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# Liquid-Liquid Extraction With and Without a Chemical Reaction

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## 1. Introduction

The extraction of mercaptans with alkaline solution is accompanied by a second- order instantaneous reaction. As explained in Section 2.2, in this case, the mass transfer coefficients can be calculated as for the physical extraction, since the mass transfer is much slower than the reaction rate. The liquid-liquid extraction is a mass transfer process between two phases. One liquid phase is *the feed* consisting of a *solute* and a *carrier*. The other phase is the *solvent*. The extraction is understood to be a transfer of the solute from the feed to the solvent. During and at the end of the *extraction* process, the feed deprived of solute becomes a *raffinate* and the solvent turns into *extract*. Extraction is a separation process aiming to purify the feed or to recover one or more compounds from it.

The mass transfer mechanism can be described by the well known double film theory, the penetration theory or the surface renewal theory. Especially the stationary double film theory describes most accurately the liquid-liquid extraction. With the means of this theory, the dimensioning of the extraction equipment can be done.

Sometimes, over the physical extraction process, a chemical reaction is superposed. Depending on the reaction rate compared with the mass transfer rate, the process can be considered driven by the mass transfer or by the chemical reaction. Also, in some cases, the chemical reaction has an effect of enhancement for the extraction, contributing to speed up the process. As a consequence, the dimensioning of the equipment is different.

Many studies have been performed in the last decades for the mathematical modelling of the processes. Accurate correlations between physical properties (densities, density difference, interfacial tension), and dimensions involved in the extraction equipment dimensioning: the drop size diameter, the characteristic velocity of the drop and the slip velocity of the phases were worked out. A smaller number of correlations are available for the calculation of the mass transfer coefficients. Some of the elements needed for the dimensioning of the extractors would be determined experimentally, if a certain accuracy is expected. The experiment is compulsory for the mass transfer coefficients when a new type of equipment is used.

The present work exemplifies the theoretical aspects of the liquid-liquid extraction with and without a chemical reaction and the dimensioning of the extractors with original

experimental work and interpretations. The experiment involved extraction of acid compounds from sour petroleum fractions with alkaline solutions in structured packing columns. Such an example is useful for understanding the principles of dimensioning the extraction equipment but also offers a set of experimental data for people developing processes in petroleum processing industry. A simple, easy to handle model composed by two equations was developed for the mercaptans (thiols) extraction.

## 2. Theoretical aspects

The immiscible liquid phases put in contact (the feed and the solvent) form a closed system evolving towards the thermodynamic equilibrium. According to the Gibbs law:

$$l = c + 2 - f = 3 + 2 - 2 = 3, \quad (1)$$

the system can be defined by three parameters ( $l=3$ ), the number of components being  $c=3$  (solvent, solute and carrier), and the phases number  $f=2$ . Usually, the parameters taken into account are the temperature ( $T$ ), the concentration of the solute in the raffinate ( $x$ ) and the concentration in the extract ( $y$ ). So, the equilibrium general equation in this case is:

$$y = f(x)_{l=\text{const}} \quad (2)$$

The equilibrium equation can have different forms, but most frequently, if the liquid phases are completely immiscible and the solute concentration is low, the Nernst law describes accurately the thermodynamic equilibrium:

$$y = m \cdot x, \quad (3)$$

where  $m$  is the repartition coefficient of the solute between the two phases. The Nernst law can be applied also at higher concentration of the solute but in a narrow range of concentrations.

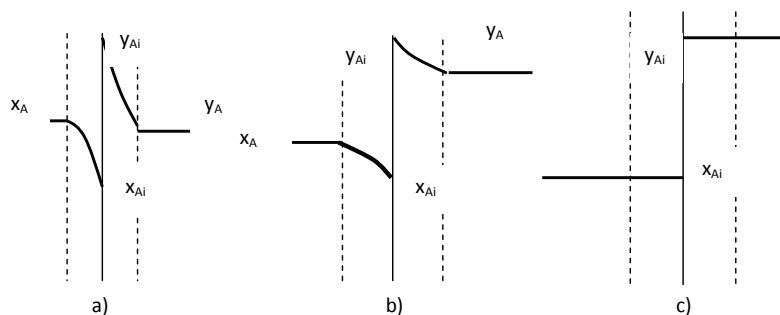


Fig. 1. The evolution of the solute concentration in the vicinity of the interface in a closed system

The double stationary film theory of Whitman leads to very good practical results for the determination of mass transfer coefficients. According to this theory, the phases are separated by an interface and a double film (one of each phase) adheres to this interface. The

mass transfer takes place exclusively in this double stationary film by the molecular diffusion mechanism. In the bulk of both phases, the concentration of the solute is considered uniform as a consequence of perfect mixing.

In Fig.1, the evolution in time is presented for a closed system approaching the equilibrium, in the light of double film theory. Notations  $x_{Ai}$  and  $y_{Ai}$  are for the concentration at the interface in raffinate and extract respectively;  $x_A$  and  $y_A$  denote the concentration of the solute A in the bulk of the raffinate and of the extract respectively. In Fig.1, the mass transfer is presented in a closed system in evolution from the initial state  $a$  to the final equilibrium state  $c$ . The concentrations at the interface are constant and linked by the equilibrium equation since the concentration of the solute in the bulk feed /raffinate decreases and the concentration of the solute in the bulk solvent/ extract increases in time until equalling the equilibrium concentrations. If the system is open,  $y_A$  and  $x_A$  are constant in time (the regime becomes stationary) and the system is maintained in the state  $a$ .

### 2.1 Mass transfer coefficients in physical extraction

In liquid-liquid extraction, the best mechanism describing the mass transfer is the unicomponent diffusion (the solute A diffusing in one direction without a counter diffusion). According to Maxwell- Stefan model, the mass transfer rate in the raffinate film is:

$$N_A = \frac{c_R \cdot D_{AR}}{l_R(1-x_A)_{ml}}(x_A - x_{Ai}) \quad (4)$$

In the Eq.4,  $N_A$  is the flow of component A transferred from the raffinate through the film to the interface;  $D_{AR}$  is the diffusion coefficient of the solute in the raffinate phase;  $c_R$  is the total concentration of components in the raffinate, usually expressed as kmol/m<sup>3</sup>;  $l_R$  is the thickness of the raffinate film;  $\frac{c_R \cdot D_{AR}}{l_R(1-x_A)_{ml}}$  denoted with  $k_R$  is the partial mass transfer

coefficient in the raffinate phase and  $1/k_R$  is the resistance to the transfer.

Similarly, Eq.5 describes the mass transfer rate in the extract film,  $E$  being the notation for "extract":

$$N_A = \frac{c_E \cdot D_{AE}}{l_E(1-y_A)_{ml}}(y_{Ai} - y_A) \quad (5)$$

During a stationary regime, the component A doesn't accumulate in the raffinate film as well as in the extract film; this means that the flux transferred in the raffinate film to the interface equals the flux transferred from the interface into the extract phase:

$$N_A = k_E(y_{Ai} - y_A) = k_R(x_A - x_{Ai}) \quad (6)$$

In Eq.6,  $(y_{Ai}-y_A)$  and  $(x_A-x_{Ai})$  are the driving forces of the mass transfer in the extract film and in the raffinate film respectively (related to the partial mass transfer coefficients). These partial driving forces can be read on the axes in the Fig. 2, where the system state is represented by the point A and the equilibrium concentrations at the interface are represented by the point  $A_i$ . The arrow  $AA_i$  denotes the distance from the actual state of the system to the equilibrium state. But the overall driving force is  $(x_A-x_{Ae})$ , related to the raffinate phase and  $(y_{Ae}-y_A)$ , related to the extract respectively. The overall driving forces

refer to the distance from the actual state of the system to an hypothetical state when the actual concentration of the raffinate ( $x_A$ ) would be in equilibrium with the extract ( $y_{Ae}$ ), or the actual concentration of the extract ( $y_A$ ) would be in equilibrium with the raffinate ( $x_{Ai}$ ).

