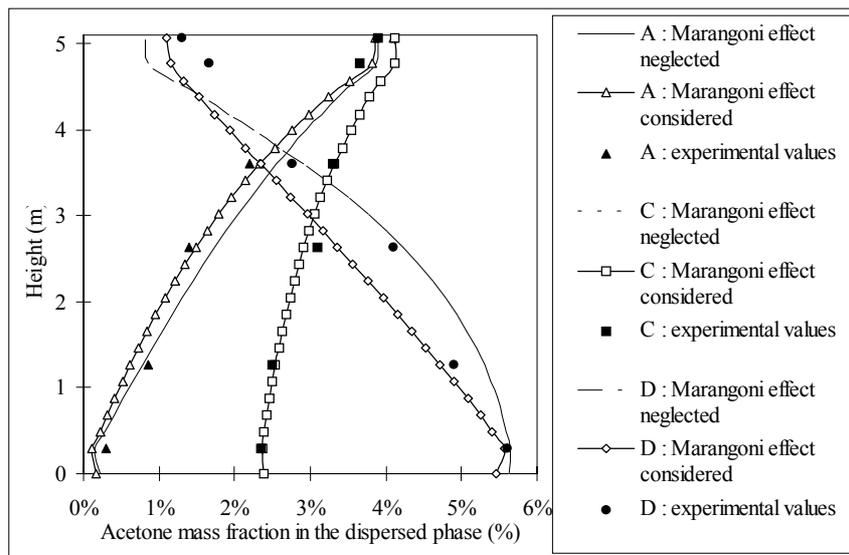
Figure 2 - Predicted and experimental Acetone

mass fraction profiles in the dispersed phase

Concerning hydrodynamics, Figures 3 and 4 highlight all the interest the introduction of the model of Chester and al. [3] represents. In all cases, the predicted profiles given by the simulation accounting for the Marangoni effect provide values in a very good agreement with the experimental measurements, especially for the hold-up of the dispersed phase. Concerning the case D, there is no measurement of the Sauter diameter, but the predicted value at the top of the column corresponds to experimental values obtained by Gourdon [12]. The detailed description of mass transfer also has a significant influence on the hydrodynamics since it directly allocates drop rising

velocities and consequently hold-up. Globally, for the transfer from continuous to dispersed phase, hold-up in the lower part of the column is essentially linked to the value of Sauter diameter while its changes in the upper part derive from the evolution of drop rising velocities due to the enrichment on solute. For the transfer from dispersed to continuous phase, interdrop coalescence is active throughout the column. This leads to large variations on hold-up, and far more pronounced ones on the Sauter diameter profile.
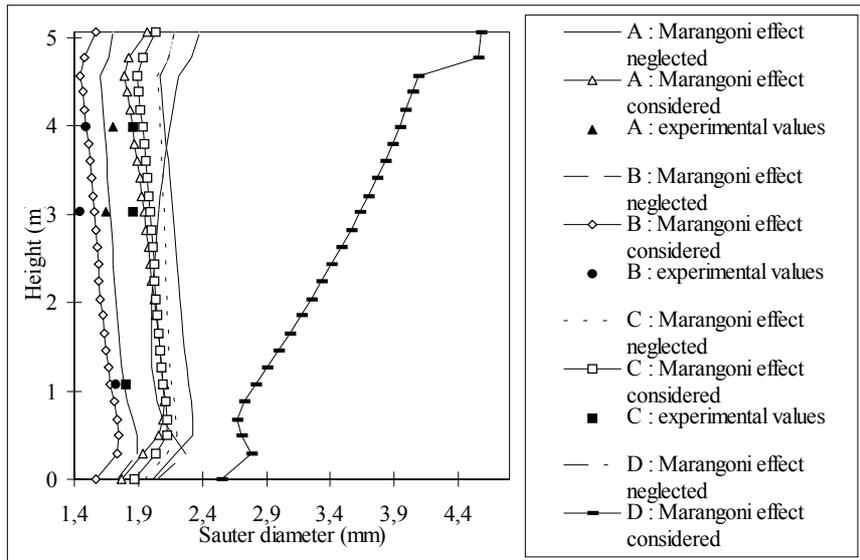

