# Transport of Butyric Acid through Layered Bulk Liquid Membranes

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Transport of butyric acid (BA) through a layered bulk liquid membrane (BLM) with trioctylamine (TOA) as carrier has been studied. With increasing concentration of TOA from 0.2 to 0.6 the flux of BA through the BLM increased only by 16 % while the permeability (in the first approximation product of the distribution and diffusion coefficients) increased 2.7 times. The flux through the stripping interface increased with temperature, while the flux through the extraction interface remained practically constant. These facts can be interpreted by a slower reaction of the complex decomposition on the stripping interface and/or by saturation of the stripping interface with the molecules of complexes. A model of transport through a BLM, taking into account adsorption equilibrium of the complex and the reaction kinetics of its decomposition on the stripping interface, is suggested. The proposed model fits experimental data well. It has been found that the pseudofirstorder rate equation can be used only as a first approximation and a more detailed description of the reaction kinetics is required. A two-compartment contactor can be useful in studying the kinetics of the decomposition or formation of complexes on the stripping or extraction interfaces in pertraction or extraction.

Integration of membrane separations with fermentation can enhance the fermenter performance by decreasing the product inhibition and allows semicontinuation of the process [1-5]. Pertraction or extraction of carboxylic acids in HF contactors has been studied in papers [4, 6-10]. The transport of butyric acid (BA) [11], C<sub>6</sub>-carboxylic acid [12], lactic acid [13-15], and lysine [16] through a layered bulk liquid membrane (BLM) has been investigated. The competitive transport of mineral acids influences the pertraction of BA [11] and lactic acid [15].

The transport of permeants through liquid membranes can be studied in contactors with a layered BLM. The advantage of these contactors is their relative simplicity, possibility of experimental identification of concentrations in all three phases, and possibility of visual observation of interfaces and phases. Different types of contactors have been described in the literature. In the early published experiments [17] a U-tube-type contactor has been utilized with a BLM placed at the bottom of the U-tube, and having a higher density than that of the aqueous phases, and the feed and the stripping solution in its arms. For a BLM with lower density than that of the aqueous phases, H-type contactors can be used [11, 13]. Two vertical tubes are connected by a neck, which is partially filled with the membrane phase, with interfaces in tubes below this neck. All three phases can be stirred. In papers [16, 18, 19] contactors with concentric cylindrical vessels were used. The smaller vessel

placed in the centre has a lower height and it is filled with aqueous phases close to its top. The solvent is layered above these phases and forms a BLM. Mixing in these contactors cannot be arranged in such a way that identical hydrodynamic conditions at both interfaces can be reached.

The aim of this paper was to study the transport of BA through layered bulk membranes in a contactor with identical hydrodynamic conditions at both interfaces and to derive a model for this transport taking into account adsorption equilibrium of the acid/carrier complexes and the reaction kinetics of the complex decomposition on the stripping interface.

## THEORETICAL

The overall reaction of the formation of a complex between acid (HA), in our case butyric acid (BA), and carrier (P), *e.g.* trioctylamine (TOA), on the feedmembrane interface can be written as

$$n\mathrm{HA} + \overline{\mathrm{P}} \Leftrightarrow \overline{(\mathrm{HA})_n \mathrm{P}} \tag{A}$$

where bars denote species dissolved in the membrane (solvent) phase. Based on the analysis and modelling of equilibrium data presented in paper [20] it has been found that the probable values of n for the complexes of BA are 1, 3, and 5. BA is dissolved in the membrane also in the form of a dimer. The monomer is practically not present in the membrane, as follows from



Fig. 1. Concentration profile of acid in pertraction through well mixed bulk liquid membranes. F - feed, M - membrane phase, R - stripping solution.

modelling, because on the interface or in the solvent phase it immediately forms a dimer. The content of individual forms of complexes and the dimer is shown in the above-mentioned paper as well. The overall reactions for the complex and the dimer decomposition on the membrane-stripping solution interface are

$$\overline{(\mathrm{HA})_{n}\mathrm{P}} + n\mathrm{HO}^{-} \rightarrow \overline{\mathrm{P}} + n\mathrm{A}^{-} + n\mathrm{H}_{2}\mathrm{O}$$
 (B)

$$\overline{(\mathrm{HA})_{2}} + 2\mathrm{HO}^{-} \rightarrow 2\mathrm{A}^{-} + 2\mathrm{H}_{2}\mathrm{O} \qquad (C)$$

The concentration profile of the permeant, *i.e.* acid in the form of different complexes and the dimer, with denotation of individual concentrations, is shown schematically in Fig. 1.