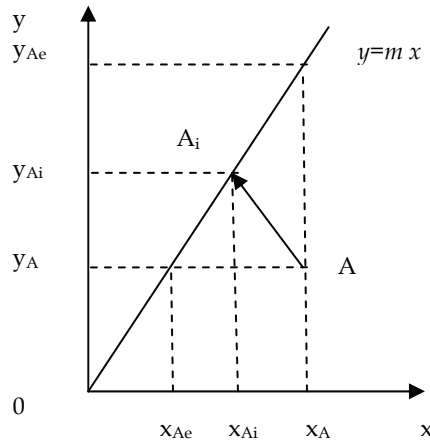


Fig. 2. The representation of the driving forces for the mass transfer (immiscible liquid phases; equilibrium described by Nernst law)

In connection with the overall driving forces, the overall mass transfer coefficients are defined in the equations (7) and (8):

$$N_A = K_R \cdot (x_A - x_{Ae}) \quad (7)$$

$$N_A = K_E \cdot (y_{Ae} - y_A) \quad (8)$$

As seen in Fig.2, the slope of the equilibrium curve ( $m$ ) can be calculated from geometrical dimensions (Eq.9):

$$m = \frac{y_{Ai} - y_A}{x_{Ai} - x_{Ae}} = \frac{y_{Ae} - y_A}{x_A - x_{Ae}} = \frac{y_{Ae} - y_{Ai}}{x_A - x_{Ai}} \quad (9)$$

By manipulating the Eq.6-9 and Fig.2, the Eq.(10) and (11) are obtained and would be used for the calculation of the overall mass transfer coefficients  $K_R$  and  $K_E$  [ $\text{m} \cdot \text{s}^{-1}$ ] when the partial coefficients  $k_R$  and  $k_E$  are known:

$$\frac{1}{K_R} = \frac{1}{k_R} + \frac{1}{m \cdot k_E} \quad (10)$$

$$\frac{1}{K_E} = \frac{1}{k_E} + \frac{m}{k_R} \quad (11)$$

More often, the mass transfer coefficients are not related to the raffinate/ extract phases but more important, to the continuous and the dispersed phase. The extraction system is in fact an emulsion: one of the phases is in form of droplets and the other one is continuous. Which

one is discontinuous, depends on the volume ratio of the phases and on the interfacial phenomena. Sometimes, the raffinate is the dispersed phase, at other times it is the continuous phase. This is why, the equations (10) and (11) are re-written in terms of *overall volumetric mass transfer coefficients* for the dispersed phase ( $d$ ) and for the continuous phase ( $c$ ),  $K_d a$  and  $K_c a$  [ $s^{-1}$ ], as the interfacial area  $a$  [ $m^2/m^3$ ] is included in their value:

$$\frac{1}{K_d \cdot a} = \frac{1}{k_d \cdot a} + \frac{\rho_d}{\rho_c \cdot m \cdot k_c \cdot a} \quad (12)$$

$$\frac{1}{K_c \cdot a} = \frac{1}{k_c \cdot a} + \frac{\rho_c \cdot m}{\rho_d \cdot k_d \cdot a} \quad (13)$$

Eq. (12) and (13) are written for the raffinate as dispersed phase. The partial coefficients in Eq. (12) and (13) can be calculated from the diffusivity coefficients  $D_{AR}$ ,  $D_{AE}$  and the thickness of the double film:  $l_R$  and  $l_E$  (Eq.4 and 5). Since for the diffusivity, there are a few accurate correlations (the most used is the correlation Wilke & Chang, 1955) or simple experiments to perform, measuring the double film thickness is more complicated. Alternatively, the partial coefficients can be calculated with criterial equations; for example, the most used correlation for the calculation of the partial coefficient for the continuous phase is Eq.14 (Treybal, 2007):

$$Sh_c = 0.725 \cdot Sc_c^{0.42} \cdot Re_c^{0.57} \cdot (1 - \varphi) , \quad (14)$$

where:

- the partial mass transfer coefficient in the continuous phase film is included in the Sherwood criterion ( $Sh_c = k_d d_{32} / D_c$ ,  $d_{32}$  being the medium Sauter diameter of the drops and  $D_c$  - diffusivity of the reactant A in the continuous phase);
- $Sc_c$  is the Schmidt criterion for the continuous phase,  $Sc_c = \mu_c / D_c$ ;
- $Re_c$  is Reynolds number for continuous phase,  $Re_c = \rho_c d_{32} V_{slip} / \mu_c$  ( $V_s$ - slip velocity of phases);
- $\varphi$  is the dispersed phase hold-up.
- The following notions: Sauter mean diameter ( $d_{32}$ ), slip velocity( $V_{slip}$ ) and dispersed phase hold up ( $\varphi$ ), will be explained in section 2.3.

The correlation recommended by Laddha and Degaleesan (1974) for the partial coefficient for the discontinuous phase is Eq.15:

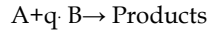
$$k_d = 0.023 \cdot V_{slip} \cdot Sc_c^{-0.5} \quad (15)$$

In practice, the calculations are done in reverse order: the overall coefficients are determined in experimental studies, as explained in Section 2.3, then the partial coefficients are calculated from Eq.(10) and (11). From these partial coefficients one can calculate the thickness of the double film. In the extreme case when the solvent has a high affinity for the solute A, much higher than the raffinate, it is accepted that  $K_E \approx k_E$ .

Knowing the overall global coefficients for a certain system is crucial, because they can't be avoided at the equipment dimensioning.

## 2.2 Mass transfer coefficients in chemical extraction

Let's consider a reaction in the liquid-liquid system:



The first phase contains the component A which diffuses from the first phase into the second one containing B, reacting with B in that phase. Then, products diffuse in the same phase 2. Reactions in liquid-liquid systems can be classified from kinetically point of view as slow, fast and instant (Sarkar *et al*, 1980).

The equation describing the diffusion of the reactant A simultaneously with the chemical reaction is (Astarita, 1967):

$$D_A \cdot \nabla^2 c_A = u \cdot \nabla c_A + \frac{\partial c_A}{\partial t} + v_{RA} \quad (16)$$

The term on the left hand side of the Eq.16 represents the molecular diffusion of the component A through the film of phase 1, The terms on the right hand sides have the following meaning: the first one describes the transport by convection through the same film, the second one is the accumulation of A in the film and the third represents the reaction rate. The Eq. 16 can be simplified in the conditions of the double film theory, where the diffusion direction of A is perpendicular to the interface (direction  $x$ ), eddies are inexistent in the film and component A doesn't accumulate in the film:

$$D_A \cdot \frac{d^2 c_A}{dx^2} = v_{RA} \quad (17)$$

The Eq.17 can be detailed for both reactants:

$$D_A \cdot \frac{d^2 c_A}{dx^2} = \frac{dc_A}{dt} \quad (18)$$

$$D_B \cdot \frac{d^2 c_B}{dx^2} = \frac{dc_B}{dt} \quad (19)$$

### Fast and instant reactions

In case of fast and instant reactions, the reaction takes place in the plane located in the film of phase 2 (phase containing the component B). The component A diffuses through the film 1 to the interface then from interface to the reaction plane (see Fig. 3 a). In Fig.3 a, a particular case of fast reaction: the irreversible instantaneous reaction is illustrated; in this case, both reactants diffuse to the reaction plane, where their concentrations equals to zero. The term "instantaneous" is idealised since the reaction rate is always finite, but in this case, the mass transfer rate is much lower than the reaction rate, so the process is entirely controlled by the diffusion mechanism.

Taking into account the position of the reaction plane (at the distance  $\lambda$  from the interface) and the stoichiometric coefficient of the reaction  $q$ , the Eq.18 and 19 considering their equality, and integrating, the Eq. 20 is obtained:

$$D_A \cdot \left( \frac{dc_A}{dx} \right)_{x=\lambda} = \frac{1}{q} \cdot D_B \cdot \left( \frac{dc_B}{dx} \right)_{x=\lambda} \quad (20)$$

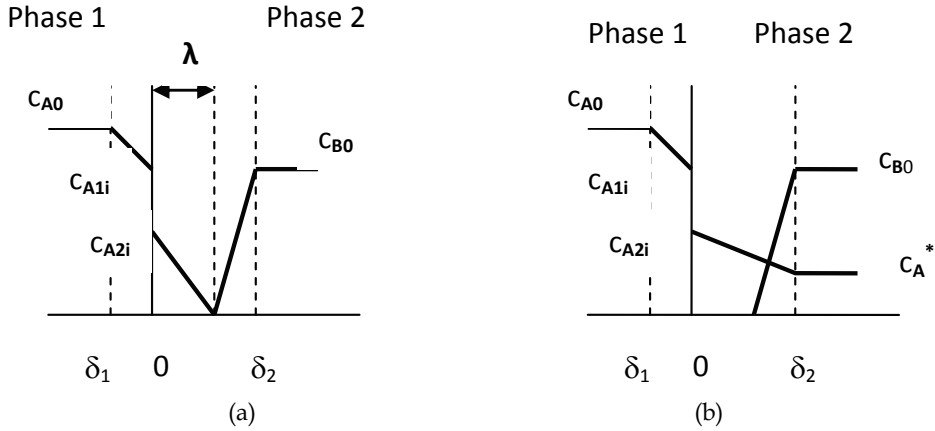


Fig. 3. Profiles of reactants concentration at the extraction with a chemical reaction: a - instantaneous irreversible reaction taking place in phase film 2; b - slow reaction taking place in the film phase 2

By integrating Eq.20 between the limits  $x=\lambda$  and  $x=l$ , ( $l$ - the film thickness), it results:

$$q \cdot D_A \cdot \frac{C_{A2i}}{\lambda} = D_B \cdot \frac{C_{B0}}{l - \lambda} \quad (21)$$

In Eq.21,  $C_{A2i}$  is the concentration of A at the interface on the film's 2 side and  $C_{B0}$  is the concentration of B in bulk of the phase 2. The Eq. 21 can be re- written in another form:

$$\lambda = l \cdot \frac{q \cdot D_A \cdot C_{A2i}}{q \cdot D_A \cdot C_{A2i} + D_B \cdot C_{B0}} \quad (22)$$

$\frac{l}{\lambda}$  is in fact the ratio between the the overall mass transfer coefficient with a chemical reaction  $Ka$ , and the overall mass transfer coefficient at the physical extraction (without a chemical reaction),  $K^0a$ :

$$\frac{K \cdot a}{K^0 \cdot a} = \frac{l}{\lambda} = 1 + \frac{D_B}{D_A} \cdot \frac{C_{B0}}{q \cdot C_{A2i}}, \quad (23)$$

So, the overall mass transfer coefficient in the case of instant reaction is proportional to the coefficient for the physical extraction. It means that the coefficient at the extraction with instant chemical reaction depends on hydrodynamics in the same extent as that for physical extraction.

