

## The Effects of a Surfactant Concentration on the Mass Transfer in a Mixer-Settler Extractor

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**ABSTRACT:** *The effects and influences of various parameters upon the efficiency and the overall volumetric mass transfer coefficients are important subjects to be studied in most liquid-liquid extraction processes. One of these important parameters is surface active agent (surfactant). In this paper, in order to study the effect of sodium dodecyl sulfate (SDS) concentration on the efficiency and the average overall volumetric mass transfer coefficients, several experiments were carried out in a ten stage mixer-settler. In these experiments the effect of surfactant concentration on above mentioned parameters at constant operational conditions are studied. In general the efficiency and mass transfer coefficients dropped significantly at low surfactant concentration and remained almost constant at the higher concentrations (Almost a minimum point was observed). Although the surfactant caused a decrease in mass transfer, but the amount of mass transfer coefficients in both phases are considerable and therefore the resistance against mass transfer in both phases cannot be neglected.*

**KEY WORDS:** *Liquid extraction, Mixer-settler, Surfactant, Efficiency, Overall mass transfer coefficient.*

### INTRODUCTION

Mixer-settler extractor as compared to other extractors, beside its large amount of hold-up which is considered a weakness, is widely used in industries due to their high capacity and low number of stages [1,2]. The efficiency and the overall volumetric mass transfer coefficient are usually considered as important parameters in selecting of optimum conditions for designing of mixer-settler extractor. Therefore, the study of efficiency and the range of the overall volumetric mass transfer coefficient help us to achieve appropriate performance of extractor. However, the existence of surfactants can affect considerably on the

efficiency and the overall volumetric mass transfer coefficient.

The surfactants consist of surface agents, impurities, softening, and or metallic colloids from pipes and fittings. The effects of surfactants on mass transfer across an interface may be placed in two categories:

- 1- They may form an interfacial barrier of a mechanical, physical, or chemical nature.
- 2- They may modify the relevant hydrodynamics by reducing the rate of internal circulation in drops, damping the interfacial waves or oscillations, decreasing the

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1021-9986/06/4/9

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terminal velocity of drops, lowering the interfacial tension, lessening the transmission of turbulence across the interface, and retarding the rate of coalescence.

Several investigators [3-12] suggest that the effects of surfactants cause a decrease in mass transfer rate. The results indicate that surfactants often reduce the mass transfer coefficient but increase the mass transfer area per unit volume. In studies performed on extraction, the decrease in the mass transfer coefficient by surfactant was attributed either to the decrease in interfacial mobility and internal circulation or to the blocking action of surfactant molecules at the interface. In the studies on equipment performance, the overall efficiencies were found to increase or decrease with the addition of surfactant on mass transfer coefficient,  $K$ , and mass transfer area,  $a$ . The net effect of surfactant on the operation efficiency of the extraction equipment or the value of the product,  $Ka$ , is rather complicated. To identify the competitive effect, it is more appropriate to study the two factors individually. Generally, the coefficients dropped significantly at low surfactant concentration, but remained almost constant (or increased slightly) at the highest surfactant level. Minima in this type of curve have been reported in different extraction equipment.

Therefore, nowadays the study of the behaviors of these effects has become one of the main and major factors in research concerning extraction processes.

### Efficiency [13]

Efficiency depends on different parameters such as impeller speed, solvent amount, hold-up and concentration of surfactant. In this paper, we studied the effect of concentration of surfactant upon the stage and the extraction efficiencies. Consider a cocurrent stage with input mass fractions  $x_1$  and  $y_1$ , and output mass fractions  $x_2$  and  $y_2$  in raffinate and extract phase respectively. If the effluent liquids had come to equilibrium, they would have left the stage with solute mass fractions  $x_e$  and  $y_e$ . Therefore, the stage efficiency (as a fraction) is defined

$$E_{\text{stage}} = \frac{x_1 - x_2}{x_1 - x_e} = \frac{y_2 - y_1}{y_e - y_1} \quad (1)$$