With increasing concentration of carrier (TOA), the flux of BA through the BLM increases only slightly, despite the fact that the values of the distribution coefficient and the permeability of the membrane are being substantially increased, as discussed later. The permeability of the LM can be in the first approximation estimated as a product of the distribution coefficient and the diffusion coefficient of species in the membrane. A possible explanation of this discrepancy is the influence of the reaction kinetics of the decomposition of acid/carrier complexes on the stripping interface. In connection with these results also the conception of interface saturation with the molecules of both complexes and the dimer, even at their low concentration in the membrane phase can arise. Adsorption equilibrium can be described by the Langmuir isotherm.

In the development of a model for the pertraction through a well mixed layered BLM in a twocompartment pertractor the following assumptions were made:

i) Chemical reactions of the complex acid/carrier formation on the extraction interface (F/M) are fast, which means that the diffusional mass-transfer resistances in boundary layers are decisive at this interface.

ii) All three phases are well mixed and hydrody-

namic conditions, as well as the structure of the transported species, at both interfaces in the membrane are identical. Hence,  $k_{\rm MF} = k_{\rm MR} = k_{\rm M}$ . The accumulation of species in the boundary layers at interfaces is negligible. This means that the fluxes through the boundary layers on both sides of the individual interface are identical.

iii) On the extraction interface an equilibrium is reached.

iv) The rate of the stripping reaction is proportional to the concentration of acid species (complexes and dimer) on the interface, which can be described by the Langmuir isotherm. The rate of the decomposition of the complexes on the stripping interface (M/R) can be described by a pseudofirst-order rate equation defined for acid concentration.

v) The excess of reagent in the stripping solution is maintained so that the concentration of the undissociated acid in the stripping solution even at the interface R/M is practically zero.

vi) The volumes of phases are functions of the concentration of the organic acid providing that the additivity of volumes is valid, which was proved experimentally. Components of the membrane phase, *i.e.* carrier, diluent (n-alkanes), and complexes are insoluble in aqueous solutions in contact.

Based on these assumptions the following model equations were derived. For the concentration of acid in individual phases differential equations have been derived

$$\frac{\mathrm{d}c_{\mathrm{F}}}{\mathrm{d}t} = -\frac{k_{\mathrm{F}}k_{\mathrm{M}}A_{\mathrm{F}}(D_{\mathrm{F}}c_{\mathrm{F}} - c_{\mathrm{M}})}{V_{\mathrm{F}}(k_{\mathrm{F}} + k_{\mathrm{M}}D_{\mathrm{F}})} \tag{1}$$

$$\frac{\mathrm{d}c_{\mathrm{M}}}{\mathrm{d}t} = \frac{k_{\mathrm{F}}k_{\mathrm{M}}A_{\mathrm{F}}}{V_{\mathrm{M}}} \left[ \frac{(D_{\mathrm{F}}c_{\mathrm{F}} - c_{\mathrm{M}})}{(k_{\mathrm{F}} + k_{\mathrm{M}}D_{\mathrm{F}})} \right] - \frac{k_{\mathrm{M}}A_{\mathrm{R}}}{V_{\mathrm{M}}} (c_{\mathrm{M}} - c_{\mathrm{MR}})$$
(2)

$$\frac{\mathrm{d}c_{\mathrm{aR}}}{\mathrm{d}t} = \frac{k_{\mathrm{M}}A_{\mathrm{R}}}{V_{\mathrm{R}}}(c_{\mathrm{M}} - c_{\mathrm{MR}}) \tag{3}$$

