Mass Transfer at Propanethiol - Buthanethiol Alkaline Extraction from Sour Petroleum Fractions

ALINA BARBULESCU*, CLAUDIA IRINA KONCSAG
Ovidius University of Constanta, Bd. Mamaia, nr.124, 900527, Constanta, Romania

The present work is a study of the extraction of some mercaptans from the liquid hydrocarbon fractions with caustic solutions. The goal was to obtain a mathematical model for the estimation of mass transfer coefficients by processing data from laboratory and pilot scale extraction columns equipped with packing.The model was established taking into account the factors influencing the extraction: the acidity of the thiol, the alkaline solution concentration, the geometrical characteristic of the packing and the superficial velocity of the dispersed phase. The general equation is:

$$K_{od} \cdot a \cdot 10^3 = \alpha\left(0.95 + \frac{c}{100}\right)^{A_1} \left(\frac{a_p}{\varepsilon}\right)^{A_2} \left(10^2 \cdot v_d\right)^{A_3}$$

The model's parametres were found for each thiol separately by applying a modified version of the least squares method. The validity of the model was checked using statistical tests on the errors.

Keywords: mass transfer, packed columns, modelling, errors analysis

The thiols extraction from sour liquid petroleum fractions is a process in the petroleum refining industry. It is a liquid - liquid extraction accompanied by a second order chemical reaction between the thiols and NaOH:

$C_3H_7SH + NaOH \leftrightarrow C_3H_7SNa + H_2O$
$C_4H_9SH + NaOH \leftrightarrow C_4H_9SNa + H_2O$

The extraction equilibrium is favoured by lower molecular weight of the mercaptan and lower temperature [1]. Also, the phase equilibrium is influenced by the feed quality (the boiling range of the petroleum fraction) and the presence of some contaminants in the NaOH solution [2].

This process can be understood under the double layer theory of Whitman. For a liquid-liquid extraction accompanied by chemical reaction, the equation describing the process is the same as that recommended by Astarita [3] for the absorption with reaction process:

$$D_A \cdot \nabla^2 C_A = u \cdot \nabla c_A + \frac{\partial C_A}{\partial t} + v_{RA} \qquad (1)$$

where:

D_A is the diffusivity of the reactant A in the film towards the reaction plane;

u – the linear velocity of the convective streams inside the film containing the reaction plane;

v_{RA} – the reaction rate related to the reactant A.

The first term of the equation 1 represents the mass transfer of A in the liquid thin film by molecular diffusion mechanism, the second is the expression of the convection mechanism inside the film, the third term represents the accumulation of the compound A in the film and the last one represents the variation of compound A concentration, as a consequence of the chemical reaction. In the frame of the twin film theory of Whitman, the second and the third terms of the equation (1) are null because there are not convective flows in the double film and no accumulation of substance occurs.

Also, there is a unique direction of diffusion, x : the direction perpendicular to the reaction plane. So, according to this theory, equation 1 becomes:

$$D_A \frac{\partial^2 c_A}{\partial x^2} = v_{RA} \qquad (2)$$

Or

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

Let's design A for a mercaptan. a similar equation can be written for the reactant B (NaOH):

$$D_B \cdot \frac{d^2 c_B}{dx^2} = \frac{dc_B}{dt}$$

Let's suppose that the reaction plane is located inside the film of the phase containing the reactant B. In this case:

$$D_A\left(\frac{dc_A}{dx}\right)_{x=\lambda} = \frac{1}{q} \cdot D_B\left(\frac{dc_B}{dx}\right)_{x=\lambda} \qquad (4)$$

where:

λ – the distance between the interface and the reaction plane;

q – the stoechiometric coefficient.