Also, the extraction efficiency in each phase is defined as the ratio of actual mass transfer to the mass transfer in which one of effluent streams approach to

equilibrium with other at its actual concentration. Thus, for the raffinate phase that is discharged at  $x_{\text{out}}$  (or  $X_{\text{out}}$ ), whereas equilibrium with extract at  $y_{\text{out}}$  is  $x^*$  (or  $X^*$ ), the extraction efficiency is:

$$E_{\text{ext}} = \frac{X_{\text{in}} - X_{\text{out}}}{X_{\text{in}} - X^*} \quad (2)$$

### Overall Volumetric Mass Transfer Coefficients [13]

The overall volumetric mass transfer coefficient can be defined as a function of the overall mass transfer coefficient ( $K$ ), the dispersed phase hold-up ( $\epsilon$ ), and the sauter mean diameter ( $d_{32}$ ), where the surface area is defined as  $\alpha = 6\epsilon/d_{32}$ . The overall mass transfer coefficient also depends on surfactant's concentration. In this paper, we studied the effect of concentration of surfactant upon the overall volumetric mass transfer coefficients.

### Overall Volumetric Mass Transfer Coefficient in Raffinate and Extract Phases

It is possible to arrive a correlation for overall volumetric mass transfer coefficients when an average mass transfer coefficient is defined throughout each stage. Assume that there is no backmixing and liquids travel only in the forward direction from inlet to outlet. Thus, the overall volumetric mass transfer coefficient in raffinate phase (light phase,  $K_R a$ ) is obtained by using material balance for each stage based on input and output solute concentrations and definition of mass flux in the raffinate phase:

$$\dot{m}_R (x_{\text{in}} - x_{\text{out}}) = K_R a \cdot V (C_{R_{\text{out}}} - C_R^*) \quad (3)$$

In the above correlation, the concentrations are by weight, therefore, we can write:

$$\dot{m}_R (x_{\text{in}} - x_{\text{out}}) = K_R a \cdot V \cdot \rho_{\text{av}} (x_{R_{\text{out}}} - x^*) \quad (4)$$

where  $\rho_{\text{av}} = \sum_{i=1}^n x_i \rho_i$ .

Also, the overall volumetric mass transfer coefficient in extract phase (heavy phase,  $K_E a$ ) is obtained by using material balance for each stage based on input and output solute concentrations and definition of mass flux in the extract phase:

$$\dot{m}_E (y_{\text{out}} - y_{\text{in}}) = K_E a \cdot V (C_E^* - C_{E_{\text{out}}}) \quad (5)$$