The concentration of acid in the membrane phase can

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be calculated from the material balance

$$c_{\rm M} = \frac{V_{\rm Fo}c_{\rm Fo} - V_{\rm F}c_{\rm F} - V_{\rm R}c_{\rm aR}}{V_{\rm M}} \tag{4}$$

Based on assumption vi), following relationships for the volumes of phases were derived

$$V_{\rm F} = \frac{V_{\rm Fo}(\rho_{\rm k} - c_{\rm Fo}M_{\rm k})}{\rho_{\rm k} - c_{\rm F}M_{\rm k}} \tag{5}$$

$$V_{\rm R} = \frac{V_{\rm Ro}\rho_{\rm k}}{\rho_{\rm k} - c_{\rm aR}M_{\rm k}} \tag{6}$$

$$V_{\rm M} = \frac{V_{\rm Mo}\rho_{\rm k}}{\rho_{\rm k} - c_{\rm M}M_{\rm k}} \tag{7}$$

where  $\rho_{\mathbf{k}}$  is the density of the pure acid, in the present paper BA.

The flux of acid in the boundary layer at the stripping interface can be expressed by the equation

$$\dot{n} = k_{\rm M} A_{\rm R} (c_{\rm M} - c_{\rm MR}) \tag{8}$$

The flux through the interface is influenced also by the reaction kinetics of the complexes and the dimer decomposition. As the first approximation, it will be assumed that this kinetics can be described by the pseudofirst-order rate equation

$$\dot{n} = r_{\rm S} A_{\rm R} c_{\rm iR} \tag{9}$$

where for the concentration of acid (in the form of different species) on the phase interface the following relation applies according to the Langmuir isotherm

$$c_{\rm iR} = c_{\rm iRmax} \frac{ac_{\rm MR}}{1 + ac_{\rm MR}} \tag{10}$$

Considering assumption ii), the fluxes in eqns (8) and (9) are equal. Taking into account eqn (10) a quadratic equation is obtained

$$-k_{\rm M}ac_{\rm MR}^2 + c_{\rm MR}(k_{\rm M}c_{\rm M}a - k_{\rm M} - Xa) + k_{\rm M}c_{\rm M} = 0 \quad (11)$$

where

$$X = r_{\rm S} c_{\rm iRmax} \tag{12}$$

with  $c_{iRmax}$  being the maximal concentration of acid on the interface. Eqn (11) enables the estimation of the concentration of acid in the membrane at the stripping interface  $c_{MR}$ . This concentration is related to the minimal area occupied by one molecule on the interface. Its value has to be, together with the value of a, estimated by an independent method. For the first orientation, for hydroxyoximes  $c_{iRmax}$  has a value around  $2 \times 10^{-6}$  mol m<sup>-2</sup> [21]. The value of a = 200m<sup>3</sup> kmol<sup>-1</sup> or 1000 m<sup>3</sup> kmol<sup>-1</sup> in eqn (10) was chosen



Fig. 2. Extraction equilibria of butyric acid in water/solvent system at 30 °C. Lines are calculated according to the model [20].

according to the assumption that the stripping interface is saturated even at lower concentrations of acid in the membrane.

The distribution coefficient of BA is concentrationdependent. Based on the reaction mechanism the following relationship has been derived with a good fit to experimental data [20], as it is shown in Fig. 2

$$D = \frac{\frac{N}{c_{\rm F}^{*}} \left(1 - \frac{c_{\rm Po}M_{\rm P}}{\rho_{\rm P}}\right) + \frac{Bc_{\rm Po}/c_{\rm F}^{*}}{1 + Yc_{\rm F}^{*}}}{1 + \frac{M_{\rm k}}{\rho_{\rm k}} \left(N \left(1 - \frac{c_{\rm Po}M_{\rm P}}{\rho_{\rm P}}\right) + \frac{Bc_{\rm Po}}{1 + Y}\right)}$$
(13)