By integrating the equation 4 between the limits $x=\lambda$ and $x=\delta$ (δ being the thickness of the film), one obtains:

$$q \cdot D_A \cdot \frac{c_{Ai}}{\lambda} = D_B \cdot \frac{c_B}{\delta - \lambda} \qquad (5)$$

where:

c_{Ai} – the concentration of A at the interface;

c_B – the concentration of B in the bulk f the phase 2,

So:

$$\lambda = \delta \cdot \frac{q \cdot D_A \cdot c_{Ai}}{q \cdot D_A \cdot c_{Ai} + D_B \cdot c_B} \qquad (6)$$

And from this, resulting:

$$\frac{K_L}{K_L^0} = \frac{\delta}{\lambda} = 1 + \frac{D_B}{D_A} \cdot \frac{c_B}{q \cdot c_{Ai}} \qquad (7)$$

K_L^0 – the overall mass transfer coefficient in the absence of chemical reaction;

K_L – the overall mass transfer coefficient with chemical reaction.

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* *email: alinadumitriu@yahoo.com*

The overall mass transfer coefficient in the case of the instant chemical reaction is proportional to the overall mass transfer for the physical reaction so, the overall mass transfer coefficient with chemical reaction depends on the hydrodynamic conditions as much as in the case of the extraction without a chemical reaction.

The determinant stage of the mass transfer is the diffusion of the reactants toward and of the products from the reaction plane. If the reaction plane is the interface itself, $\lambda=\delta$. Since the chemical reaction of mercaptans with NaOH is very fast, the reactant A disappears instantaneously at the reaction plane and the process is controlled by the diffusion rate. So, the estimation of the mass transfer coefficients, as the expression of the process rate, could be used for the design and the simulation of the industrial extraction process.

In the present work, the authors established a mathematical model for the estimation of mass transfer coefficients in the case of buthanethiol and propanethiol extraction with NaOH solutions, by analyzing and processing original experimental data obtained in laboratory and in a pilot plant, in extractors equipped with structured packing.

Experimental part

In laboratory, an Elgin extractor was available. It had the following dimensions: 26 mm - the inner diameter and 700-800 mm - the active height. The extraction column was used in two variants: as a dispersion column and then packed with a handicraft-structured packing of metal gauze type, with the specific area $a=60 m^2/ m^3$ and the porosity $\varepsilon = 0.98$ [4].

The pilot scale column has a diameter of 76 mm and an active height of approximately 1000 mm, from which the packing layer represents 840 mm. The structured packing was of corrugated metal sheet type (Sulzer SMV350Y), with the specific area of $a=340 m^2/ m^3$ and the porosity, $\varepsilon = 0.96$ [5].

The continuous phase (NaOH solution) and the dispersed one (gasoline) flew in countercurrent. The experiences took place in a steady state. The continuous phase had a constant flow. The solvent-to-feed ratio was variable. The extraction of the buthanethiol (propanethiol, respectively) was performed with NaOH solutions 5%, 10% and 15% wt.

In order to obtain accurate experimental data, the influence of any impurifying substance was eliminated by using the hydrogenated gasoline (max.0.5 ppm sulphur) enriched in 1-buthanethiol (1-propanethiol, respectively), the thiols being pure reagents from Merck. Also the alkaline solutions were made-up with Merck reagent of analysis grade.

The thiol concentration in the feed and in the raffinate was determined with the standard STAS 8042/1983, in use; the thiol concentration in the extract (NaOH solution) was found by material balance.

The calculation of the overall drop-side mass transfer coefficients ($K_{od}\cdot a$) followed the steps described below [4,6,7]:

- the calculation of the number of theoretical extraction stages NTT, NTT being defined as the number of equilibriums needed to reach the concentration in raffinate, for a certain solvent – to - feed ratio (S/A). The number of the theoretical extraction stages NTT was graphically determined in a McCabe-Thiele plotting, using the distribution coefficients, K determined previously [1,2];
- the calculation of the number of the transfer units related to the drop-side, NUT_{od} , where the mass transfer unit is defined as the height of the column along which the driving force of the mass transfer changes by a factor of e=2.71;

For systems following the Nernst law (a linear correlation between the concentrations of the solute in both liquid phases) and for high values of the extraction factor ($E= K\cdot S/A$), the number of the transfer units NUT_{od} can be calculated with equation 8 knowing the number of theoretical stages NTT:

$$\frac{NTT}{NUT_{od}} = \frac{1-\frac{1}{E}}{\ln E} \qquad (8)$$

- the calculation of the mass transfer unit height HUT_{od}, by dividing the active height of the experimental column H to the number of transfer units NUT_{od}.
- the calculation of overall mass transfer drop-side coefficients ($K_{od}\cdot a$), from the HUT_{od} values, using the formula (9):

$$K_{od}a = \frac{v_d}{HUT_{od}} [s^{-1}] \qquad (9)$$

where the superficial velocity of the disperse phase (v_d) is defined as the volumetric flow of the dispersed phase divided by the free cross - sectional area of the column.