For instantaneous irreversible reactions, the enhancement factor  $E_i$  is defined (Pohorecki, 2007) by Eq.24:

$$E_i = \frac{Q(\text{instantaneous reaction})}{Q(\text{physical})} \quad (24)$$



where  $Q$  is the quantity transferred through the interface ( $\text{mol m}^{-2}$ ). If this quantity is divided by time, the enhancement factor is defined as the factor by which the reaction increases the overall transfer rate compared to the rate of physical transfer (in the absence of the reaction). Taking into account Eq.23, the enhancement factor at the interface can be calculated by the formula:

$$E_i = 1 + \frac{D_B}{D_A} \cdot \frac{c_{B0}}{q \cdot c_{A2i}} \quad (25)$$

As seen in Eq.25, the enhancement factor can be calculated with the diffusivities of the reactants and their concentrations in bulk of phase and at the interface; because the concentration is difficult to be determined at the interface, the following approach is more feasible:

- The overall mass transfer coefficient for the physical extraction of component A from the phase 1 in phase 2,  $K^0 a$ , is calculated with Eq.14 or 15, depending on the phase where the reaction takes place; the individual transfer coefficients can be estimated with Eq.16 and 17 or other correlations found in literature (Treybal, 2007 and Pratt, 1983); the slip velocity  $V_{slip}$  intervening in the Eq.15 directly or in Eq.14 in the Reynolds number, can be calculated, as it will be seen in Section 2.3;
- The actual overall mass transfer coefficient including the chemical reaction is determined experimentally,  $K a$ , as it will be seen in Section 2.3;
- The ratio  $\frac{K \cdot a}{K^0 \cdot a}$  represents the enhancement factor  $E$ ; it is higher than 1, sometimes  $\gg 1$ , depending on the physical properties of the system ( $D_A$ ,  $K^0 a$ ) and the constant of reaction rate; the values of  $E$  experimentally determined are useful for the calculation of the concentration of the reactant A at the interface  $c_{Ai}$  (Eq.25) needed in further calculations.

The intensification of the mass transfer during the chemical reaction was explained here in the frame of the film theory but in fact, the renewal of interface theory could better explain what happens: the interfacial tension depends on the concentration of the transferred substance and as a result, spontaneous interfacial convection is initiated, so a more intensive renovation of the interface and, correspondingly, an increase in the mass transfer coefficient is achieved (Ermakov *et al*, 2001)

#### Slow reactions

The slow reaction can take place in the film but more probably, in the bulk of the solvent phase 2. In Fig.3b, the reaction takes place in the film phase 2. The process can be considered a physical diffusion of component A in the phase 2 film followed by reaction between A and B in the film of the phase 2. Unlike the fast reaction, part of component A remains unreacted and diffuses further in the phase 2, where its concentration is  $c_A^*$ . In Fig.3.b it is illustrated the case when component B is completely consumed in the reaction, but there are more complicated cases when B is not consumed in the film phase 2 but diffuses further in the phase 1 and reaction could take place in one or both phases.

In a steady state, there is no accumulation of component A in any point of the system; this means that the rate of physical transfer process equals the consumption rate of A in reaction:

$$K \cdot a = k_E a \cdot (c_{A2i} - c_A^*) = \frac{1}{\tau} (c_{A0} - c_{A1i}) + r(c_A, c_B) \quad (26)$$

where  $c_{A1i}$  and  $c_{A2i}$  are the concentrations of A at the interface (see Fig.3) in thermodynamic equilibrium. The mass transfer depends on the contact time of phases in the extractor. The contact time is the same as the residence time  $\tau$ , defined in Eq.27:

$$\tau = \frac{V}{Q}, \quad (27)$$

where  $V$  is the active volume of the extractor (the volume occupied by the emulsion in the extractor) and  $Q$  is the total volumetric flow of the phases.

For the first order irreversible reaction:  $r = -k_1 \cdot c_A^*$  ( $k_1$ - reaction rate constant) and taking into account the equilibrium correlation:  $c_{A1i} = m \cdot c_{A2i}$  ( $m$ - the repartition coefficient, Eq.3), the Eq.26 becomes:

$$K \cdot a = k_E a \cdot (c_{A2i} - c_A^*) = \frac{1}{\tau} (c_{A0} - m \cdot c_{A2i}) - k_1 \cdot c_A^* \quad (28)$$

In the Eq.28, only  $c_{A2i}$  can't be measured, so the equation is re-arranged in all measurable or calculable terms (Sarkar *et al*, 1980):

$$K \cdot a = \frac{1}{\tau} \cdot \left( c_{A0} - m \cdot \frac{k_E + k_1}{k_E \cdot a - \frac{m}{\tau}} \right) - k_1 \cdot c_A^* \quad (29)$$

As seen in Eq.29, the rate of transfer for the extraction with slow reaction, depends both on the mass transfer coefficient ( $K_E$ ) and on the reaction rate constant ( $k_1$ ). The process is controlled by the slowest step: the mass transfer or the reaction.

### 2.3 The dimensioning of the extractors. The column with continuous differential contact of phases

All the theory about the mass transfer coefficients has as a practical goal the dimensioning of the industrial equipment for liquid-liquid extraction.

Dimensioning and extractor means to find its main geometrical dimensions. As an example, the column type extractors are presented here but for other type of equipment, the dimensioning is very different (Godfrey & Slater, 1994). Dimensioning a column means to find its diameter and height.

For the columns with continuous differential contact, the phases flow in countercurrent, one of the phases being continuous, the other one dispersed (drops).

#### 2.3.1 The column diameter

The diameter of the column is correlated with the processing capacity of the column (the flow of the phases) and the flooding capacity. The synthetic form of this correlation was expressed by Zhu and Luo (1996):

$$D_c = \sqrt{\frac{4 \cdot (Q_c + Q_d)}{\pi \cdot k \cdot B_{max}}} \quad (30)$$

where:  $Q_c$  is the continuous phase volumetric flow,  $[\text{m}^3\cdot\text{s}^{-1}]$

$Q_d$  the dispersed phase volumetric flow,  $[\text{m}^3\cdot\text{s}^{-1}]$

$B_{max}$  is the flooding capacity,  $[\text{m}^3\cdot\text{m}^{-2}\cdot\text{s}^{-1}]$ ; considering the flow in the free cross-sectional area of the column. The flooding capacity  $B_{max}$  is in fact the sum of the flooding velocities of phases; it depends on the physical properties of the system: the density ( $\rho_c$  and  $\rho_d$ ), the viscosity ( $\mu_c$  and  $\mu_d$ ) and the interfacial tension  $\sigma$ . The flooding capacity can be predicted following extensive studies, as exemplified in Section 3.

$k$ - the flooding coefficient, with values from 0.4 (dispersion column) to 0.8 (column equipped with structured packing); this coefficient would be kept as high as possible, in order to increase the mass transfer rate and the processing capacity of the column.

The flooding capacity is experimentally determined for each type of column. It consists in derangements of the countercurrent flow bringing about entrainment of one phase in the other one, or the impossibility for one flow to enter the column. There are three main mechanisms of flooding:

- The phase inversion provoked by the excessive increasing of dispersed phase flow;
- The entrainment of the drops in the continuous phase when the flow of continuous phase increases too much;
- The flooding due to the contaminants at the interface creating instability of the interface or even inversion of the phases.