where the quantities N, B, and Y are defined by the equations

$$N = 2 \frac{K_{\rm d}(c_{\rm F}^{*})^2}{1 - K_{\rm d}(c_{\rm F}^{*})^2 \frac{M_{\rm k}}{\rho_{\rm k}}}$$
(14)

$$B = K_{1,1}c_{\rm F}^* + 3K_{1,1}K_{3,1}(c_{\rm F}^*)^3 + 5K_{1,1}K_{3,1}K_{5,1}(c_{\rm F}^*)^5$$
(15)

$$Y = K_{1,1}c_{\rm F}^* + K_{1,1}K_{3,1}(c_{\rm F}^*)^3 + K_{1,1}K_{3,1}K_{5,1}(c_{\rm F}^*)^5$$
(16)

Estimated equilibrium constants of the formation of both the dimer and the complexes with BA TOA mole ratios 1 1, 3:1, 5 1 have respective values  $K_{\rm d}$ = 0.669 m<sup>3</sup> kmol<sup>-1</sup>,  $K_{1,1}$  = 1.67 m<sup>3</sup> kmol<sup>-1</sup>,  $K_{3,1}$  = 167.7 (m<sup>3</sup> kmol<sup>-1</sup>)<sup>2</sup>,  $K_{5,1}$  = 2.58 (m<sup>3</sup> kmol<sup>-1</sup>)<sup>2</sup> [20].

The concentration of undissociated acid in the feed phase at  $pH_F$  was calculated from the overall (analytical) concentration estimated according to the equation

$$c_{\rm F} = \frac{c_{\rm aF}}{1 + 10^{(\rm pH_F - pK_a)}} \tag{17}$$

Table 1. Distribution Coefficient of BA, D (at  $pH_F = 2.6$ ), Kinematic Viscosity of the Membrane Phase,  $\nu$ , and Diffusion Coefficients of the Complex BA—carrier (3 1) in a Solvent or of the Dimer of BA in n-Alkanes,  $\mathcal{D}$ . Temperature: 30 °C

	D		$     \frac{\nu_{M} \cdot 10^{6}}{1} $	ρ	$\mathcal{D}\cdot 10^{10}$	$+D\cdot D\cdot 10^{10}$
Membrane phase						
	0.15 <sup>a</sup>	0.4ª	$m^2 s^{-1}$	kg m $^{-3}$	$m^2 s^{-1}$	$m^2 s^{-1}$
M1: 0.2 kmol m <sup><math>-3</math></sup> TOA	1.8	2.0	1.792	746.6	3.83	6.9
M2: 0.4 kmol m <sup><math>-3</math></sup> TOA	3.8	3.3	2.026	751.9	3.54	13.4
M3: 0.6 kmol m <sup><math>-3</math></sup> TOA	6.2	4.2	2.297	757.9	2.96	18.4
M4: pure n-alkanes	0.5	0.6	1.596	741.4	10.23	5.1

a)  $c_{\rm F}$  in kmol m<sup>-3</sup> at which D is determined. + for  $c_{\rm F} = 0.15$  kmol m<sup>-3</sup>.

where for BA  $pK_a = 4.83$  at 25 °C [22].

By numerical solution of a set of differential and algebraic equations (1-7) and (11-16) parameters of the model have been estimated.

Both the initial flux of acid through the extraction interface, what is its maximum value, and the maximum flux of acid through the stripping interface were estimated from the equations

$$J_{\rm Fo} = -\frac{V_{\rm F}}{A_{\rm F}} \frac{{\rm d}c_{\rm F}}{{\rm d}t} \tag{18}$$

$$J_{\rm Rmax} = -\frac{V_{\rm R}}{A_{\rm R}} \frac{{\rm d}c_{\rm R}}{{\rm d}t} \tag{19}$$

where the values of derivations were estimated from empirical functions correlating experimental data. The second-order power law was used for  $c_{\rm F}$  for the initial period and the linear function for  $c_{\rm R}$  in the linear part of this dependence which is around the maximum in the plot  $c_{\rm M}$  vs. time. Of course, values of these derivations can be obtained from eqns (1) and (3), when model parameters are available.