Results and discussions

The experimental data processed as described in the previous section are shown in figures 1-6.

In [8] we gave different models for each set of data from figures 1-6. The best one was of Weibull type, a simple correlation between the mass transfer coefficient and the superficial velocity of the dispersed phase. That model was not satisfactory because the values of the parametres do not take into account all the factors affecting the mass transfer. As seen at a first glance, the mass transfer coefficients increase with the acidity of the solute (1-

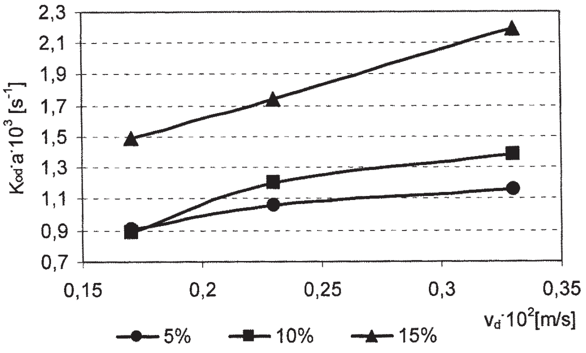

Fig. 1. The overall drop-side mass transfer coefficients at the extraction of 1-buthanethiol in the dispersion column

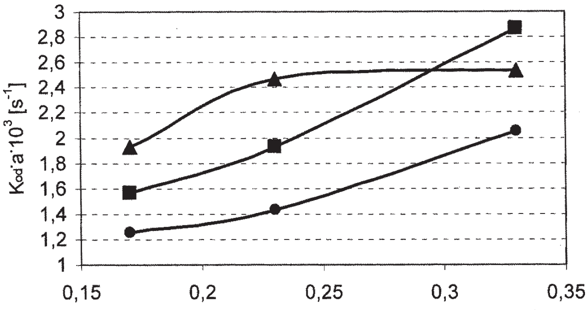

Fig. 2. The overall drop-side mass transfer coefficients at the extraction of 1-buthanethiol in the laboratory packed column

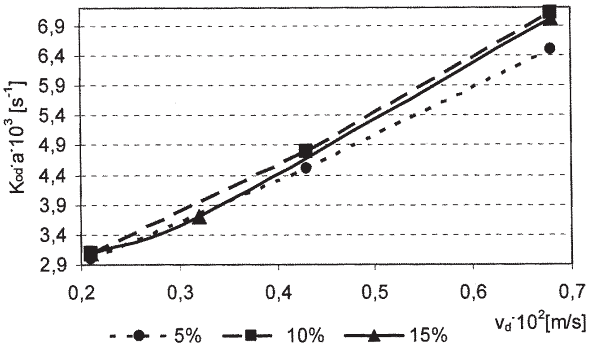

Fig. 3. The overall drop-side mass transfer coefficients at the extraction of 1-buthanethiol in the pilot packed column

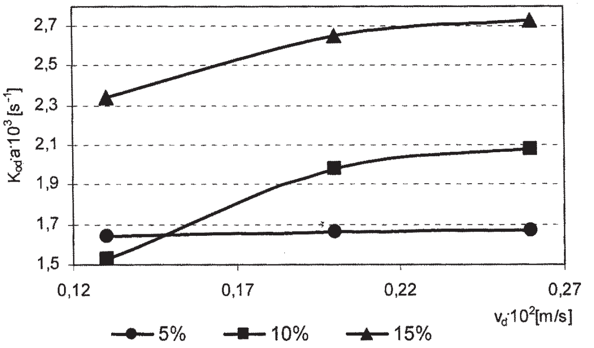

Fig. 4. The overall drop-side mass transfer coefficients at the extraction of 1-propanethiol in the dispersion column

Propanethiol being more acid than 1-Buthanethiol) and with the concentration of the alkaline solution. Also, the geometrical characteristics of the packing, especially the specific area *a*, strongly influence the mass transfer coefficients. The superficial velocity of the dispersed phase is also of great importance, by increasing the mass transfer coefficients with the velocity.