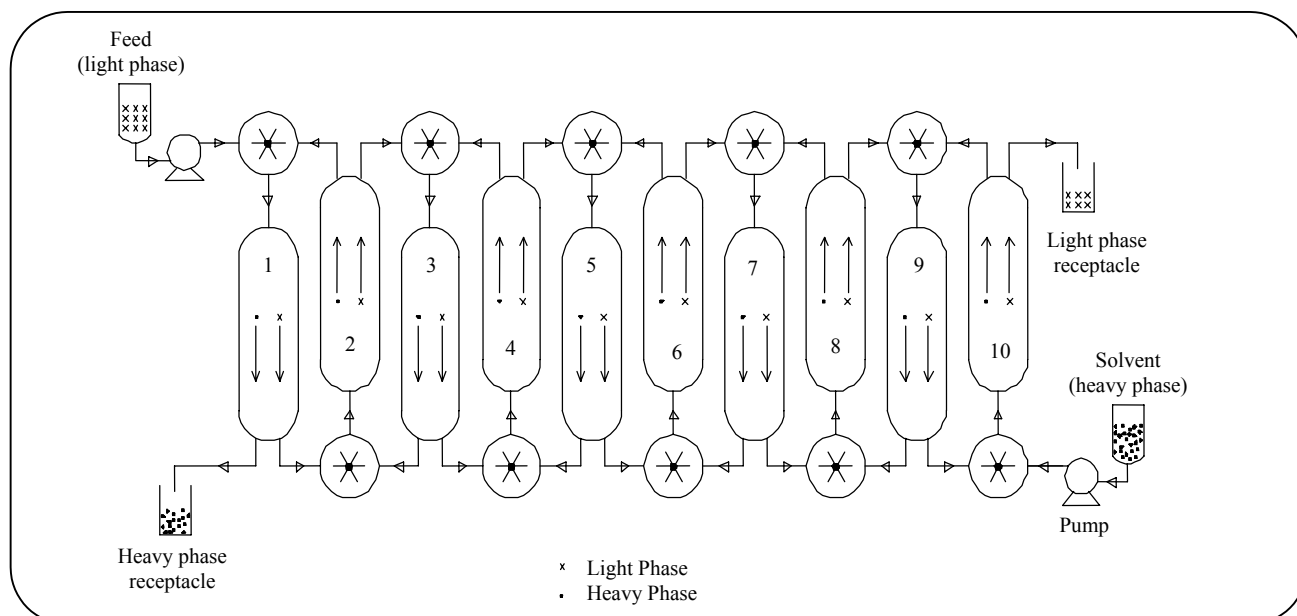


Fig. 1: Schematic of a horizontal mixer-settler.

In the above correlation, the concentrations are by weight, therefore, we can write:

$$\dot{m}_E (y_{out} - y_{in}) = K_E a \cdot V \cdot \rho_{av} (y^* - y_{out}) \quad (6)$$

$$\text{where } \rho_{av} = \sum_{i=1}^n x_i \rho_i$$

#### APPARATUS AND EXPERIMENTAL METHOD

The counter current mixer-settler used in these experiments consisted of ten stages in cascade with a pump-type pattern propeller in each stage, which could pump the solution between stages. All stages are made of glass in order to observe two phases. The interface level of the two phases in every settler can be controlled by level controller and also samples can be taken from two phases by a sampling device mounted on each settler. The rotor speed and the pumping degree, which are digitally adjusted, can be easily controlled. A drawing of the mixer-settler and one of stages used in these experiments are shown in Figs. 1 and 2 respectively. Also table 1 shows the characteristics of the mixer settler. In each stage, the light and the heavy phases are mixed in a mixing chamber and the mixed liquid (dispersion) is transferred to the settling chamber (settler). Of course, in first the calibration curves for the feed and the solvent pumps were also obtained.

In order to start up operations, at the beginning of

experiments, the two pumps for the feed and the solvent phases were turned on until all of stages fill with two phases. Then the interface level in each settler was carefully controlled by level controller to bring the system to steady-state condition.

To obtain optimum results, before collecting samples from each stage, enough time was given to the system to let the two phases to leave the stages. The concentration of acetone was measured by gas chromatography method. Some experiments were repeated two or three times in order to eliminate any error and to confirm the results.

The chemical system used in these experiments is water/acetone/toluene/SDS, where water is considered as the continuous phase, toluene as the dispersed phase, acetone as a solute and SDS as a surface active agent (surfactant). At the beginning of the operation, water and toluene are brought to saturation. Acetone with a known concentration is then added to the toluene phase (feed phase) and SDS with known and different concentrations are added to the water phase (solvent phase). The mass transfer direction in this system is from raffinate phase to extract phase.

