Membrane-Based Extraction Joined with Membrane-Based Stripping in a Circulating Arrangement
III. Extraction of Zinc*

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The aim of this work was to determine mass transfer coefficients for membrane-based extraction joined with membrane-based stripping (re-extraction). For the integrated system of batch extraction and back extraction (re-extraction) in a hollow fibre contactor, and for the extraction system exhibiting a high value of the distribution coefficient a model, which simplifies our previously derived model (parts I and II of this article), was proposed. This model consists of three relations resulting from analytical integration of the differential equations, which were used in the previous model. The model allows determining the overall mass transfer coefficients simultaneously for batch extraction and back extraction from the experimental time dependences of concentration of the transferred component in the reservoirs of the feed and stripping phases. The proposed model was applied for extraction of Zn from an aqueous phase to the solvent with DEHPA carrier and for simultaneous back extraction from the solvent to diluted sulfuric acid. For the extraction system with high distribution coefficient the resistance against mass transfer is concentrated predominantly in the aqueous phase. In this case, the particular coefficient, k_e, could be considered to be equal to the overall coefficient, K_e. The dependence of the measured values k_e *vs.* *Re* in lumens was compared to k_e values available in the literature. Moreover, a good agreement of the measured and calculated dependence of the concentration of the transferred component in the feed and stripping reservoirs confirmed the suitability of the presented model for the batch extraction/re-extraction circulating arrangement in case of membrane-based extraction joined with membrane-based stripping.

During membrane extraction carried out in a hollow fibre contactor (HFC), the two phases are contacted through immobilized interface formed by one of the liquid in the micropores of the wall of the hollow fibre. Large specific area for mass transfer, no flooding, the possibility of achieving extreme phase ratios, and nondispersive phase contact are the advantages over traditional equipment. To avoid entrainment of the liquid wetting material of the fibres, pressure of the other liquid has to be kept higher.

The system integrating batch extraction and back extraction is used in laboratories for the determination of mass transfer coefficients. This arrangement of the process permits a significant saving of the volume of phases, particularly the volume of the solvent. This configuration assures that saturation of the carrier in the solvent does not occur, as it is continuously regenerated and the carrier concentration can be reduced maintaining the mass transfer rate, thus decreasing the operating costs of the process.

Membrane extraction processes have been applied in a large variety of systems including separation of organic acids [1—3], pollutants [4], pharmaceutical products [5], and metals [6—9]. For a constant value of the partition coefficient in batch extraction *D'elia et al.* [1], *Dahuron* and *Cussler* [10], *Viegas et al.* [11], and *Coelhoso et al.* [12] derived integrated relations of the time dependence of the solute concentration in the feed/raffinate reservoir. On the basis of these relations the overall mass transfer coefficient was determined. Numerical integration of differential equations of the mass balance of solute in the feed and stripping reservoirs was proposed by *Coelhoso et al.* [12, 13] for the integrated system of extraction and back extraction and for the partition coefficient dependent on the solute concentration. The authors supposed a constant driving force in HFC. *Escalante et al.* [14] proposed four different models. In the first two models a constant driving force in HFC was supposed. In the second two models the authors supposed that the time

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change of the concentration in HFC could not be neglected. For mathematical evaluation of these changes two couples of partial differential equations were used. One couple was used for the extraction HFC and the other for stripping HFC. For the integrated system of batch extraction and extraction system with high value of the distribution coefficient *Schöner et al.* [8] implied the relation for mass transfer in HFC into the mass balance of the feed reservoir. Thus, an integrated form of the relation for calculation of the time course of the solute in the feed reservoir necessary for determination of the extraction mass transfer coefficient was obtained. *Marriott et al.* [15] proposed a general form of model equations for HFC. *Lin* and *Juang* [16] supposed pseudosteady-state condition for mass-transfer rate through all interfaces. Their system of equations included also the rate constant of surface reaction between carrier and the transferred component.