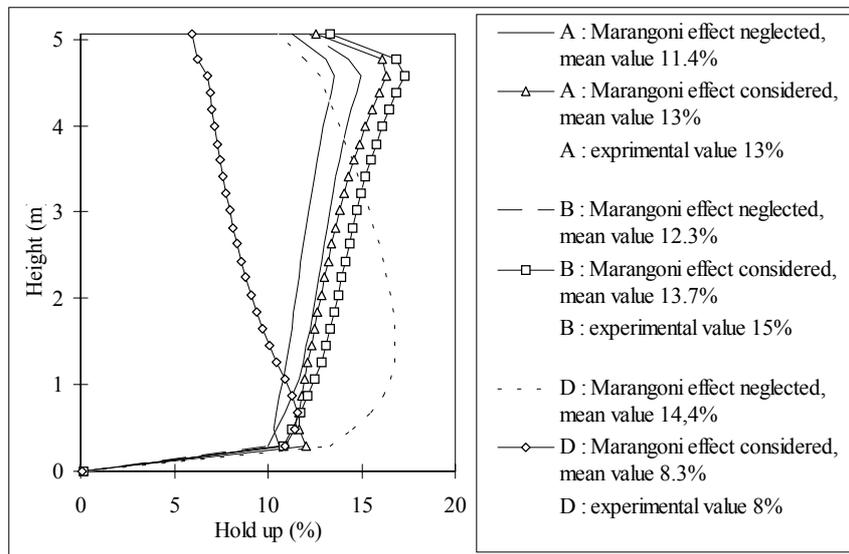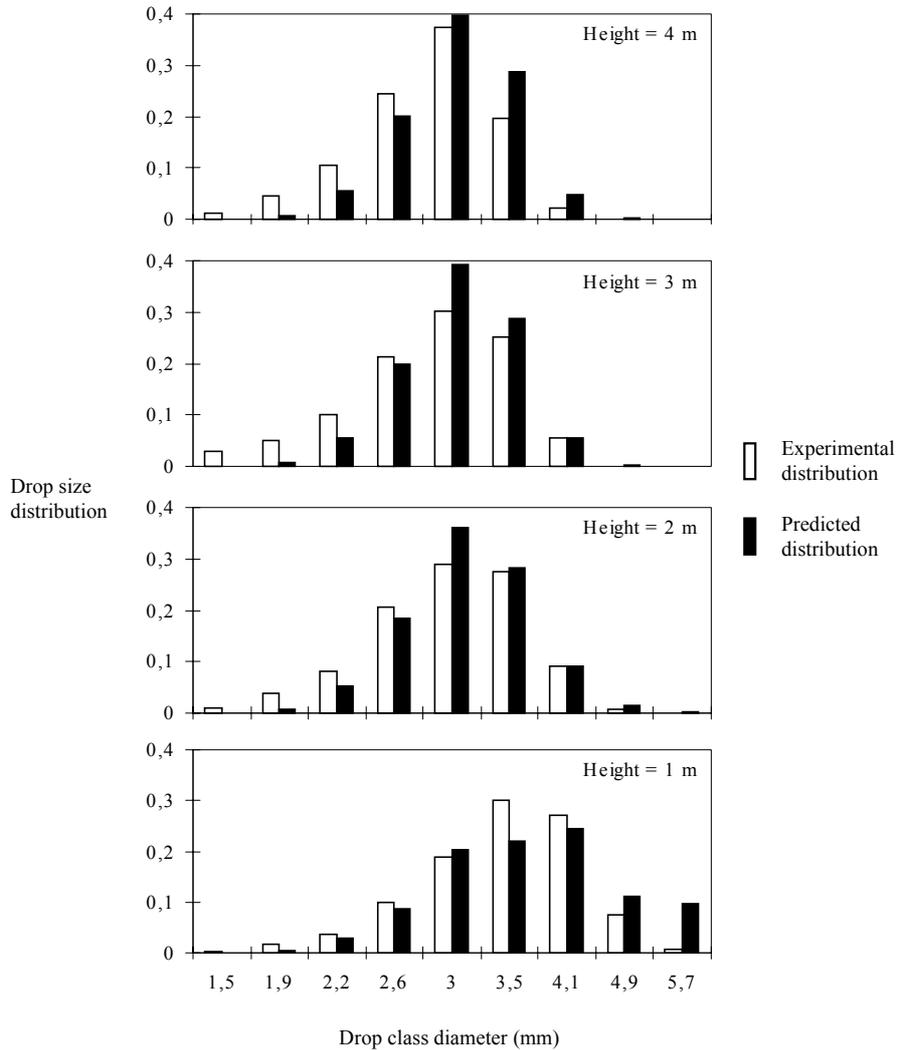Figure 3 - Predicted and experimental Sauter diameter profiles