Totally, five experiments were carried out in order to study the effect of surfactant concentration on the efficiency and the overall volumetric mass transfer coefficients. These experiments were made with the following parameters:

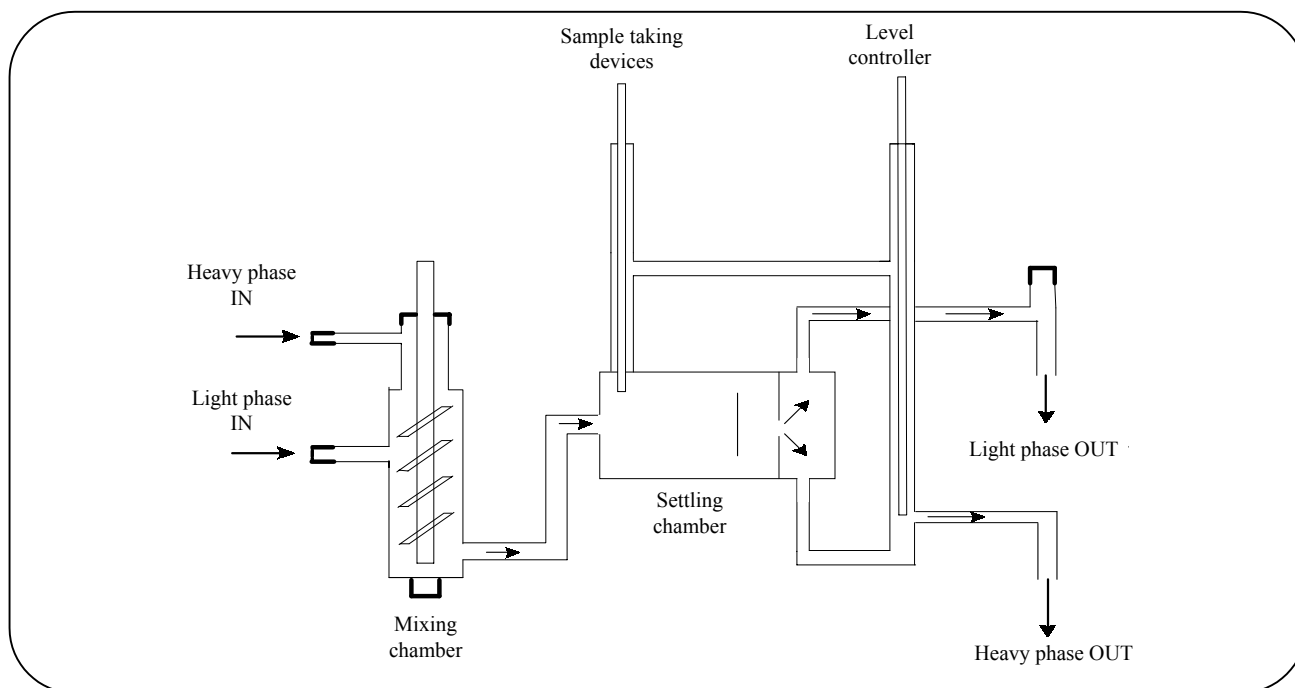


Fig.2: Schematic of a single stage.

Table 1: The characteristics of mixer settler.

Volume of mixing chamber	150 ml
Volume of settling chamber	250 ml
Diameter of mixing chamber	38 mm
Diameter of impeller	34 mm
Diameter of settlr chamber	50 mm
Length of settler	200 mm
Number of Settler	10
Material	Glass

- A constant impeller speed.
- A known and constant volumetric flow rate for two phases.
- A known mass fraction of acetone in toluene (3% by weight).
- Different mass fractions for SDS in water phase.

With the measured mass fractions of acetone and with the equilibrium curve and the mentioned correlation, we were able to obtain the efficiency and the overall volumetric mass transfer coefficients. The characteristics of experiments are shown in table 2.

## RESULTS AND DISCUSSION

Fig. 3 shows the effect of surfactant concentration on

Table 2: The characteristics of experiments for used chemical system.

Exp.	$Q_d$ ml/min	$Q_c$ ml/min	N rpm	Mass fraction of Surfactant, wt%
1	52.9	47.05	800	0
2	52.9	47.05	800	0.00677
3	52.9	47.05	800	0.01425
4	52.9	47.05	800	0.03287
5	52.9	47.05	800	0.05547

interfacial tension. This curve shows an increase of surfactant concentration results in a decrease in interfacial tension. The interfacial tension dropped approximately 50% by increasing small amount of SDS surfactant.