THEORETICAL

Kinetic experiments were performed in the system composed of Zn in a form of $ZnSO_4$ diluted in water and bis(2-ethylhexyl) phosphate (DEHPA) in alkanes. The chemical extraction of Zn^{2+} ions with DEHPA can be described by the overall reaction scheme

$$\mathrm{Zn^{2+}} + 1.5\left(\overline{\mathrm{RH}}\right)_2 \Leftrightarrow \overline{\mathrm{ZnR_2RH}} + 2\mathrm{H^+} \qquad (A)$$

The value of the equilibrium constant was determined experimentally as (5.0 ± 0.8) × 10^{-2} (kmol $\mathrm{m^{-3}})^{1/2}$. At the equilibrium constant of the extraction of zinc [7]

$$K_{\mathrm{Zn}} = \frac{\left[\overline{\mathrm{MeX_2}\left(\mathrm{HX}\right)_{2n-2}}\right]\left[\mathrm{H^+}\right]^2}{\left[\mathrm{Zn^{2+}}\right]\left[\left(\overline{\mathrm{HX}}\right)_2\right]^n} = 0.05 \qquad (1)$$

by DEHPA in isododecane the value of the distribution coefficient for pH > 3 in the aqueous phase is higher than 1000. These results agree with those published by *Forgóová* and *Schlosser* [17]. Their dependence of the distribution coefficient on pH in the aqueous phase for a system, composed of a solution of $ZnSO_4$ in an aqueous solution of Na_2SO_4 (0.1 kmol $\mathrm{m^{-3}}$)—DEHPA (0.2 kmol $\mathrm{m^{-3}}$) in alkanes, has the following form

$$\log D_{\mathrm{F}} = -2.53537 + 1.61287\mathrm{pH} \qquad (2)$$

The back chemical extraction was induced by diluted sulfuric acid

$$\overline{\mathrm{ZnR_2RH}} + \mathrm{H_2SO_4} \rightarrow 1.5\left(\overline{\mathrm{RH}}\right)_2 + \mathrm{ZnSO_4} \qquad (B)$$

The value of the equilibrium constant of this reaction is shifted to the right and the value of the distribution coefficient D_{R} can be considered as extremely high.

For membrane-based extraction joined with membrane-based stripping in the circulating arrangement a following set of model equations was derived in our previous articles [18—20].

Governing Equations of the Model

Feed/Raffinate Loop

For

$$D_{\mathrm{F}} = \frac{c_{\mathrm{org}}}{c_{\mathrm{aqu}}} = f\left(c_{\mathrm{S0}t}\right) \qquad (3)$$

(usually a polynomial form of the relation)

and countercurrent arrangement of the flow of phases through the extraction HFC, time dependence of the concentration of the transferred component in the extraction reservoir is described by the equations [19]

$$-\frac{\mathrm{d}c_{\mathrm{F1}t}}{\mathrm{d}t} = \frac{1-\mathrm{e}^{-W}}{\tau_{\mathrm{F}}\left(1-E_{\mathrm{F}}\mathrm{e}^{-W}\right)}\left(c_{\mathrm{F1}t} - \frac{c_{\mathrm{S0}t}}{D_{\mathrm{F}}}\right) \qquad (4)$$

$$c_{\mathrm{F2}} = c_{\mathrm{F1}}\frac{\left(1-E_{\mathrm{F}}\right)\mathrm{e}^{-W}}{1-E_{\mathrm{F}}\mathrm{e}^{-W}} + c_{\mathrm{S0}t}\frac{1-\mathrm{e}^{-W}}{D_{\mathrm{F}}\left(1-E_{\mathrm{F}}\mathrm{e}^{-W}\right)} \qquad (5)$$

For cocurrent arrangement of the flow of phases through HFC similar equations are valid for time dependence of the concentration of the transferred component in the extraction reservoir

$$-\frac{\mathrm{d}c_{\mathrm{F1}t}}{\mathrm{d}t} = \frac{1-\mathrm{e}^{-O}}{\tau_{\mathrm{F}}\left(1+E_{\mathrm{F}}\right)}\left(c_{\mathrm{F1}t} - \frac{c_{\mathrm{S0}t}}{D_{\mathrm{F}}}\right) \qquad (6)$$

$$c_{\mathrm{F2}} = c_{\mathrm{F1}}\frac{E_{\mathrm{F}}+\mathrm{e}^{-O}}{1+E_{\mathrm{F}}} + c_{\mathrm{S0}t}\frac{1-\mathrm{e}^{-O}}{D_{\mathrm{F}}\left(1+E_{\mathrm{F}}\right)} \qquad (7)$$