So, another model was developed empirically, following these observations [9].

The equation has the general form described in formula 10 with different parametres for the buthanethiol and propanethiol extraction:

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

where:

K_{od} - overall drop-side mass transfer coefficient, s^{-1};

c - the concentration of NaOH solution, % wt;

a_p - the specific area of the packing, in m^2/m^3;

ε - the porosity of the packing, in m^3/m^3;

v_d - the superficial velocity of the dispersed phase, m/s;

α - constant depending on the thiol acidity;

A_1, A_2, A_3- other constants, model's coefficients.

Taking the logarithms in the formula (10) and denoting by

$$Y=\ln\left(K_{od}\cdot a\cdot 10^3\right),\ A_0=\ln\alpha,\ X_1=\ln\left(0.95+\frac{c}{100}\right),$$

$$X_2=\ln\left(\frac{a_p}{\varepsilon}\right),\ X_3=\ln\left(10^2\cdot v_d\right)$$

we obtain the model:

$$Y=A_0+A_1X_1+A_2X_2+A_3X_3+\varepsilon', \qquad (11)$$

where ε' is the error of the model.

These parameters of the model were calculated separately for the propanethiol and for the buthanethiol.

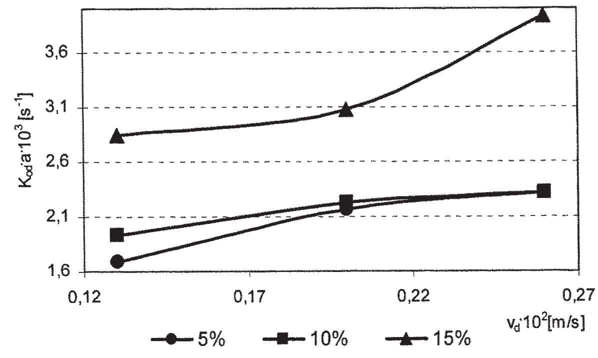

Fig. 5. The overall drop-side mass transfer coefficients at the extraction of 1-propanethiol in the laboratory packed column

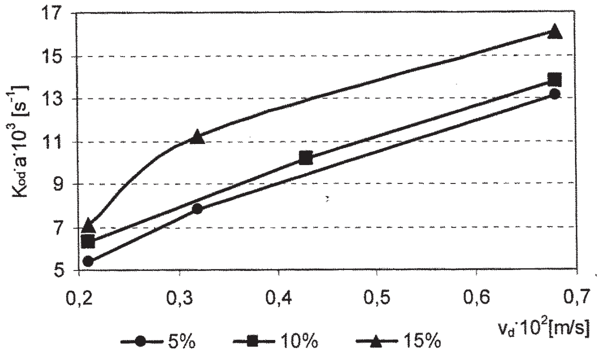

Fig. 6. The overall drop-side mass transfer coefficients at the extraction of 1-propanethiol in the pilot packed column

The model of buthanethiol extraction

Using a modified version of the least squares method, the solution of the equation (10) is:

$$\hat{A}_0=1.455,\ \hat{A}_1=3.464,\ \hat{A}_2=0.0925,\hat{A}_3=0.825,$$

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

$$\hat{\sigma}^2(\varepsilon')=\frac{e'e}{n-k-1}=0.03908, \qquad (12)$$

where:

n=27 is the number of observations;

k = 3 is the number of explicative variables (three, in our case: X_1, X_2, X_3);

e is the vector that contains the residuals;

e_t, t=1, ... , 27 (the difference between the experimental values, y_t and the calculated values, $\hat{y}_t$).

The estimated variance is very small and making the calculus, it results that the residuals sum is zero.