Fig. 4 shows the effect of surfactant mass fraction upon the average overall volumetric mass transfer coefficients. In each experiment, no more differences were observed between the overall volumetric mass transfer coefficient of one stage and other stages. Therefore we can define an average overall volumetric mass transfer coefficient for all stages and we can use it for designing and computations. In other words, the driving force of concentration and mass transfer amount in all stages are almost the same. In this figure, each point

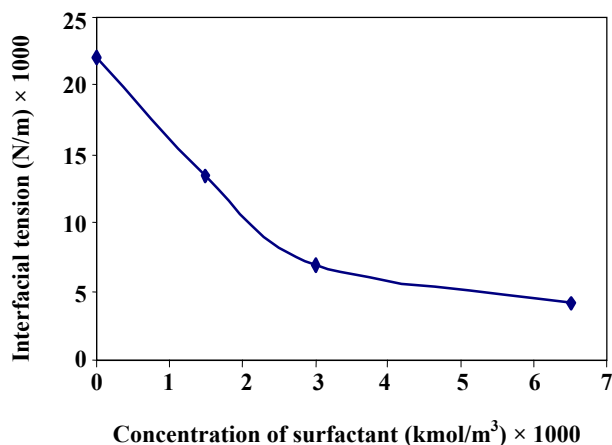


Fig. 3: Effect of surfactant concentration on interfacial tension at 298 K.

shows average overall volumetric transfer coefficient for all ten stages in each experiment. This curve shows an increase of surfactant mass fraction results in a decrease approximately 30% to 40% in the average overall volumetric mass transfer coefficients. In fact, the use of surfactants causes a reduction of the internal circulations, turbulences in drops and also a decrease of oscillations and waves on the surfaces of drops. It also causes a big drop to act as a small drop. All these phenomena cause molecular diffusion mechanism to govern the system and therefore mass transfer rate and mass transfer coefficients decrease. However, the above achieved results are still not clear, but the reason may be similar to that governing damping of waves by surfactants. This refers to the optimum concentration of soluble surfactant often found to give maximum damping of waves on a free liquid surface; increase or decrease in concentration of surfactant about this optimum value leads to considerable intensification of rippling [3,8].

Fig. 5 shows the effect of surfactant mass fraction upon extraction efficiency. The curve shows that an increase of surfactant mass fraction results in a decrease approximately 5% to 10% of extraction efficiency. In fact, the surfactant is placed on the external surface of drops and gives rise to decrease of internal circulation and turbulences in drops and in conclusion by changing of mass transfer mechanism to molecular diffusion, the rate of mass transfer and also the amount of solute extraction decreases or in other words, the separation efficiency (or extraction efficiency) decreases.

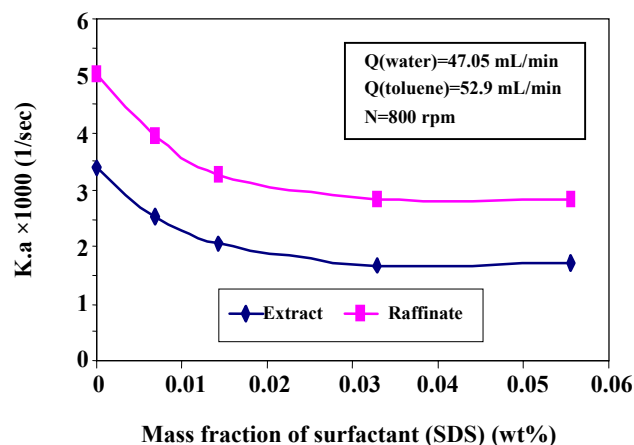


Fig. 4: Effect of surfactant mass fraction on the average overall volumetric mass transfer coefficient.

Fig. 6 shows the effect of surfactant mass fraction on the average stage efficiency. In this figure, each point shows average stage efficiency of all stages in each experiment. The curve shows the existence of surfactant causes a decrease approximately 15% to 20% of stage efficiency.