Solvent Loop

For

$$D_{\mathrm{R}} = \frac{c_{\mathrm{org}}}{c_{\mathrm{aqu}}} \rightarrow \infty \qquad (8)$$

eqns (*40*) and (*41*) in [19] describing concentration changes of the transferred component with time in the solute reservoir were reduced to only one equation [20]

$$-\frac{\mathrm{d}c_{\mathrm{S0}t}}{\mathrm{d}t} = \tau_{\mathrm{S}}^{-1}\Big\{c_{\mathrm{S0}t}\left[1-\exp\left(-N_{\mathrm{S}}\right)\right] - \\ - \frac{\dot{V}_{\mathrm{F}}}{\dot{V}_{\mathrm{S}}}\left(c_{\mathrm{F1}t} - c_{\mathrm{F2}t}\right)\exp\left(-N_{\mathrm{S}}\right)\Big\} \qquad (9)$$

Further, eqn (*33*) from [19] was transformed to the form [20]

$$c_{\mathrm{S2}t} = c_{\mathrm{S1}t}\exp\left(-N_{\mathrm{S}}\right) \qquad (10)$$

and

$$c_{\mathrm{S1}t} = c_{\mathrm{S0}t} + \frac{\dot{V}_{\mathrm{F}}}{\dot{V}_{\mathrm{S}}}\left(c_{\mathrm{F1}} - c_{\mathrm{F2}}\right) \qquad (11)$$

Stripping Phase Loop

As for the solvent loop, for the stripping phase loop only the following equation was obtained for high values of D_R [20]

$$\frac{\mathrm{d}c_{\mathrm{R}0t}}{\mathrm{d}t} = \tau_\mathrm{R}^{-1}\frac{\dot{V}_\mathrm{S}}{V_\mathrm{R}}\left[c_{\mathrm{S}0t} + \frac{\dot{V}_\mathrm{F}}{\dot{V}_\mathrm{S}}\left(c_{\mathrm{F}1t} - c_{\mathrm{F}2t}\right)\right] \cdot \cdot \left[1 - \exp\left(-N_\mathrm{S}\right)\right] \qquad (12)$$

Note: Designation of concentrations of the transferred component in the particular streams is clear from the scheme depicted in Fig. 1.

Auxiliary Equations of the Model

$$E_\mathrm{F} = \frac{\dot{V}_\mathrm{F}}{D_\mathrm{F}\dot{V}_\mathrm{S}} \qquad (13)$$

$$N_\mathrm{F} = \frac{K_\mathrm{e}A_\mathrm{e}}{\dot{V}_\mathrm{F}} \qquad (14)$$

$$W = \left(1 - E_\mathrm{F}\right)N_\mathrm{F} \qquad (15)$$

$$O = N_\mathrm{F}\left(1 + E_\mathrm{F}\right) \qquad (16)$$

$$E_\mathrm{S} = \frac{\dot{V}_\mathrm{S}}{D_\mathrm{R}\dot{V}_\mathrm{R}} \qquad (17)$$

$$N_\mathrm{S} = \frac{K_\mathrm{s}A_\mathrm{s}}{\dot{V}_\mathrm{S}} \qquad (18)$$

$$\tau_\mathrm{F} = \frac{V_\mathrm{F}}{\dot{V}_\mathrm{F}} \qquad (19)$$

$$\tau_\mathrm{S} = \frac{V_\mathrm{S}}{\dot{V}_\mathrm{S}} \qquad (20)$$

$$\tau_\mathrm{R} = \frac{V_\mathrm{R}}{\dot{V}_\mathrm{R}} \qquad (21)$$

EXPERIMENTAL

Bis(2-ethylhexyl) phosphate (DEHPA) (Merck), molar mass 322.43 kg kmol^{-1}, technical purity, was used as received. Alkanes, a dodecane fraction of alkanes (Slovnaft, Bratislava), were used as diluents. The composition, estimated by GC (w/mass %) was 5.4 C_{10}, 40.6 C_{11}, 40.4 C_{12}, and 13.1 C_{13}, and the mean molar mass was 164.2 kg kmol^{-1}. Density and kinematic viscosity at 25 °C were $\rho = 743.0$ kg m^{-3} and $\upsilon = 1.62 \times 10^{-6}$ m^2 s^{-1}. Sulfuric acid, sodium hydroxide (Mikrochem, Bratislava), zinc sulfate heptahydrate, and sodium sulfate (Lachema, Brno) were all of p.a. purity.