The estimation quality can be pointed out using the determination and the modified determination coefficients, defined respectively by:

$$R^2=1-\frac{\sum_{t=1}^{27}e_t^2}{\sum_{t=1}^{27}\left(y_t-\bar{y}\right)^2}\ \text{and}\ \bar{R}^2=1-\frac{n-1}{n-k-1}\cdot\left(1-R^2\right). \qquad (13)$$

If these values are close to 1, the fitting quality is good.

In our case: R^2 = 0.907 and R^2 =0.875.

I. The first step to validate the model is to verify if the explicative variables had significant contributions to the explanation of the dependent variable and if the model is globally significant. To do it, Student test and F-test were applied [10].

In this case:

- the values of t-statistic calculated at the significance level of α=5% ($t^*_{\hat{A}_0} = 9.736, t^*_{\hat{A}_1} = 3.541, t^*_{\hat{A}_2} = 7.928, t^*_{\hat{A}_3} = 8.482$) are higher than 2.069, which is the value of the quantile in Student table,

- the value of F-statistic calculated at the significance level of α=5% (F* = 48.294) is higher than 3.028, which is the value of the quantile in Fisher table, for k=3 and n - k - 1- = 23 degrees of freedom, so the model's coefficients proved to be right.

II. The second step was to study the errors.

- Analysing the P-P plot diagram (fig.7) we accept the hypothesis that the errors have a normal distribution, since the points in the graph are situated around the straight line that represents the theoretic normal distribution.

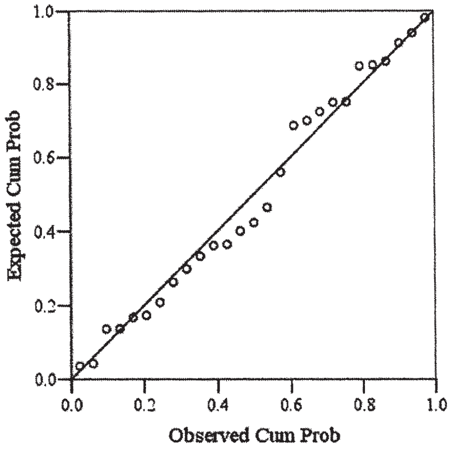

Fig. 7. The P-P plot for the residuals

- Using the autocorrelation function (ACF), plotted in figure 8, we accept the hypothesis that the errors are uncorrelated, since all the values of ACF are inside the confidence interval, at the confidence level of 95%.

- Bartlett's test was used to verify the hypothesis H_0 that the errors have the same variance.

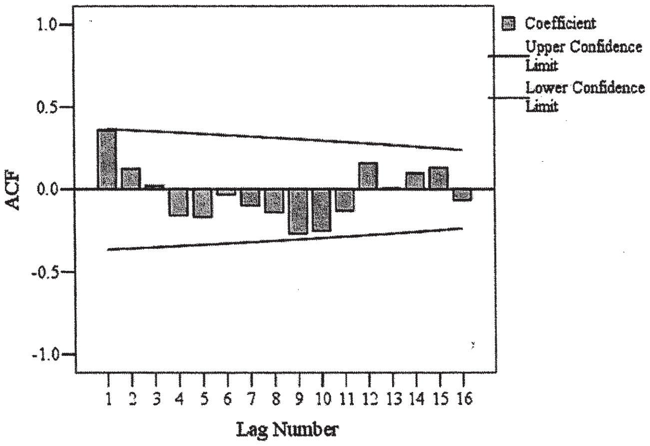

Fig. 8. The ACF for the residuals in the model for buthanethiol

The experimental data were divided in i = 3 groups, each of them containing n_i =9 data. Denoting by s_1^2, s_2^2, s_3^2 the selection variance of the groups, s^2 - the selection variance of the sample and $\aleph_\alpha^2(i-1)$ the value of the quantile given in the tables of $\aleph^2$ distribution, with i - 1 degrees of freedom, at the significance level α=5% and by:

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

if, $X^2 < \aleph^2(i-1)$ then the hypothesis H_0 is accepted.