According to authors after Hanson (1971), the diameter calculation is made using the concept of *slip velocity*,  $V_{slip}$ , which is the velocity of the dispersed phase related to the continuous phase; the *slip velocity* is in fact, the sum of linear velocities of the phases, not in the free cross-sectional area but in the actual cross-sectional area, taking into account the internal parts of the column and the dispersed phase holdup,  $\phi$ . According to this definition, in the dispersion column (without any internal parts, such as trays or packing), the slip velocity is:

$$V_{slip} = \frac{V_d}{\phi} + \frac{V_c}{1 - \phi} \quad (31)$$

The dispersed phase holdup is the fraction occupied by the drops in the free cross sectional area of the column. In fact, the holdup is not uniformly distributed in the column because the drops are of various dimensions, with an irregular shape, oscillating. For approximate calculations, a mean diameter would be taken into consideration. The most usual expression of this is the Sauter mean diameter,  $d_{32}$ :

$$d_{32} = \frac{\sum n_i \cdot d_i^3}{\sum n_i \cdot d_i^2} \quad (32)$$

The mean diameter  $d_{32}$ , is correlated with the holdup  $\phi$  and the interfacial area  $a$ :

$$a = \frac{6 \cdot \phi}{d_{32}} \quad (33)$$

Empirical correlations can be used to correlate Sauter mean diameter  $d_{32}$  with physical properties of the system. It can be calculated with the formula recommended by Seibert & Fair (1988) and verified by Iacob & Koncsag (1999) on systems with high interfacial tension:

$$d_{32} = 1.15 \left( \frac{\sigma}{\Delta \rho \cdot g} \right)^{0.5} \quad (34)$$

where  $\Delta \rho$ - density difference of phases,  $g$  -gravitational constant.

It is difficult to determinate the slip velocity, but it can be easier done but an easier by correlating it with the singular drop's characteristic velocity,  $V_K$ , which can be determined experimentally.  $V_K$  is defined as the ratio between the distance travelled by the singular drop in the column and the time of this trip. The singular drop's characteristic velocity is uninfluenced by the presence of other drops but is influenced by the presence of the internal parts of the equipment. For example, in the case of packed column,  $V_K$  can be correlated with the physical properties of the liquid-liquid system and the geometrical characteristics of the packing:

$$V_K = 0.637 \left( \frac{a_p \cdot \rho_c}{\varepsilon^3 \cdot g \cdot \Delta \rho} \right)^{-0.5} \quad (35)$$

There are correlations between the slip velocity and the singular drop's characteristic velocity. A simple correlation is the Pratt- Thornton equation which is valid for rigid (non-oscillating) drops and low values of the holdup (Thornton, 1956):

$$V_{slip} = V_K \cdot (1 - \phi) \quad (36)$$

For higher values of holdup, a more accurate equation would be used (Misek, 1994):

$$V_{slip} = V_K \cdot (1 - \phi) \exp(a\phi) \quad (37)$$

### 2.3.2 The column height

For extractors with countercurrent flow of the phases, the active height is calculated on the basis of the *mass transfer unit* notion. In the hypothesis of the plug flow, the height of the column is:

$$H = [NTU]_{od} \cdot [HTU]_{od} = [NTU]_{oc} \cdot [HTU]_{oc} \quad (38)$$

where  $[NTU]_{od}$  and  $[NTU]_{oc}$  are the number of transfer units relative to the dispersed and to the continuous phase respectively, when expressing the mass transfer rate as the overall mass transfer coefficients.  $[HTU]_{od}$  and  $[HTU]_{oc}$  are the height of the transfer unit relative to the overall mass transfer coefficient in the same phases.

The height of the transfer unit is the height of the column which ensures the decreasing by  $e$  ( $=2.71\dots$ ) of the driving force defined as in the Eq.7 and 8, taking into account which is the dispersed phase and the continuous one.

$[NTU]_{od}$  and  $[NTU]_{oc}$  are calculated taking into account the equilibrium data. The relationships given in Eq.39 and 40 are related to the extract ( $E$ ) and the raffinate ( $R$ ) and it is to see which equation applies to the continuous phase or the dispersed phase (e.g. the raffinate can be dispersed phase in one application and continuous phase in another one):

$$[NTU]_{oR} = \int_{x_1}^{x_2} \frac{dx}{x - x_e} \quad (39)$$

$$[NTU]_{oE} = \int_{y_1}^{y_2} \frac{dy}{y - y_e} \quad (40)$$

where:

$x_1, x_2, y_1, y_2$  are the solute concentration in the raffinate (x) and in the extract respectively (y) in the flow entering (1) or exiting (2) the column.

$x_e, y_e$  are the solute concentrations in raffinate and in the extract respectively, in equilibrium conditions in every point along the column.

$[HTU]_{od}$  and  $[HTU]_{oc}$  are experimentally found by dividing the active height of the column (the height of the column where the dispersed phase and the continuous phase co-exists) by the  $[NTU]_{od}$  or  $[NTU]_{oc}$ .

Let's express the mass transfer for the dispersed phase. The volumetric overall mass transfer coefficients related to the dispersed phase  $K_{od}a$  are correlated with the height of the mass transfer unit  $[HTU]_{od}$  and the superficial velocity of the dispersed phase  $v_d$  (which is defined as the volumetric flow divided by the cross-sectional area of the column):

$$K_{od} \cdot a = \frac{v_d}{HTU_{od}} \quad (41)$$

In practice, the height of the column is calculated starting with the experimental determination of mass transfer coefficients, continuing by the calculation of HTU with Eq.41 and finally, applying the Eq. 38.

### 3. Experimental data

The theoretical aspects presented here are very general. In fact, an engineer needs mathematical models for the dimensioning of the industrial equipment, specific for a given type of extractor. Here we present the process of the model's development, using a large database, partially relying on our original experiment, partially on data from literature, for the dimensioning of a packed column.

The original experimental data were obtained in a 76 mm diameter column with structured packing type Sulzer SMV 350 Y. The specific area of the packing was:  $a_p = 340 \text{ m}^2/\text{m}^3$  and the void fraction  $\varepsilon = 0.96$ . The packing bed was made of 4 structured packing elements with a total height of 840 mm. The detailed description of the pilot plant was presented in a previous work (Koncsag & Barbulescu, 2008). Another type of ordered packing -corrugated metal gauze- was used in a mass transfer study at laboratory scale, also described in (Koncsag & Barbulescu, 2008). The experiment at laboratory scale was performed in another installation including a glass column with the internal diameter of 3 cm and an active height of 70 cm. The handicraft packing was made of corrugated metal gauze and had the following geometric characteristics:  $\varepsilon = 0.98$  and  $a_p = 60 \text{ m}^2/\text{m}^3$ . Taking into account the small opening of the spiral, the drops are forced to detour and the tortuosity of their motion increases; as a consequence, the residence time of the drops in the column increases and the mass transfer improves comparing with the simple dispersion column. Also, the experiment was performed for the dispersion column (the column unpacked).

So, three sets of data were obtained: for the Sulzer SMV350 packing, for the corrugated metal gauze packing and without packing (Table1).

The studied systems were: water- gasoline, NaOH solution 20%wt – gasoline and carbon tetrachloride- water. These systems were very different from the viewpoint of density, interfacial tension and viscosity. The first and the third systems are usually taken into account in the hydrodynamic studies and the second one is common in the purifying of hydrocarbon streams. The results of the flooding tests are expressed as pairs of limiting superficial velocities of the phases (continuous and dispersed), in flooding conditions:  $V_{cf}$ ,  $V_{df}$ .

Other experimental data from the literature were connected to the results of the original experiment (Table 1), in order to have a larger database for the mathematical model (Table 2). The data were chosen for hydrocarbon – water systems (gasoline- water or toluene- water) and for very different types of packing: Raschig rings of different size (Crawford & Wilke, 1951); Norton ordered packing (Seibert & Fair, 1988) and Intalox saddles (Seibert *et al*, 1990).

Flooding superficial velocities for the system gasoline- water , $d_{32} = 0.0052$ m, $\rho_c=996$ kg/m <sup>3</sup> , $\rho_d=740$ kg/m <sup>3</sup> , $\mu_c = 0.000993$ kg/m·s, $\sigma = 52.0 \cdot 10^{-3}$ N/m , $v_K = 0.055$ m/s				
1	2	3	4	5
0.88	0.84	0.69	0.32	0.21
0.17	0.27	0.43	0.84	1.00
Flooding superficial velocities for the system gasoline- 20%NaOH solution, $d_{32} = 0.0047$ m, $\rho_c=1220$ kg/m <sup>3</sup> , $\rho_d=740$ kg/m <sup>3</sup> , $\mu_c = 0.00366$ kg/m·s, $\sigma = 78.6 \cdot 10^{-3}$ N/m, $v_K = 0.067$ m/s				
1	2	3	4	5
0.80	0.68	0.43	0.32	0.27
0.11	0.17	0.84	1.17	1.31
Flooding superficial velocities for the system water – CCl <sub>4</sub> at 5°C, $d_{32} = 0.0035$ m, $\rho_c=1610$ kg/m <sup>3</sup> , $\rho_d=996$ kg/m <sup>3</sup> , $\mu_c = 0.00123$ kg/m·s, $\sigma = 47.3 \cdot 10^{-3}$ N/m, $v_K = 0.0604$ m/s				
1	2	3	4	5
0.64	0.62	0.58	0.35	0.24
0.17	0.27	0.37	1.17	1.43

Table 1. Experimental data at the hydrodynamic test in the column equipped with Sulzer packing ( $a_p = 340$  m<sup>2</sup>/m<sup>3</sup>,  $\epsilon = 0.96$ ,  $D_{col} = 0.076$  m)

The second part of the experiment consisted of a mass transfer study concerning the extraction of mercaptans from petroleum fractions with alkaline solutions, a process encountered in the oil processing industry.