Feed: aqueous solution of zinc sulfate in aqueous solution of Na_2SO_4 with concentration 0.1 kmol m^{-3}, $c_{\mathrm{F}0} = 7.6 \times 10^{-3}$ kmol m^{-3} (ρ(Zn) = 0.5 kg m^{-3}), $\mathrm{pH}_{\mathrm{F}0}$ = 5.4—5.6 (pH was adjusted by sulfuric acid).

Solvent: 0.2 kmol m^{-3} DEHPA in alkanes, density and kinematic viscosity at 25 °C were $\rho = 748.9$ kg m^{-3} and $\upsilon = 1.89 \times 10^{-6}$ m^2 s^{-1}.

Stripping solution: aqueous solution of H_2SO_4 with a concentration of 2.5 kmol m^{-3}.

For simultaneous extraction and stripping, two hollow fibre contactors Liqui-Cel Extra-Flow 2.5″ × 8″ (Hoechst-Celanese, USA) with a cross-flow of phases were used. The characteristics of modules and fibres are presented in Table 1. The scheme of the experimental apparatus is in Fig. 1.

Procedure

The feed solution circulated from the reservoir through the fibre lumen and back into the reservoir. The solvent circulated in the shell sides of the modules. The organic phase circulated countercurrently in the shell side of the extraction module and cocurrently in the shell side of the stripping module. During the experiments a solution of NaOH (5 kmol m^{-3}) was added into the feed phase for keeping pH at a value about 3.3.

The pressure of the aqueous phase was maintained higher (about 40 kPa) than the pressure of the organic phase, since the hydrophobic fibres were wetted by the organic phase. The pressure was adjusted using valves at the outlet of the modules. The pressure and

Table 1. Characteristics of the Hollow-Fibre Module and Membrane Celgard X-30

Module		Hollow fibres Celgard X-30	
Diameter/cm	6.3	Internal diameter/μm	240
Length of module/cm	20	Wall thickness/μm	30
Effective fibre length/cm	15	Porosity/%	40
Number of fibres	10000	Effective pore size/μm	0.03
Inner effective area/m^2	0.56	Tortuosity	2.0
Specific area/(m^2/m^3)	2930		

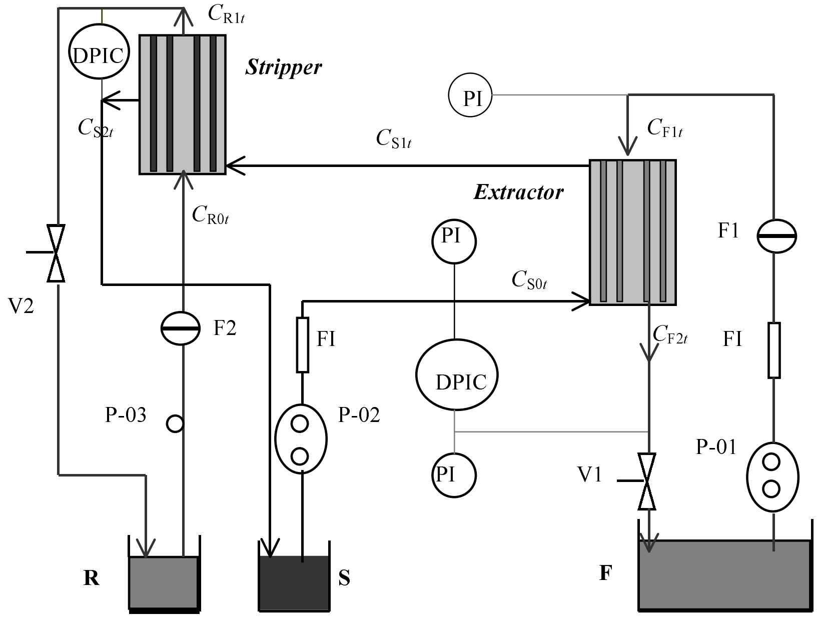

Fig. 1. Scheme of the extraction and stripping unit: F – feed reservoir, S – solvent reservoir, R – stripping reservoir, FI – flow indication (rotameters), PI – pressure indication, DPIC – difference pressure indication and control, F1, F2 – sintered glass filters, V1, V2 – metering valves for the adjustment of pressures of the aqueous phases, P-01, P-02 – gear pumps, P-03 – peristaltic pump.

pressure differences were measured with piezoelectric sensors (Omega, USA) connected to a control unit.