Figure 4 - Predicted and experimental Hold up profiles

Finally, the Figure 5 presents a comparison between predicted and experimental drop size distribution. In this case, there is no transfer between the phases. Therefore, there is

no Marangoni effect. Once again, predicted profiles are in very good agreement with experiments [4].

Figure 5 - Predicted and experimental drop size distribution profiles

CONCLUSION

The simulation tool incorporates a rate-based approach coupled with a drop population balance. It includes the resolution of Maxwell-Stefan equations for multi-component mass transfer. The coupling effects of mass transfer and hydrodynamics are here strengthened by taking into account the Marangoni effect with a view to evaluating production terms relative to interdrop coalescence. At the moment, this simulation tool, which has been tested using experimental data taken from the literature, is proving to be very useful in order to explain and interpret very spectacular behaviour observed in extraction columns, according to the choice of the phase to be dispersed. This highlights the advantage of the coupling of the two main approaches in the simulation model. It shows that the variation of only one, albeit important, hydrodynamic parameter can vary the concentration profiles. Thus, hold-up and drop size profile heterogeneities have been enlightened, all the more when mass transfer direction accelerates interdrop coalescence.

NOTATION

D	diffusion coefficient	(cm^2/s)
d_{32}	Sauter diameter	(mm)
Ga	Galilei number	(-)
μ	dynamic viscosity	(kg/m/s)
P	hydrodynamic number	(-)
σ	interfacial tension	(N/m)
Sc	Schmidt number	(-)
Sh	Sherwood number	(-)
x	molar fraction	(-)
Y	mass fraction in the continuous phase	(-)

Subscripts, superscripts

∞	infinite dilution
C	continuous phase
D	dispersed phase
I	interface
i,j	component number

REFERENCES

[1] Krishnamurthy R. and Wesselingh J.A., The Maxwell-Stefan Approach to Mass Transfer, Chem. Engng. Sci., 52, 6, 861-911, 1997

[2] Zimmermann A., X. Joulia, C. Gourdon and A. Gorak, Maxwell-Stefan Approach in Extractor Design, Chem. Engng. J., 57, 229-236, 1995

[3] Chesters A.K. and Gourdon C., The Influence of Interphase Mass Transfer on the Drainage of Partially-Mobile Liquid Films Between Drops Undergoing a Constant Interaction Force, to be published in Chem. Engng. Sci., 1998

[4] Vogelpohl A., Lorenz M. and Sievers M., Einfluß des Stoffaustausches auf die Hydrodynamik und die Trennleistung einer pulsierten Siebboden-Extraktionskolonne, Diplomarbeit am ITV, Technische Universität Clausthal, Germany, 1989

[5] Baldauf W., Experimentelle Ermittlung binärer diffusionkoeffizienten für einige testgemische der flügssig-flügssig extraktion, Dissertation an der TU Berlin, 1981

[6] Sherwood T.K., Pigford R.L. and Wilke C.R., Mass transfer , McGraw Hill, New York 1979

[7] Tyn M.T., Calus W.F., Diffusion coefficients in dilute binary mixture, J. Chem. Eng. Data, 56, 106, 1975

[8] Vignes A., Diffusion in binary solutions , I&EC Fundamentals, 5, 5, 1966

[9] Molinier J., «Fonctionnement des colonnes pulsées en extraction liquide-liquide , Thèse de Docteur ès Sciences, INP Toulouse, 1976

[10] Malmary G., Influence de la viscosité de la phase continue sur le transfert de matière entre une goutte et un liquide non-miscible , Thèse de Doctorat, INPT, 1986

[11] Misek T., Recommanded systems for liquid extraction studies, Summer School on Liquid-Liquid Extraction, Toulouse, 8-11 July, 1991

[12] Gourdon C., "Les colonnes d'extraction par solvant : modèles et comportement", Thèse de Docteur d'Etat, INP Toulouse, 1989