The raw material was the gasoline enriched in mercaptans (ethanethiol or 1-propanethiol or 1-buthanethiol) and pumped into the column where it forms the dispersed phase; after the extraction and the coalescence, the gasoline exits the column at the top, as a refined phase. The solvent – the continuous phase- is in fact a caustic solution (NaOH) with concentration in range of 5-15% wt. The continuous phase enters the column free of mercaptans and exits as an extract enriched in the said mercaptans. Samples of feed and refined phase are

collected and the mercaptans concentration is analyzed by a volumetric method using  $\text{AgNO}_3$ . The concentration of the mercaptans in the extract is calculated by material balance. The volumetric overall mass transfer coefficients were calculated by Eq.37, 38 and 40 and are presented in Table 3.

Flooding superficial velocities for the system gasoline- water in case of the contactor equipped with Raschig rings 1/ 2" ( $a_p = 310 \text{ m}^2/\text{m}^3$ , $\varepsilon = 0.71$ , $D_{\text{col}} = 0.305 \text{ m}$ ), $d_{32} = 0.0052 \text{ m}$ , $\rho_c = 996 \text{ kg}/\text{m}^3$ , $\rho_d = 740 \text{ kg}/\text{m}^3$ , $\mu_c = 0.000993 \text{ kg}/\text{m} \cdot \text{s}$ , $\sigma = 42.4 \cdot 10^{-3} \text{ N}/\text{m}$ , $v_K = 0.037 \text{ m}/\text{s}$					
Superficial velocities of phases, m/s	1	2	3	4	
$10^2 \cdot V_{df}$	0.88	0.58	0.38	0.13	
$10^2 \cdot V_{cf}$	0.25	0.44	0.60	0.97	
Flooding superficial velocities for the system gasoline- water in case of the contactor equipped with Raschig rings 1" ( $a_p = 195 \text{ cm}^2/\text{cm}^3$ , $\varepsilon = 0.74$ , $D_{\text{col}} = 0.305 \text{ cm}$ ); $d_{32} = 0.0052 \text{ m}$ , $\rho_c = 996 \text{ kg}/\text{m}^3$ , $\rho_d = 740 \text{ kg}/\text{m}^3$ , $\mu_c = 0.000993 \text{ kg}/\text{m} \cdot \text{s}$ , $\sigma = 42.4 \cdot 10^{-3} \text{ N}/\text{m}$ , $v_K = 0.05 \text{ m}/\text{s}$					
Superficial velocities of phases, m/s	1	2	3	4	5
$10^2 \cdot V_{df}$	1.64	1.10	0.88	0.67	0.36
$10^2 \cdot V_{cf}$	0.54	0.83	1.00	1.23	1.69
Flooding superficial velocities for the system toluene- water in case of the contactor equipped with Norton packing ( $a_p = 213 \text{ m}^2/\text{m}^3$ , $\varepsilon = 0.97$ , $D_{\text{col}} = 0.425 \text{ m}$ ); $d_{32} = 0.0055 \text{ m}$ , $\rho_c = 996 \text{ kg}/\text{m}^3$ , $\rho_d = 864 \text{ kg}/\text{m}^3$ , $\mu_c = 0.00089 \text{ kg}/\text{m} \cdot \text{s}$ , $\sigma = 30.0 \cdot 10^{-3} \text{ N}/\text{m}$ , $v_K = 0.0497 \text{ m}/\text{s}$					
Superficial velocities of phases, m/s	1	2	3	4	5
$10^2 \cdot V_{df}$	1.13	0.93	0.72	0.60	0.30
$10^2 \cdot V_{cf}$	0.9	1.01	1.14	1.30	1.60
Flooding superficial velocities for the system toluene- water in case of the contactor equipped with Intalox saddles No25 IMTP ( $a_p = 226 \text{ m}^2/\text{m}^3$ , $\varepsilon = 0.95$ , $D_{\text{col}} = 0.102 \text{ m}$ ); $d_{32} = 0.0055 \text{ m}$ , $\rho_c = 996 \text{ kg}/\text{m}^3$ , $\rho_d = 864 \text{ kg}/\text{m}^3$ , $\mu_c = 0.00089 \text{ kg}/\text{m} \cdot \text{s}$ , $\sigma = 30.0 \cdot 10^{-3} \text{ N}/\text{m}$ , $v_K = 0.0477 \text{ m}/\text{s}$					
Superficial velocities of phases, m/s	1	2	3	4	5
$10^2 \cdot V_{df}$	1.44	1.32	0.93	0.72	0.51
$10^2 \cdot V_{cf}$	0.79	1.05	1.40	1.58	1.75

Table 2. Experimental data from literature concerning the hydrodynamic tests in the columns equipped with other type of packing

## 4. Discussion

The original experimental data about the flooding- linked to the column capacity- (Table 1) were compared with the predicted data from older models in the literature for packed columns, in order to see if they are satisfactory models or should be improved. If not, a new model would be developed.

### 4.1 The Crawford-Wilke model

A good old model is the Crawford- Wilke correlation curve (Crawford & Wilke, 1951). At the beginning, this model correlated a total of 160 experimental points for a large range of random packing but relatively few liquid systems.

	NaOH conc.	Dispersion column		Laboratory packed column		Pilot packed column	
		Dispersed phase velocity, $V_d$ ( $\times 10^2$ , m/s)	$K_{oda}$ ( $\times 10^3$ , s $^{-1}$ )	Dispersed phase velocity, $V_d$ ( $\times 10^2$ , m/s)	$K_{oda}$ ( $\times 10^3$ , s $^{-1}$ )	Dispersed phase velocity, $V_d$ ( $\times 10^2$ , m/s)	$K_{oda}$ ( $\times 10^3$ , s $^{-1}$ )
Buthanethiol	5%	0.17	0.91	0.17	1.25	0.21	3.0
		0.23	1.06	0.25	1.43	0.43	4.5
		0.33	1.16	0.33	2.05	0.68	6.5
	10%	0.17	0.89	0.17	1.56	0.21	3.1
		0.23	1.20	0.25	1.93	0.43	4.8
		0.33	1.38	0.33	2.87	0.68	7.1
	15%	0.17	1.49	0.17	1.93	0.21	3.1
		0.23	1.74	0.25	2.47	0.43	3.7
		0.33	2.19	0.33	2.54	0.68	7.0
Propanethiol	5%	0.13	1.64	0.13	1.69	0.21	5.4
		0.20	1.66	0.20	2.17	0.32	7.8
		0.26	1.77	0.26	2.62	0.68	13.1
	10%	0.13	1.53	0.13	1.94	0.21	6.3
		0.20	1.98	0.20	2.23	0.32	10.2
		0.26	2.08	0.26	2.32	0.68	13.8
	15%	0.13	2.34	0.13	2.85	0.21	7.1
		0.20	2.65	0.20	3.08	0.32	11.2
		0.26	2.73	0.26	3.94	0.68	16.1
Ethanethiol	5%	0.17	2.78	0.17	6.02	0.21	8.3
		0.23	3.66	0.23	6.27	0.32	11.4
		0.33	4.31	0.33	8.34	0.58	18.2
	10%	0.17	5.06	0.17	6.45	0.21	9.3
		0.23	5.36	0.23	8.26	0.32	13.3
		0.33	8.21	0.33	13.87	0.58	22.2
	15%	0.17	5.77	0.17	7.84	0.21	10.2
		0.23	6.43	0.23	10.30	0.43	19.2
		0.33	11.67	0.33	14.46	0.68	28.6

Table 3. Experimental data at the mercaptans extraction



This model started from the premise that the sum of the square roots of the flooding velocity of both phases is a constant. This seemed reasonable for a large range of packing and systems, even that it has no a theoretical basis. The sum:  $(V_{cf}^{1/2} + V_{df}^{1/2})^2 = \text{constant}$ , is correlated with the physical properties of the liquids and the characteristics of the packing ( $a_p, \epsilon$ ):

$$\frac{(V_{cf}^2 + V_{df}^2) \cdot \rho}{a_p \cdot \mu_c} = f \left[ \left( \frac{\sigma}{\rho_c} \right)^{0.2} \left( \frac{\mu_c}{\Delta \rho} \right) \left( \frac{a_p}{\epsilon} \right) \right] \quad (42)$$

The variables of Eq.42 are plotted in Figure 4.