Streams entering the contactors, especially the fibre lumen, were filtered through sintered glass filters. The flow rates of both, the feed solution and the organic phase were measured using rotameters at the inlet of the modules. The feed and organic phase were fed by gear pumps (Verder, USA), and the stripping solution by a peristaltic pump. Maximum of the volume flow achieved by the gear pump for the aqueous phase was approximately 0.95 $\mathrm{dm}^3\ \mathrm{min}^{-1}$, *e.g.* the maximum average speed in the fibres was 3.4 cm s^{-1}. The tube-side Reynolds numbers ranged from 0.5 to 9.3.

At the beginning of measurement both the contactors were filled with aqueous phases and their pressure was adjusted and then pumping of solvent could start. The experiment started when the extractor was filled with the organic phase. The samples from the feed and stripping reservoirs were collected for the analysis as a function of time. The samples of the organic phase were taken before the start and after completion of the extraction process. After completion of the experiment the contactors were emptied.

For the determination of the concentration of Zn in the aqueous phases a colour reaction of Zn with Zincon sodium salt was used. The colour intensity was determined by the spectrophotometer UNICAM 8625 (UNICAM, UK). The concentration of Zn in the organic phase was also determined by this spectrophotometer after stripping Zn to a solution of H_2SO_4 with concentration of 2.5 kmol m^{-3}.

RESULTS AND DISCUSSION

The high value of the distribution coefficient, D_F, caused that mass transfer resistance in extraction occurred exclusively in the aqueous phase.

For a very high value of D_F ($D_\mathrm{F} \to \infty$) eqns (*4—7*) are transformed to the simpler forms, which are independent of arrangement of flow through contactors

$$-V_\mathrm{F}\frac{\mathrm{d}c_{\mathrm{F1}t}}{\mathrm{d}t} = \dot{V}_\mathrm{F}\left(c_{\mathrm{F1}t} - c_{\mathrm{F2}t}\right) \qquad (22)$$

$$c_{\mathrm{F2}t} = c_{\mathrm{F1}t}\exp\left(-N_\mathrm{F}\right) \qquad (23)$$

In the membrane-based extraction joined with membrane-based stripping, when extraction and stripping distribution coefficients are of very high values, the integral form can be obtained from eqns (*22*), (*9*), (*12*) of the proposed model.

Thus, one obtains the following relation for feed/raffinate loop

$$c_{\mathrm{F1}t} = c_{\mathrm{F0}}\exp\left(-\frac{P}{\tau_\mathrm{F}}t\right) \qquad (24)$$

where $P = 1 - \exp\left(-N_\mathrm{F}\right)$.

For the solvent loop the integral form of eqn (*9*) is

$$c_{\mathrm{S0}t} = c_{\mathrm{F0}}\frac{\dot{V}_\mathrm{F}P\exp\left(-N_\mathrm{S}\right)}{V_\mathrm{S}\left(\dfrac{P}{\tau_\mathrm{F}} - \dfrac{Q}{\tau_\mathrm{S}}\right)}\cdot$$
$$\cdot\left[\exp\left(-\frac{Q}{\tau_\mathrm{S}}t\right) - \exp\left(-\frac{P}{\tau_\mathrm{F}}t\right)\right] \qquad (25)$$

where

$$Q = 1 - \exp\left(-N_\mathrm{S}\right) \tag{26}$$

For the stripping phase the integral form of eqn (*12*) has the following form

$$\begin{aligned} c_{\mathrm{R}0t} = c_{\mathrm{F}0}\Bigg\{ & \frac{V_\mathrm{F}}{V_\mathrm{R}}\left[1 - Q\exp\left(-\frac{P}{\tau_\mathrm{F}}t\right)\right] + \\ & + \frac{\dot{V}_\mathrm{F} P Q \exp\left(-N_\mathrm{S}\right)}{V_\mathrm{R}\tau_\mathrm{S}\left(\dfrac{P}{\tau_\mathrm{F}} - \dfrac{Q}{\tau_\mathrm{S}}\right)} \cdot \\ & \cdot \left[\frac{\tau_\mathrm{F}}{P}\exp\left(-\frac{P}{\tau_\mathrm{F}}t\right) - \frac{\tau_\mathrm{S}}{Q}\exp\left(-\frac{Q}{\tau_\mathrm{S}}t\right)\right]\Bigg\} \end{aligned} \tag{27}$$