It is the case: $X^2 = 1.35351 < 5.991 = \aleph^2(2)$ .So, the model determined by us is right from the viewpoint of statistics.

The model of propanethiol extraction

We tried to develop an analogue model for propanethiol extraction.

Following the same calculus way, it was obtained:

$$\hat{A}_0 = 2.255, \hat{A}_1 = 3.589, \hat{A}_2 = 0.0878, \hat{A}_3 = 0.957,$$

$$-\hat{\sigma}^2(\varepsilon') = 0.09528, R^2 = 0.853, \overline{R}^2 = 0.834.$$

Since the sample variance and the determination coefficients are very small, the fitting quality is good. Also, the errors sum is zero.

To validate the model, the same procedure as in buthanethiol case was followed.

I. Student test and F-test, at the significance level of α=5%, were used to verify that the coefficients are significants:

- $t^*_{\hat{A}_0} = 9.378, t^*_{\hat{A}_1} = 2.35, t^*_{\hat{A}_2} = 4.641, t^*_{\hat{A}_3} = 7.102$ that are higher than 2.069, which is the value of the quantile in Student table;

- the value of F-statistic calculated at the significance level of α=5%, F* = 44.514 which is higher than 3.028, the value of the quantile in Fisher table.

II. The second step was to study the errors.

- Using the P-P plot diagram or the Kolmogorov - Smirnov test, the hypothesis that the errors have a normal distribution is accepted.

- From Bartlett test, $X^2 = 1.35351 < 5.991 = \aleph^2(2)$ it results that the errors have the same variance.

- Using the autocorrelation function (fig. 9), we reject the hypothesis that the errors are uncorrelated, since there are some values of ACF outside the confidence interval at the confidence level of 5%.

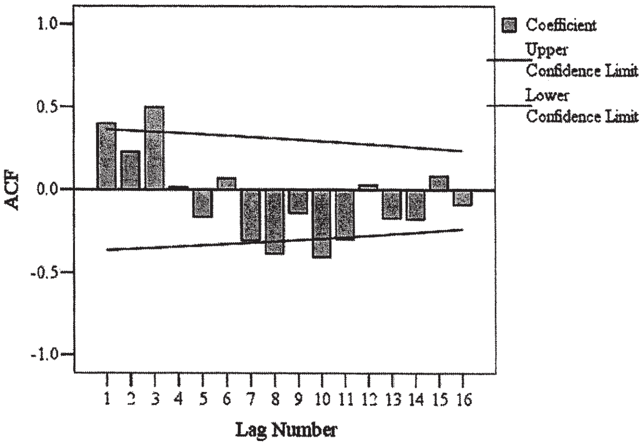

Fig. 9. The ACF for the residuals in the model for propanethiol

Conclusions

The comparative study of the propanethiol and buthanethiol extraction from a petroleum fraction (gasoline) proved that the presence of the packing in the extraction column leads to increased mass transfer coefficients. They increase proportionally with the specific area of the packing, the acidity of the thiol and the concentration of the alkaline solution but the effect of this last factor is feeble for packing with high specific area.

Also, the mass transfer coefficients depend strongly on the superficial velocity of the dispersed phase.

In this work, an estimation model for the mass transfer coefficients at the alkaline extraction of the buthanethiol and propanethiol from sour petroleum fractions, in packed columns, was established. The model has an empirical basis since it follows the observations concerning the extraction process but not the dimensional analysis. Given the complexity of the phenomena implied in the process, it would be difficult to find an accurate model of this kind.

The model established here proved to be right. All the explicative variables have a significant contribution in the definition of the dependent variable. The errors have a normal distribution, the same variance and are uncorrelated, in the first model and correlated in the second one. It can be due to the measurement accuracy. The residual sum is practically zero in all the cases and their variances are small. The coefficients are of the same order of magnitude.

When correlating the model's coefficients, it was interesting to observe that $\hat{A}_0$ is higher for propanethiol than for buthanethiol,relative to their acidity, since $A_1, \hat{A}_2$ and $\hat{A}_3$ have very close values in both cases, which conducted us to the conclusion they are common for all the mercaptans. Future studies would demonstrate this.

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