## EXPERIMENTAL

Feed: Aqueous solution of butyric acid (Reachim) with  $pH_{Fo} = 2.6$ . The density of the pure BA is 959 kg m<sup>-3</sup> at 30 °C.

Stripping solution: Aqueous solution of NaOH with the concentration of 0.5-1 kmol m<sup>-3</sup>.

Components of the membrane phase: Trioctylamine (TOA, Fluka) was used as carrier increasing the value of the distribution coefficient of the acid. The density of TOA at 30 °C is 804.3 kg m<sup>-3</sup> A fraction of n-alkanes with a composition in mass % 5.4 (C<sub>10</sub>), 40.6 (C<sub>11</sub>), 40.4 (C<sub>12</sub>), and 13.1 (C<sub>13</sub>) (Slovnaft, SK) was used as a diluent. The composition of the membrane phases and their characteristics are listed in Table 1. The diffusion coefficients of permeants were estimated by the Wilke—Chang equation.

## Two-Compartment Contactor

The contactor used was made of glass with a bulk liquid membrane layered above the aqueous feed and



Fig. 3. Scheme of a two-compartment pertraction cell. F - feed, M - layered membrane phase, R - stripping solution. 1. Sampling ports, 2. disc mixers, 3. magnetic Teflon rod mixers.

the stripping phases, as it is shown in Fig. 3. The diameters of cylindrical arms of the contactor, in places where the feed and the strip interfaces are located, are nearly the same (50.3 mm and 50.6 mm). These interfaces are positioned 2.5 mm below the bottom of the neck with a length of 15.4 mm and a rectangular crosssection 50.4 mm  $\times$  37 mm (height) connecting both arms. The membrane phase with a height 18 mm was stirred with Teflon disc mixers (29 mm in diameter, distance between the centre of the disc and the interface was 12 mm) driven by the same motor. The circulation of the membrane phase in all the space occupied is quite vigorous. The aqueous feed and the stripping phases were mixed by magnetic rod mixers with a diameter of 5 mm and a length of 25 mm. Stirrers in the membrane and aqueous phases rotated in opposite directions to keep undisturbed interfaces. The frequency of mixers was adjustable and based on earlier experience it was set to  $120 \text{ min}^{-1}$  and  $100 \text{ min}^{-1}$  for mixers in the membrane phase and in the aqueous phases, respectively. Additionally, the frequency was monitored by a microprocessor tachometer CT6 (Compact, UK).



Fig. 4. Initial flux of BA through the extraction interface ( $\Box$ ) and the maximum flux through the stripping interface (0) vs. concentration of the carrier (TOA) in a BLM for  $c_{Fo} = 0.48$  kmol m<sup>-3</sup> (a), and initial feed concentration for  $c_{Po} = 0.4$  kmol m<sup>-3</sup> (b).

Around frequencies applied, the interfaces were flat and the flux practically did not change with the frequency.

The respective initial volumes of phases were for the feed, the membrane, and the stripping solution  $V_{\rm Fo} = 300 \text{ cm}^3$ ,  $V_{\rm Mo} = 90 \text{ cm}^3$ , and  $V_{\rm Ro} = 135 \text{ cm}^3$ The interfacial areas were  $A_{\rm F} = 20.13 \text{ cm}^2$  and  $A_{\rm M} =$ 19.86 cm<sup>2</sup> The contactor was placed in a closed space with the air thermostat and the temperature was kept at  $(30 \pm 0.5)$  °C, if not otherwise stated.

At chosen times, samples of the feed and the stripping solutions have been taken into a syringe with a longer Teflon capillary on the tip, which was inserted through the sampling ports. The amount of samples estimated from differential weighing was around 2 g. The same amount of the feed and the fresh stripping solution, and later in the experiment, solutions with adjusted concentration of BA were returned back to both compartments, without longer delay, to keep the volumes of solutions without change due to the sampling. Tubes below the sampling ports were emptied during the experiment by the help of elevated pressure to have interface close to the connection with the cell wall.