From the integral form of equations following properties of the proposed model can be demonstrated:

If extraction proceeds for a long time, concentration of extracted component in the feed is approaching zero. Thus, a following expression is valid for the quantity of the extracted component

$$\begin{aligned} m_{\mathrm{e,tot}} &= \int_0^\infty \dot{m}_{\mathrm{e}t}\,\mathrm{d}t = \\ &= \rho_{\mathrm{F}0}\dot{V}_\mathrm{F} P \int_0^\infty \exp\left(-\frac{P}{\tau_\mathrm{F}}t\right)\,\mathrm{d}t = V_\mathrm{F}\rho_{\mathrm{F}0} \end{aligned} \tag{28}$$

For the above-mentioned conditions the following relation gives the quantity of the extracted component from solvent to the stripping phase

$$\begin{aligned} m_{\mathrm{s,tot}} = \dot{V}_\mathrm{S}\rho_{\mathrm{F}0} P Q \Bigg\{ & \frac{\dot{V}_\mathrm{F}\exp\left(-N_\mathrm{S}\right)}{V_\mathrm{S}\left(\dfrac{P}{\tau_\mathrm{F}} - \dfrac{Q}{\tau_\mathrm{S}}\right)} \cdot \\ & \cdot \int_0^\infty \left[\exp\left(-\frac{Q}{\tau_\mathrm{S}}t\right) - \exp\left(-\frac{P}{\tau_\mathrm{F}}t\right) + \right. \\ & \left. + \frac{\dot{V}_\mathrm{F}}{\dot{V}_\mathrm{S}}\exp\left(-\frac{P}{\tau_\mathrm{F}}t\right)\right]\mathrm{d}t\Bigg\} = V_\mathrm{F}\rho_{\mathrm{F}0} \end{aligned} \tag{29}$$

If membrane-based extraction joined with membrane-based stripping proceeds for a very long time, the extracted component is accumulated in the stripping reservoir. Integration of eqn (*27*) in time interval (0,∞) yields

$$c_{\mathrm{R}0\infty} = c_{\mathrm{F}0}\frac{V_\mathrm{F}}{V_\mathrm{R}} \tag{30}$$

The value of the coefficient K_e may be estimated from the time course of the extracted component in the feed reservoir. In semilogarithmic coordinates the experimental values have the shape of a straight line and K_e is determined from the slope of this straight line according to relation (*25*). The exemplary results of the changes of zinc concentration in the feed/raffinate reservoir are shown in Fig. 2.