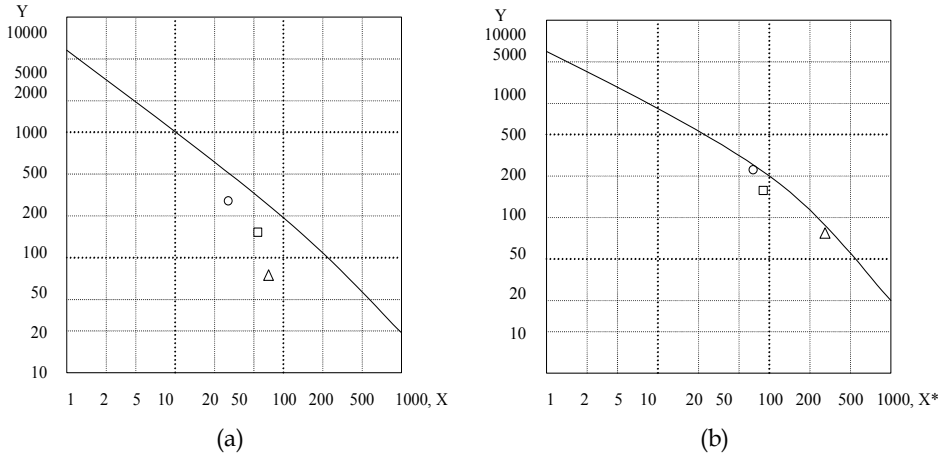


Fig. 4. The correlation between the flooding velocity of the phases - the Crawford-Wilke model. Legend: a- the original correlation ( $X = \frac{(V_{cf}^{1/2} + V_{df}^{1/2}) \cdot \rho}{a_p \cdot \mu_c}$ ,  $Y = \left( \frac{\sigma}{\rho_c} \right)^{0.2} \left( \frac{\mu_c}{\Delta \rho} \right)^{1.0} \left( \frac{a_p}{\epsilon} \right)^{1.5}$ );

b- the modified correlation ( $X^* = ([V]_{cf}^{1/2} + k_1[V]_{df}^{1/2}) \cdot \rho / (a_p \cdot \mu_c)$ ); square for the system water- gasoline, circle for the system NaOH solution- gasoline and triangle for the system  $\text{CCl}_4$ - water

As one can see from Figure 4.a, our experimental points are pretty far from the original curve. Other authors (Nemunaitis *et al* 1971) reported the same. They found that flooding occurred at loading only 20% of those predicted by the flooding correlation of Crawford and Wilke. An explanation could be that the assumption of the sum  $(V_{cf}^{1/2} + V_{df}^{1/2})$  constancy is not true. Even Crawford and Wilke (1951) expressed their doubts, however they considered this hypothesis as reasonable.

The sum  $(V_{cf}^{1/2} + V_{df}^{1/2}) = \text{constant}$  indicates that the curves  $V_{df}^{1/2}$  vs  $V_{cf}^{1/2}$  are lines with a slope of (-1):

$$V_{cf}^{1/2} + V_{df}^{1/2} = k_2 \quad (43)$$

Eq. 43 does not describe correctly the flooding line. The sum  $(V_{cf}^{1/2} + V_{df}^{1/2})$  should be modified as follows:  $(V_{cf}^{1/2} + k_1 V_{df}^{1/2})$  with respect to the real slope of the flooding line. In

this case,  $k_1 = -1/m'$  where ( $m'$ ) is the real slope of the flooding line. For the systems studied in my experiment, it was found:

- $k_1 = 1.17$  - for Water-Gasoline; ( $m' = -0.85$ )
- $k_1 = 2.44$  - for NaOH sol.20%wt- Gasoline ; ( $m' = -0.41$ )
- $k_1 = 2.63$  - for  $\text{CCl}_4$  - Water; ( $m' = -0.38$ )

As one can see, slope  $m'$  is in fact very different from the original (-1). This wasn't obvious when Crawford and Wilke established their model, because the liquid- liquid systems taken into account at that time were (all) low interfacial tension systems. In the present work, very different systems have been considered, proceeding from present authors' original experimental data as well as from other authors' data, e.g. (Nemunaitis *et al* 1971), (Watson *et al*, 1971), (Seibert & Fair, 1998), (Seibert *et al*.1990). It is to say that the scientific literature is very poor in flooding data in case of liquid-liquid countercurrent contactors.

In order to fit all these data and to have a model responding to systems with very different physical properties, the Crawford- Wilke correlation should be modified as follows: on the

X- axis would appear the expression  $X^* = \frac{(V_{cf}^{1/2} + k_1 \cdot V_{df}^{1/2}) \cdot \rho}{a_p \cdot \mu_c}$  instead of the expression

$$X = \frac{(V_{cf}^{1/2} + V_{df}^{1/2}) \cdot \rho}{a_p \cdot \mu_c}.$$

The  $k_1$  constant should be calculated with Eq.43 as recommended by Watson *et al* (1975):

$$k_1 = 0.466 \cdot \rho_c^{+0.5} \cdot \sigma^{+0.25} \cdot \mu_c^{+0.25} \cdot \varepsilon^{+0.5} \cdot d_{32}^{-1} \quad (44)$$

From Fig. 4b, one can see that it is a better accordance of experimental data with the Crawford- Wilke model when the real slope of the flooding line is considered. The maximum error of the modified model for our experimental points was 24%, lower than that reported by the authors of the original correlation: 35% for their own data.

## 4.2 The Seibert- Fair model

This model was developed after Eighties, when structure packing type was introduced, but it can be also applied to the random type packing as well. The models presented previously were empirical but this one is analytical, starting from the following assumption: the drops are rigid and spherical, the drop size can be represented by a Sauter mean diameter  $d_{32}$ , the axial mixing of the continuous and of the dispersed phase can be neglected. The authors consider a drop traveling at an *angle of ascent*  $\theta$ , in order to avoid the packing surface in its path. In a spray column, the mean angle of ascent is  $90^\circ$  but in a packed column the angle is smaller and depends on the drop size and the packing specific area. The packing increases the droplet velocity and the path length. This can be expressed as a *tortuosity factor*  $\xi$ :

$$\xi = a_p \cdot d_{32} / 2 \quad (45)$$

Manipulation of the classic equations of hydrodynamics and the use of the maximum theoretical holdup value of 0.52 lead to the final expression of the model:

$$1.08 \cdot V_{cf} + \left[ \cos\left(\frac{\pi \xi}{4}\right) \right]^2 \cdot V_{df} = 0.192 \cdot \varepsilon \cdot V_{s0} \quad (46)$$

where  $V_{s0}$  is the slip velocity of the singular drop in the dispersion column defined by hydrodynamic Eq. 47:

$$V_{s0} = [(\Delta \rho g d_{32}) / (3 \rho_c C_D)]^{0.5} \quad (47)$$

The dispersed phase holdup at flooding point  $\phi_f$  depends on the the phases flow ratio and by consequence, on their superficial velocities ratio ( $V_d$  and  $V_c$ ). Seibert & Fair (1988) proposed the empirical Eq.48:

$$\phi_f = \frac{V_d \cdot \left[ \cos\left(\frac{\pi \cdot \xi}{4}\right) \right]^{-2}}{\varepsilon \cdot V_{s0} \exp(-1.92 \cdot \phi_f) - \frac{V_c}{1 - \phi_f}} \quad (48)$$

This correlation is used especially for the prediction of the holdup at flooding, by trial-error method.

Legend: square for the system water- gasoline, circle for the system NaOH solution-gasoline and triangle for the system  $\text{CCl}_4$ - water.

The Fair- Sibert model was verified by its authors and gave good results for their own data obtained on a small diameter (100 mm) column (Seibert & Fair 1988). At larger scale: 400 mm diameter, the model gave bigger errors (Seibert *et al.* 1990). Also, the model was verified with data obtained in the original experiment (Koncsag & Stratula 2002) giving a maximum error of 26.4%. The parity plot for the original data is shown in Figure 5.

It seems to be a good accordance of the original data with the model but in fact the errors are systematic; for example, in the case of  $\text{CCl}_4$ - water system, the errors go continuously from negative to positive values. This could be explained either by non- reliable data or by a non-reliable model. The authors of the present work tend to consider a non- reliable model as long as the authors of the model themselves had a parity plot which indicated exclusively negative values for the standard errors (Seibert *et al.*1990).