The concentration of BA in the aqueous phases was determined using the isotachophoretic analyzer EA 100 (Villa, SK) using HCl and a histidine solution with pH = 6.0 as the leading electrolyte. The pH of the feed samples was measured by an ion meter 3040 (Jenway, UK).

## **RESULTS AND DISCUSSION**

It has been found that the overall maximum flux through the LM, *i.e.* the maximum flux through the stripping interface,  $J_{\text{Rmax}}$ , does not change much with

the carrier concentration (Fig. 4*a*). This does not reflect the fact that the distribution coefficient of BA as well as the permeability of the LM, defined in the first approximation as product of the distribution and diffusion coefficients,  $D \cdot D$ , increases greatly, as it is shown in Table 1. By increasing the TOA concentration from 0.2 to 0.6 kmol m<sup>-3</sup>, the permeability increases by 2.7 times but the flux increases only by about 16 %. The maximal flux through the extraction interface, *e.g.* its initial value is in all experiments higher than the maximal flux through the stripping interface, as shown in Figs. 4*a* and 4*b*. This supports the assumption on the influence of the slower kinetics



Fig. 5. Influence of temperature on the initial flux of BA through the extraction interface,  $J_{Fo}$ , and the maximum flux through the stripping interface,  $J_{Rmax}$ .  $c_{Fo} = 0.48$  kmol m<sup>-3</sup>, membrane: M2 (0.4 kmol m<sup>-3</sup> TOA).



Fig. 6. Time course of BA concentrations in three phases of a two-chamber contactor.  $c_{Fo} = 0.48 \text{ kmol m}^{-3}$ .  $\Delta$  Feed,  $\bigcirc$  membrane phase,  $\square$  stripping solution. a)  $c_{Po} = 0.2 \text{ kmol m}^{-3}$ , estimated:  $k_{M} = 4.4 \times 10^{-6} \text{ m s}^{-1}$ , b)  $c_{Po} = 0.4 \text{ kmol m}^{-3}$ , estimated:  $k_{M} = 3.32 \times 10^{-6} \text{ m s}^{-1}$ , c)  $c_{Po} = 0.6 \text{ kmol m}^{-3}$ , estimated:  $k_{M} = 3.7 \times 10^{-6} \text{ m s}^{-1}$ . Lines are correlated for fixed values of parameters:  $X = 1.0 \times 10^{-6} \text{ kmol m}^{2} \text{ s}^{-1}$ ,  $a = 200 \text{ m}^{3} \text{ kmol}^{-1}$ , and  $k_{F} = 5.2 \times 10^{-6} \text{ m s}^{-1}$ .

of the stripping reaction on the overall transport rate. Another reason explaining this observation can be saturation of the interface with the molecules of complexes and the dimer even at their relatively low concentration in the membrane. This results in a steady rate of the complex decomposition, because this rate is a function of the concentration of species on the interface. When this concentration is close to saturation, the flux through the stripping interface as well as through the LM is increasing only slightly, as can be seen in Fig. 4a.

With increasing temperature, the initial flux

through the extraction interface practically does not change. However, the maximum flux through the stripping interface, where slower reaction of decomposition takes place, increases with temperature (Fig. 5). The temperature dependences of the fluxes through interfaces support the interpretation based on the reaction kinetics of decomposition of the complexes.