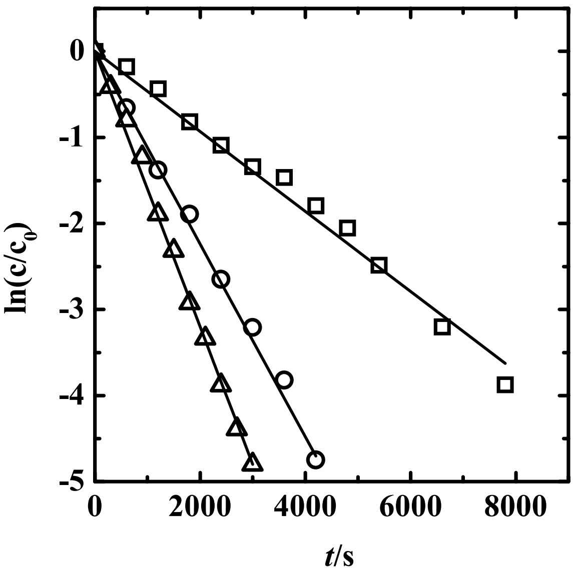

Fig. 2. Decline of the dimensionless concentration of Zn *vs.* time in the feed/raffinate reservoir for different flow rates: □ $V_\mathrm{F} = 4.909 \times 10^{-3}$ m^3, $\dot{V}_\mathrm{F} = 2.7 \times 10^{-6}$ m^3 s^{-1}, $K_\mathrm{e} = 8.9 \times 10^{-6}$ m s^{-1}; ○ $V_\mathrm{F} = 5.083 \times 10^{-3}$ m^3, $\dot{V}_\mathrm{F} = 9.9 \times 10^{-6}$ m^3 s^{-1}, $K_\mathrm{e} = 1.51 \times 10^{-5}$ m s^{-1}; Δ $V_\mathrm{F} = 5.02 \times 10^{-3}$ m^3, $\dot{V}_\mathrm{F} = 14.8 \times 10^{-6}$ m^3 s^{-1}, $K_\mathrm{e} = 2.07 \times 10^{-5}$ m s^{-1}.

The value of the coefficient K_s may be estimated from the time corresponding to the maximum on the curve of the time dependence of the extracted component concentration in the solvent reservoir. From the derivative form of eqn (*25*) the following equation is obtained

$$t_\mathrm{max} = \frac{\tau_\mathrm{F}\tau_\mathrm{S}}{Q\tau_\mathrm{F} - P\tau_\mathrm{S}}\ln\left(\frac{Q\tau_\mathrm{F}}{P\tau_\mathrm{S}}\right) \tag{31}$$

where t_max is the time corresponding to the maximum concentration on the experimental time dependence of the concentration of extracted component in the solvent reservoir. From this equation the quantity Q has to be found.

Concentrations of the transferred component in the organic phase were not measured except of the start and after completion of the experiment. Therefore, the starting value K_s was considered to be the value of the individual mass transfer coefficient

$$k_\mathrm{m} = D(\delta\tau)^{-1} \tag{32}$$

from which according to *Fernandez et al.* [21] $D = 1.33 \times 10^{-10}$ m^2 s^{-1}, and for $\tau = 2$, the coefficient k_m was calculated. For the determination of the value K_s the calculated time dependence of the solute concentration was fitted with experimentally obtained solute

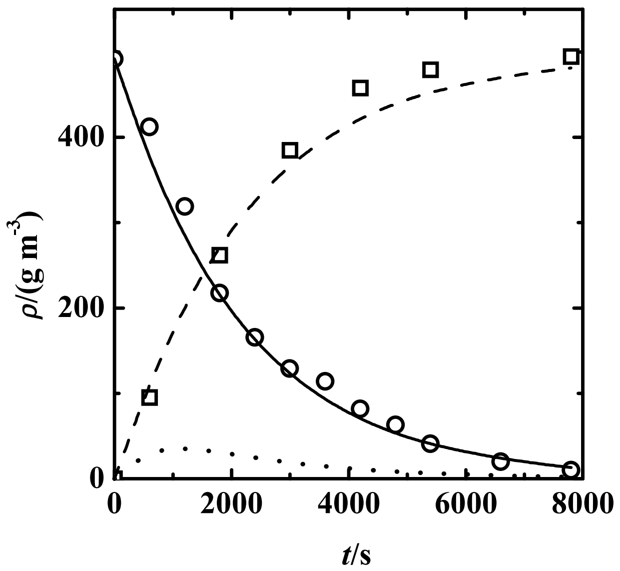

Fig. 3. Time dependence of the concentration of Zn^{2+} in feed/raffinate, and stripping phase reservoirs: ○ $V_F = 4.909 \times 10^{-3}\ m^3$, $\dot{V}_F = 2.7 \times 10^{-6}\ m^3\ s^{-1}$, $K_e = 8.9 \times 10^{-6}\ m\ s^{-1}$; □ $V_R = 0.975 \times 10^{-3}\ m^3$, $\dot{V}_R = 3.0 \times 10^{-6}\ m^3\ s^{-1}$ ($V_S = 1.083 \times 10^{-3}\ m^3$, $\dot{V}_S = 2.3 \times 10^{-6}\ m^3\ s^{-1}$, $K_s = 9.3 \times 10^{-7}\ m\ s^{-1}$). Data fitted by eqns (*25*) (solid line), (*27*) (dotted line), and (*29*) (dashed line).