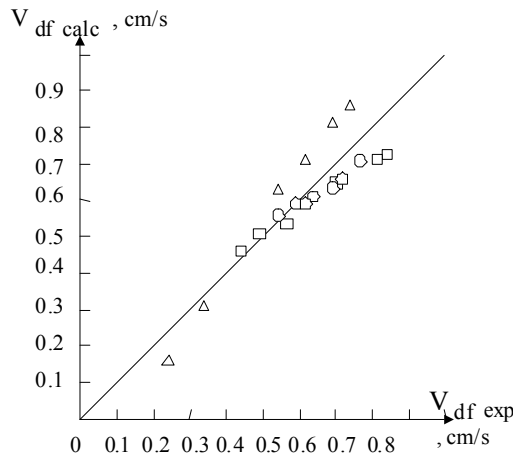


Fig. 5. The parity plot:  $V_{df \text{ calc}}$  (Seibert -Fair model) vs. original experimental values

## 5. Modelling the removal of mercaptans from liquid hydrocarbon streams in structured packing columns

### 5.1 Calculating the diameter

The data from Tables 1 and 2 were processed by dimensional analysis, with the goal of finding a mathematical model, which gives the limiting capacity of the contactor, expressed as *slip velocity of the phases* in flooding conditions.

The relevant list of dimensional parameters and dimensional constant describing this process is:

$$d_{32}, \sigma, \rho_c, \mu_c, V_{slip}, a_p, g \quad (49)$$

According to the dimensional analysis theory, this set of 7 dimensional parameters and constants, reduces to a set of only 4 dimensionless numbers. These numbers are chosen by us according to their physical significance for the extraction process:

$$Re, C_D, Ar, \Pi_4 \quad (50)$$

where Re is the Reynolds number, proportional to the ratio between the inertial force and the viscous force,  $(\rho_c \cdot d_{32} \cdot V_{slip}) / \mu_c$ ;

- $C_D$  - the drag coefficient, proportional to the ratio between the gravitational force and the inertial force,  $(g \cdot \Delta \rho \cdot d_{32}) / (\rho_c \cdot V_{slip}^2)$ ;
- $Ar$  - the Archimedes number, proportional to the ratio between the gravitational force and the viscous force,  $(g \cdot \rho_d \cdot d_{32}^3 \cdot \Delta \rho) / \mu_c^2$ ;
- $\Pi_4$  - a dimensionless number, which combines the geometrical characteristics of the packing and of the drops,  $s \cdot (1 - \phi) \cdot \frac{\varepsilon}{a_p}$ ,  $s$  being the characteristic surface of the mean

drop ( $= 6 / d_{32}$ ) and  $\phi$  being the hold-up of the dispersed phase in the column.

So, the criterial equation for the process would be:

$$Re^a \cdot C_D^b \cdot Ar^c \cdot \Pi_4^d = \text{const.} \quad (51)$$

The linear velocity which intervenes in the Re and  $C_D$  numbers is *the slip velocity*.

By processing the data from Tables 1 and 2, the exponents  $a, b, c, d$  and the constant in the Eq.51 were found and the general model is the following:

$$Re \cdot C_D \cdot Ar^{-0.6} \cdot \Pi_4 = 2.97 \quad (52)$$

The average deviation of this model is 7.7% and the absolute maximum error is 11.8%.

Replacing the dimensionless numbers with their definition correlations, the Eq.52 turns into Eq.53 for the calculation of the slip velocity in flooding conditions:

$$V_{slip} = 0.33 \cdot \Delta \rho^{0.4} \cdot \rho^{-0.6} \cdot d_{32}^{-0.8} \cdot \mu_c^{0.2} \cdot \left( \frac{\varepsilon}{a_p} \right) \cdot (1 - \phi) \quad (53)$$

Or, taking into consideration the Eq. 36, the characteristic velocity of the singular drop is:

$$V_K = 0.33 \cdot \Delta \rho^{0.4} \cdot \rho^{-0.6} \cdot d_{32}^{-0.8} \cdot \mu_c^{0.2} \cdot \left( \frac{\varepsilon}{a_p} \right) \quad (54)$$

The new model can serve for dimensioning the liquid- liquid countercurrent contactor equipped with packing: random or ordered. The steps of the dimensioning are:

- the calculation of the characteristic velocity (Eq.54);
- the choice of the desired ratio of the phases ( $V_d/V_c$ );
- the calculation of the dispersed phase holdup by trial- error method (Eq.48);
- the calculation of slip velocity (Eq.53 applied to the flooding conditions,  $\phi_f$  );
- the prediction of the throughputs limit ( $V_{df}$  and  $V_{cf}$ ), knowing their ratio ( $V_d/V_c = V_{df}/V_{cf}$ );
- the calculation of the diameter with Eq. 30, where  $B_{\max} = V_{df} + V_{cf}$  .

## 5.2 Calculating the active height of the column

The extraction of mercaptans with alkaline solution is accompanied by a second- order instantaneous reaction. As explained in Section 2.2, in this case, the mass transfer coefficients can be calculated as for the physical extraction, since the mass transfer is much slower than the reaction rate.

The calculation of the active height of the column is performed with Eq.38-41. The main difficulty consists of calculating the integrals (Eq.39 and 40) because one should know the concentrations profiles along the column. For systems following the Nernst law (Eq.3) and for very high values of the extraction factor (defined by Eq.56), the number of the transfer units  $NTU_{od}$  can be calculated from the number of theoretical stages  $NTT$ , with the Eq.55:

$$\frac{NTT}{NTU_{od}} = \frac{1 - \frac{1}{E}}{\ln E} \quad (55)$$

$NTT$  can be found graphically in a McCabe-Thiele- type construction.

The extraction factor  $E$  is defined by the Eq.56:

$$E = m \cdot \frac{S}{A} \quad (56)$$

where  $S/A$  is the solvent- to- feed gravimetric ratio.

As seen in Eq.56, the phase ratio refers to the solvent and feed and not to dispersed and continuous, as in diameter calculation. In mass transfer, the direction of the transfer is very important. Always, the direction is from the feed to the solvent, whatever the dispersed phase is.

The data used in modelling the extraction of the buthanethiol, propanethiol and ethanethiol are given in Table 3.

A model of the same type for all the data in Table 3 was developed, taking into account the factors determining the mass transfer rate:  $c$ - the concentration of NaOH solution (%wt), the geometrical characteristics of the packing ( $\varepsilon$ ,  $a_p$ ), the dispersed phase (the feed) superficial velocity and the acidity of the mercaptans:

$$K_{od} \cdot a \cdot 10^3 = \alpha_i \left( 0.95 + \frac{c}{100} \right)^{A_1} \left( \frac{a_p}{\varepsilon} \right)^{A_2} (10^2 \cdot V_d)^{A_3}, i = 1, 2, 3 \quad (57)$$

In Eq.57, the coefficients  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$  correspond to different mercaptans, respectively buthanethiol, propanethiol and ethanethiol.

The inferior limit value for  $a_p$  in Eq.57 is  $0.01 \text{ m}^2/\text{m}^3$ , being assigned to the unpacked column.

Taking the logarithms in the previous formula and denoting by  $Y = \ln(K_{od} \cdot a \cdot 10^3)$ ,

$$A_0 = \ln \alpha, \quad X_1 = \ln \left( 0.95 + \frac{c}{100} \right), \quad X_2 = \ln \left( \frac{a_p}{\varepsilon} \right), \quad X_3 = \ln(10^2 \cdot V_d), \quad C_i = \ln \alpha_i, i = 1, 2, 3,$$

the model becomes:

$$Y = A_0 + A_1 X_1 + A_2 X_2 + A_3 X_3 + \xi, \quad (58)$$

where  $Y$  is the dependent variable,  $X_1, X_2, X_3$  are independent (explicative) variables and  $\xi$  is the specification error of the model. In a equivalent form, the system can be written:

$$y = xA + \xi. \quad (59)$$

Using the least squares method, the solution of Eq.58 is:

$$\begin{pmatrix} \hat{C}_1 \\ \hat{C}_2 \\ \hat{C}_3 \\ \hat{A}_1 \\ \hat{A}_2 \\ \hat{A}_3 \end{pmatrix} = \begin{pmatrix} 1.442 \\ 2.048 \\ 2.867 \\ 4.119 \\ 0.091 \\ 0.837 \end{pmatrix} \quad (60)$$

In what follows,  $\hat{y}_t$  is the estimated (computed) value of  $y_t$  and  $e_t$  the residual, i.e  $e_t = y_t - \hat{y}_t$ ,  $t = 1 \dots 81$ .

**Remark.** A distinction has to be made between the specification error of the model,  $\xi_t$  which is and remains unknown and the residual, which is known.