The suggested model correlates experimental data well, as shown in Figs. 6 and 7. The nonzero value of the BA concentration in the membrane at the stripping interface,  $c_{\rm MR}$ , was estimated and it is depicted in these figures together with other concentrations at



Fig. 7. Time course of butyric acid concentration in three phases of a two-compartment contactor. Membrane: M2 (0.4 kmol m<sup>-3</sup> TOA).  $\Delta$  Feed, O membrane phase,  $\Box$  stripping solution. Lines are correlated for fixed values of parameters:  $a = 200 \text{ m}^3$  kmol<sup>-1</sup>,  $k_{\rm F} = 5.2 \times 10^{-6} \text{ m s}^{-1}$ ,  $k_{\rm M} = 3.9 \times 10^{-6} \text{ m s}^{-1}$ . a)  $c_{\rm Fo} = 0.25$  kmol m<sup>-3</sup>, estimated:  $X = 0.43 \times 10^{-6}$  kmol m<sup>-2</sup> s<sup>-1</sup>, b)  $c_{\rm Fo} = 0.74$  kmol m<sup>-3</sup>, estimated:  $X = 1.22 \times 10^{-6}$  kmol m<sup>-2</sup> s<sup>-1</sup>.



Fig. 8. Parameters of the model vs. concentration of carrier in the membrane.  $c_{\rm Fo} = 0.48$  kmol m<sup>-3</sup>. Fixed values of parameters:  $\circ a = 200 \text{ m}^3 \text{ kmol}^{-1}, \Delta a = 1000 \text{ m}^3 \text{ kmol}^{-1}. a) k_{\rm F} = 5.2 \times 10^{-6} \text{ m s}^{-1}, X = 1.0 \times 10^{-6} \text{ kmol m}^{-2} \text{ s}^{-1}, b) k_{\rm F} = 5.2 \times 10^{-6} \text{ m s}^{-1}, X = 1.0 \times 10^{-6} \text{ kmol m}^{-2} \text{ s}^{-1}, b) k_{\rm F} = 5.2 \times 10^{-6} \text{ m s}^{-1}, X = 1.0 \times 10^{-6} \text{ kmol m}^{-2} \text{ s}^{-1}, b) k_{\rm F} = 5.2 \times 10^{-6} \text{ m s}^{-1}, X = 1.0 \times 10^{-6} \text{ kmol m}^{-2} \text{ s}^{-1}, b) k_{\rm F} = 5.2 \times 10^{-6} \text{ m s}^{-1}, x = 1.0 \times 10^{-6} \text{ kmol m}^{-2} \text{ s}^{-1}, b) k_{\rm F} = 5.2 \times 10^{-6} \text{ m s}^{-1}, x = 1.0 \times 10^{-6} \text{ kmol m}^{-2} \text{ s}^{-1}, b) k_{\rm F} = 5.2 \times 10^{-6} \text{ m s}^{-1}, x = 1.0 \times 10^{-6} \text{ kmol m}^{-2} \text{ s}^{-1}, b) k_{\rm F} = 5.2 \times 10^{-6} \text{ m s}^{-1}, x = 1.0 \times 10^{-6} \text{ kmol m}^{-2} \text{ s}^{-1}, b) k_{\rm F} = 5.2 \times 10^{-6} \text{ m s}^{-1}, x = 1.0 \times 10^{-6} \text{ kmol m}^{-2} \text{ s}^{-1}, b) k_{\rm F} = 5.2 \times 10^{-6} \text{ m s}^{-1}, b = 0.0 \times 10^{-6} \text{ m s$ 

the feed interface. In the initial period of identification of model parameters only the constant *a* was fixed to 200 m<sup>3</sup> kmol<sup>-1</sup> or 1000 m<sup>3</sup> kmol<sup>-1</sup>, which are only estimates. This constant should be independently determined from experimental data, *e.g.* from the measurements of interfacial tensions. From the first trials, the mean value of the individual mass-transfer coefficient in the feed boundary layer was found to be  $5.2 \times 10^{-6}$  m s<sup>-1</sup> and in further correlations it was fixed. As can be seen from Figs. 8*a* and 8*b* both the remaining parameters are more or less independent of the concentration of the carrier. The value of the adsorption isotherm parameter a in the tested interval does not influence the value of the model parameters, as shown in Figs. 8b and 9b.