## CONCLUSIONS

According to the above experiments, the following conclusions can be made:

1- The results exhibit a reduction in the average overall volumetric mass transfer coefficients with increasing surfactant concentration. Generally, the coefficients dropped significantly (approximately 30% to 40%) at low surfactant concentration, but remained almost constant (or increased slightly) at the highest surfactant level. Minima in this type of curve have been observed such as other extraction equipments [3,8,12].

2- Also, existence of surfactants causes a decrease of extraction efficiency. In general, the extraction efficiency dropped significantly (approximately 5% to 10%) at low surfactant concentration such as mass transfer coefficients.

3- According to the obtained results, it could be concluded that the surfactants cause a decrease of stage efficiency. In general, the stage efficiency dropped significantly (approximately 15% to 20%) at low surfactant concentration such as mass transfer coefficients and extraction efficiency. Therefore, we can conclude that the stage efficiency had large effect on the extraction efficiency and mass transfer coefficients.

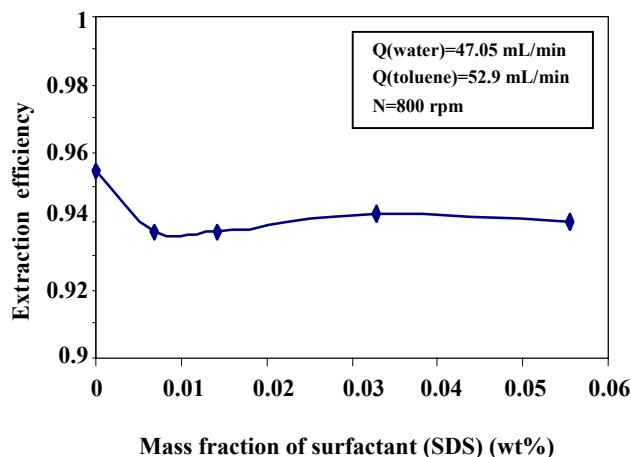


Fig. 5: Effect of surfactant mass fraction on the extraction efficiency.

4- According to the obtained results from Fig. 4 we can conclude that in the mixer-settler extractor, the amount of average overall volumetric mass transfer coefficients in two phases are considerable and therefore the resistance against mass transfer is important in both phases and in conclusion none can be ignored.

5- In industry, some materials such as impurities, plasticizers from tubing used in equipment, and or metallic colloids from pipes and fittings have similar effects as surfactants. Therefore, the study of the effects of these materials in commercial extraction equipments is widely recognized and certainly some such studies will ultimately be needed for design guidance. In general, According to the obtained results, we must reduced amounts of these materials in processes in order to increase mass transfer.

#### Acknowledgments

The authors would like to thank Ms. M. Mokhtari, P. Nourozi and Chemical Department of Engineering Faculty of Tehran University who have contributed to the success of this work.

#### Nomenclatures

$a$	Specific surface area, ( $\text{cm}^2/\text{cm}^3$ )
$C_{E_{\text{out}}}$	Mass concentration of acetone in output of extract phase, ( $\text{gr}/\text{cm}^3$ )
$C_E^*$	Equilibrium mass concentration of acetone in extract phase corresponding to raffinate phase, ( $\text{gr}/\text{cm}^3$ )

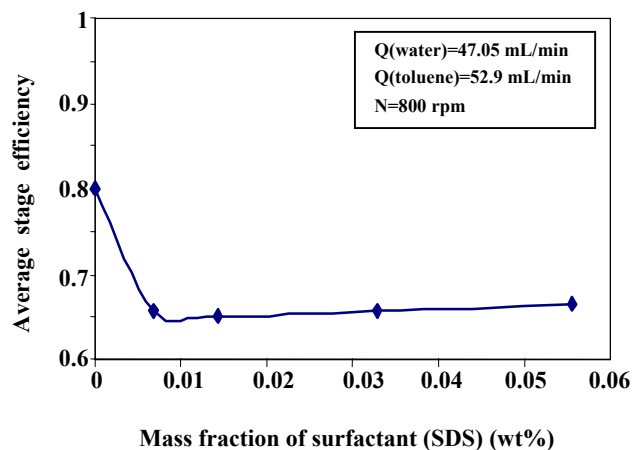


Fig. 6: Effect of surfactant mass fraction on the stage efficiency.