The variance of the error  $\sigma^2(\varepsilon)$  can be estimated by:

$$\hat{\sigma}^2(\varepsilon) = \frac{ee'}{n - k - 1} = 0.059, \quad (61)$$

where:  $n = 81$  is the observations number,  $k = 3$  is the number of explicative variables and  $e$  is the vector containing the residuals,  $e_t$ ,  $t = 1 \dots 81$ .

Making the calculus, it can be seen that the residuals sum is zero. Since the residual variance is closed to zero, the residuals in the model are very small.

From 60, the fitting quality is measured using the determination coefficient,  $R^2$ :

$$R^2 = 1 - \frac{\sum_{t=1}^{27} e_t^2}{\sum_{t=1}^{81} (y_t - \bar{y})^2} = 0.925 \quad (62)$$

and the modified determination coefficient,  $\bar{R}^2$ :

$$\bar{R}^2 = 1 - \frac{n-1}{n-k-1} (1 - R^2) = 0.922 \quad (63)$$

Since these values are closed to 1, the fitting quality is very good.

#### I. Tests on the model coefficients

- i. It was verified if the explicative variables have significant contributions to the explanation of the dependent variable, by testing the hypothesis:

$$H_0 : A_i = 0, i = 0, 1, 2, 3, \quad (64)$$

at the significance level  $\alpha = 5\%$ .

It has been done by a  $t$  test, that rejected the null hypothesis  $H_0$ , so the model coefficients are significant.

- ii. The global significance of the model has been tested by a  $F$  test, for which the null hypothesis is:

$$H_0 : A_0 = A_1 = A_2 = A_3 = C_1 = C_2 = C_3 = 0$$

The hypothesis  $H_0$  was rejected, at significance level  $\alpha = 5\%$

From i. and ii. it results that the model coefficients are well chosen.

#### II. Tests on the errors

We saw that the residual sum is zero and the residual variance is 0.059.

We complete the information on the errors distribution providing the results concerning their normality, homoscedasticity and correlation.

- i. Normality test

In order to verify the normality of the errors, the well-known Kolmogorov-Smirnov test has been used, as well as the Jarque Bera test (Barbulescu & Koncsag, 2007).

Both tests lead us to accept the normality hypothesis.

- ii. Homoscedasticity test

The test Bartlett is used to verify the errors homoscedasticity.

The hypothesis which must be tested is:

$$H_0: \text{the errors have the same variance.}$$

First, the selection values are divided in  $i = 3$  groups, each of them containing  $n_i = 27$  data, and the test statistic is calculated by the formula:

$$X^2 = \frac{-\sum_{j=1}^i n_j \ln \frac{s_j^2}{s^2}}{1 + \frac{1}{i-1} \sum_{j=1}^i \left( \frac{1}{n_j} - \frac{1}{n} \right)} \quad (65)$$

where  $s_1^2, s_2^2, s_3^2, s$  are respectively the selection variance of the groups and of the sample.

The hypothesis  $H_0$  is accepted at the significance level  $\alpha = 5\%$  since  $X^2 = 0.1138 < 5.991 = \chi^2(2)$ , where  $\chi^2(2)$  is the value given in the tables of the repartition  $\chi^2$  with two degrees of freedom.

iii. Correlation test

In order to determine if there exists a correlation of first order between the errors, the test Durbin Watson is used, for which the statistics test is defined by Barbulescu & Koncsag (2007):

$$DW = \frac{\sum_{t=2}^{81} (e_t - e_{t-1})^2}{\sum_{t=1}^{81} e_t^2} = 1.268$$

Since  $DW = 1.268 < d_1$  (the critical value in the Durbin- Watson tables), it results that the errors are correlated at the first order.

## 6. Conclusions

The result of this work consists on a model for the calculation of the industrial scale column serving to the extraction of mercaptans from hydrocarbon fractions with alkaline solutions. The work is based on original experiment at laboratory and pilot scale. It is a simple, easy to handle model composed by two equations.

The equation for the slip velocity, linked to the throughputs limit of the phases and finally linked to the column diameter, shows the dependency of the column capacity on the physical properties of the liquid- liquid system and the geometrical characteristics of the packing:

$$V_{slip} = 0.33 \cdot \Delta \rho^{0.4} \cdot \rho^{-0.6} \cdot d_{32}^{-0.8} \cdot \mu_c^{0.2} \cdot \left( \frac{\varepsilon}{a_p} \right) \cdot (1 - \phi)$$

It is recommended for the usual commercial packing having  $a_p$  in range of 195-340 m<sup>2</sup>/m<sup>3</sup> and  $\varepsilon$  in range of 0.74-0.96 and for liquid-liquid systems with interfacial tension in the range of 30-80 · 10<sup>-3</sup> N/m. The average deviation of the model is 7.7% and the error's maximum maximorum is 11.8%.

The equation for the mass transfer coefficients at the extraction of different mercaptans is linked to the calculation of the active height of the column:

$$K_{od} \cdot a \cdot 10^3 = \alpha_i \left( 0.95 + \frac{c}{100} \right)^{A_1} \left( \frac{a_p}{\varepsilon} \right)^{A_2} (10^2 \cdot V_d)^{A_3}, i = 1, 2, 3$$

where  $A_1 = 4.119$ ;  $A_2 = 0.091$ ;  $A_3 = 0.835$ .  $\alpha$  has different values for buthanethiol, propanethiol and ethanethiol respectively: 1.442; 2.0867; 2.867.

The residual sum is zero and the residual variance is 0.059, so the accuracy of the model is very good. The fitting quality is confirmed by the high values of the determination coefficients. The model is satisfactory also points of view of statistics, since its coefficients are significant and the errors have a normal repartition and the same dispersion.

The model works for all type of packing, structured or bulk.



## 7. Nomenclature

$a$  - the interfacial area,  $\text{m}^2/\text{m}^3$

$a_p$  - packing specific area,  $\text{m}^2/\text{m}^3$

$Ar$ - Archimedes number,  $g \cdot \rho_d \cdot d_{32}^3 \cdot \Delta\rho / \mu_c^2$ , dimensionless

$A_0, A_1, A_2, A_3$ - constants, dimensionless

$c$  - the concentration of NaOH solution, % wt

$C_D$ - drag coefficient,  $(g \cdot \Delta\rho \cdot d_{32}) / (\rho_c \cdot V_{slip}^2)$ , dimensionless

$d_{32}$ - Sauter mean diameter of drops,  $(\sum n_i d_i^3) / (\sum n_i d_i^2)$ , m

$D$ - diffusivity,  $\text{m}^2/\text{s}$

$D_c$ -column diameter, m

$E$ - extraction factor, dimensionless

$g$ - gravitational constant,  $\text{m}/\text{s}^2$

$H$ - active height of the column, m

$HTU$ - height of mass transfer unit, m

$k$ - partial mass transfer coefficient

$k$ - reaction rate constant

$K$ - overall mass transfer coefficient

$K_{od}$ - overall volumetric mass transfer coefficient related to the dispersed phase,  $\text{s}^{-1}$

$m$ - repartition coefficient, Nernst law

$NTU$ - number of mass transfer units, dimensionless

$Re$ -Reynolds number,  $(\rho \cdot d_{32} \cdot v_{slip}) / \mu$ , dimensionless

$s$ - characteristic surface of the mean drop,  $6 / d_{32}$

$Sc$ -Schmidt criterion,  $Sc = \mu / D$ , dimensionless

$Sh$ -Sherwood criterion,  $Sh = k_d \cdot d_{32} / D$ , dimensionless

$V_{cf}, V_{df}$ - superficial velocities of the continuous phase and the dispersed phase respectively,  $\text{m}/\text{s}$

$V_K$ - characteristic velocity of drops,  $\text{m}/\text{s}$

$V_{slip}$  - slip velocity of phases,  $\text{m}/\text{s}$

$\alpha$ - coefficient, dimensionless

$\varepsilon$  - void fraction of the packing,  $\text{m}^3/\text{m}^3$

$\mu$  - viscosity,  $\text{kg}/\text{m}\cdot\text{s}$

$\rho$  - density,  $\text{kg}/\text{m}^3$

$\Delta\rho$ - density difference of the phases,  $\text{kg}/\text{m}^3$

$\sigma$  - interfacial tension,  $\text{N}/\text{m}$

$\phi$  - holdup of the dispersed phase,  $\text{m}^3/\text{m}^3$

$\Pi_4$ - dimensionless number,  $s \cdot (1 - \phi) \cdot \varepsilon / a_p$

### Subscripts:

$c$ - continuous phase

$d$ -dispersed phase

$D$ - drag (coefficient)

$E$ -extract

$f$ - in flooding conditions

i- at interface

o- overall

p- packing

R-raffinate

0-single drop

**Superscripts:**

0-in absence of chemical reaction

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