For fixed parameters a, X, and  $k_{\rm F}$  also the value of the individual mass-transfer coefficient seems to be constant, but larger fluctuations in the values of  $k_{\rm M}$ at lower concentrations have been observed (Fig. 9a). The assumption of constant individual mass-transfer coefficients at both interfaces,  $k_{\rm F}$  and  $k_{\rm M}$  is reasonable and reflects the same hydrodynamic conditions



Fig. 9. Parameters of the model *us.* concentration of acid in the feed.  $c_{Po} = 0.4 \text{ kmol m}^{-3}$ . Fixed values of parameters:  $0 a = 200 \text{ m}^3 \text{ kmol}^{-1}$ ,  $\Delta a = 1000 \text{ m}^3 \text{ kmol}^{-1}$ .  $a) k_F = 5.2 \times 10^{-6} \text{ m s}^{-1}$ ,  $X = 1.0 \times 10^{-6} \text{ kmol m}^{-2} \text{ s}^{-1}$ ,  $b) k_F = 5.2 \times 10^{-6} \text{ m}^{-2} \text{ m}^{-1}$ .  $s^{-1}, k_{\rm M} = 3.9 \times 10^{-6} \text{ m s}^{-1}.$ 

at interfaces. When fixing them it was found that the value of the kinetic parameter X increases with the concentration of BA in the feed, as shown in Fig. 9b. This may be the consequence of changing distribution of acid/carrier complexes with a different structure, as it is presented in paper [20]. The mole ratio of acid

carrier in complexes is equal to 1 1 at low concentrations. This ratio changes to 3 1 and even to 5 1 at higher concentrations, which may be reflected in the kinetics of the decomposition reactions. A more detailed analysis of the decomposition kinetics will be the subject of further study.

A two-compartment contactor can be useful in studying the kinetics of the decomposition or formation of complexes on the stripping or extraction interfaces in pertraction or extraction.

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#### SYMBOLS

a	parameter in the Langmuir ad-	
	sorption isotherm, eqn $(10)$	${ m m}^3~{ m kmol}^{-1}$
Α	surface area	$m^2$
В	variable defined by eqn $(15)$	
с	molar concentration of permeant	
	(undissociated acid or acid in the	
	form of complexes)	$ m kmolm^{-3}$
$c_{a}$	analytical (overall) molar con-	

centration of the permeant

$c_{iR}$	molar concentration of BA at the	
	stripping interface (in the form of	
	the dimer or complex)	$ m kmolm^{-2}$
CР	molar concentration of the free	
	carrier	$ m kmolm^{-3}$
$\mathcal{D}$	diffusion coefficient	$m^2 s^{-1}$
D	distribution coefficient,	
	$D=c_{ m M}^{*}/c_{ m F}^{*}$	
J	molar flux density of permeant	$ m kmolm^{-2}$
		$s^{-1}$
$\boldsymbol{k}$	individual mass-transfer coeffi-	
	cient	$m s^{-1}$
$K_{d}$	equilibrium constant of forma-	
	tion of the acid dimer	
$K_{1,1}, K_{2}$	$_{3,1}, K_{5,1}$ equilibrium constants	
	of formation of complexes $m(acid)$	
	:n(carrier) (1:1, 3:1, 5:1)	
M	molar mass	kg kmol <sup>-1</sup>
n	stoichiometric coefficient for acid	
	in reactions $(A)$ and $(B)$	
Ν	variable defined by eqn $(14)$	
'n	molar flux	kmol s <sup>-1</sup>
V	volume	m <sup>3</sup>
X	variable defined by eqn $(11)$	
Y	variable defined by eqn $(16)$	
ν	kinematic viscosity	$m^2 s^{-1}$
ρ	density	kg m <sup>-3</sup>

## Indices

 $kmol m^{-3}$ 

d dimer F aqueous phase, interface on the feed side F/M

- k organic acid (BA)
- M membrane phase
- o initial value
- P free carrier (TOA)
- R stripping solution, interface on the strip side M/R
- TOA trioctylamine (carrier)
- \* equilibrium value

## Abbreviations

- BA butyric acid
- HA organic acid
- HF hollow fibre
- P carrier (extractant)
- TOA trioctylamine

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