$C_{R_{\text{out}}}$	Mass concentration of acetone in output of raffinate phase, ( $\text{gr}/\text{cm}^3$ )
$C_R^*$	Equilibrium mass concentration of acetone in raffinate phase corresponding to extract phase, ( $\text{gr}/\text{cm}^3$ )
$d_{32}$	Sauter mean diameter, (cm)
$E_{\text{ext}}$	Extraction efficiency
$E_{\text{stage}}$	Stage efficiency
$K_E$	Overall mass transfer coefficient in extract phase, (cm/sec)
$K_R$	Overall mass transfer coefficient in raffinate phase, (cm/sec)
$\dot{m}_E$	Mass flow rate of extract phase, (gr/sec)
$\dot{m}_R$	Mass flow rate of raffinate phase, (gr/sec)
$N$	Impeller speed, (rpm)
$n$	Number of components
$Q_c$	Volumetric flow rate of continuous phase, (mL/min)
$Q_d$	Volumetric flow rate of dispersed phase, (mL/min)
$V$	Volume of a stage, ( $\text{cm}^3$ )
$X_{\text{in}}$	Mass ratio of acetone to toluene in input of raffinate phase
$X_{\text{out}}$	Mass ratio of acetone to toluene in output of raffinate phase
$X^*$	Equilibrium mass ratio of acetone to toluene in raffinate phase corresponding to extract phase
$x_1$	Mass fraction of acetone in input of raffinate phase for each stage

$x_2$	Mass fraction of acetone in output of raffinate phase for each stage	<b>18</b> (6), 1154 (1972).
$x_e$	Equilibrium mass fraction of acetone in raffinate phase	[9] Takahiko, B. et al., <i>Ind. Eng. Chem. Res.</i> , <b>41</b> , 5477 (2002).
$x_{in}$	Mass fraction of acetone in input of raffinate phase for each stage	[10] Wieneck, J. M. et al., <i>Journal of Colloid and Interface Science</i> , <b>266</b> , 430 (2003).
$x_{out}$	Mass fraction of acetone in output of raffinate phase for each stage	[11] Tatsumi, Y. et al., <i>Journal of Chemical Engineering of Japan</i> , <b>36</b> (8), 963 (2003).
$x^*$	Equilibrium mass fraction of acetone in raffinate phase corresponding to extract phase	[12] Logsdail, D. H., Slarer, M. J., <i>Elsevier Science Publishers Ltd</i> , <b>1</b> , 445 (1993).
$y_1$	Mass fraction of acetone in input of extract phase for each stage	[13] Treybal, R.E., "Liquid Extraction", Mc Graw-Hill Book Company Inc., 150-195, 396-461 (1963).
$y_2$	Mass fraction of acetone in output of extract phase for each stage	
$y_e$	Equilibrium mass fraction of acetone in extract phase	
$y_{in}$	Mass fraction of acetone in input of extract phase for each stage	
$y_{out}$	Mass fraction of acetone in output of extract phase for each stage	
$y^*$	Equilibrium mass fraction of acetone in extract phase corresponding to raffinate phase	
$\rho_{av}$	Average density in each phase, (gr/cm <sup>3</sup> )	
$\rho_i$	Density of each component, (gr/cm <sup>3</sup> )	
$x_i$	Mass fraction of each component	
$\varepsilon$	Hold-up of dispersed phase	

Received : 4<sup>th</sup> September 2005 ; Accepted : 20<sup>th</sup> February 2006

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