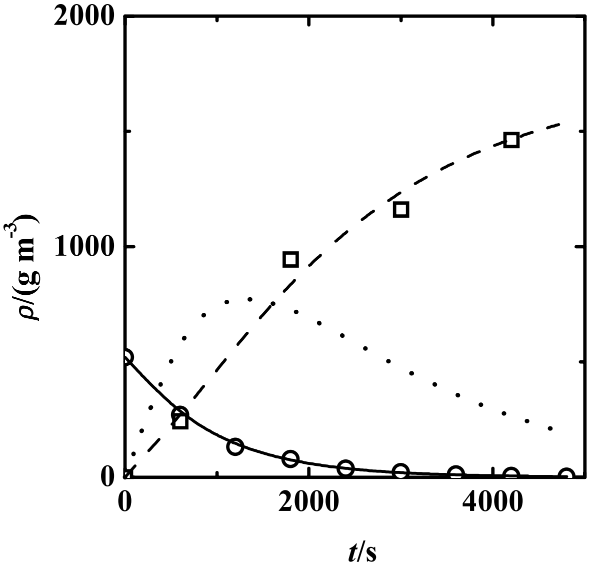

Fig. 4. Time dependence of the concentration of Zn^{2+} in feed/raffinate, and stripping phase reservoirs: ○ $V_F = 5.083 \times 10^{-3}\ m^3$, $\dot{V}_F = 9.9 \times 10^{-6}\ m^3\ s^{-1}$, $K_e = 1.51 \times 10^{-5}\ m\ s^{-1}$; □ $V_R = 0.772 \times 10^{-3}\ m^3$, $\dot{V}_R = 2.1 \times 10^{-6}\ m^3\ s^{-1}$ ($V_S = 0.670 \times 10^{-3}\ m^3$, $\dot{V}_S = 2.3 \times 10^{-6}\ m^3\ s^{-1}$, $K_s = 7.7 \times 10^{-7}\ m\ s^{-1}$). Data fitted by eqns (*25*) (solid line), (*27*) (dotted line), and (*29*) (dashed line).

concentration values in the stripping reservoir using standard Scientist programs. Fitting of experimental data [22], [24] is shown in Figs. 3—5.

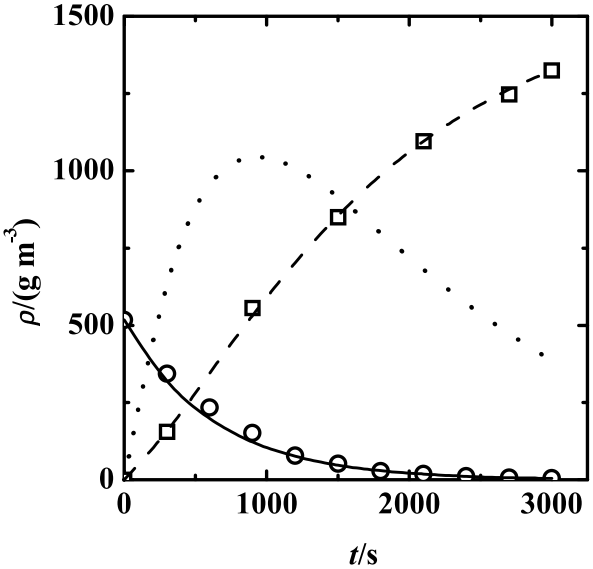

Fig. 5. Time dependence of the concentration of Zn^{2+} in feed/raffinate, and stripping phase reservoirs: ○ $V_F = 5.020 \times 10^{-3}\ m^3$, $\dot{V}_F = 14.8 \times 10^{-6}\ m^3\ s^{-1}$, $K_e = 2.07 \times 10^{-5}\ m\ s^{-1}$; □ $V_R = 0.819 \times 10^{-3}\ m^3$, $\dot{V}_R = 3.0 \times 10^{-6}\ m^3\ s^{-1}$ ($V_S = 0.523 \times 10^{-3}\ m^3$, $\dot{V}_S = 2.3 \times 10^{-6}\ m^3\ s^{-1}$, $K_s = 7.6 \times 10^{-7}\ m\ s^{-1}$). Data fitted by eqns (*25*) (solid line), (*27*) (dotted line), and (*29*) (dashed line).

Mixing in the reservoirs was sufficiently vigorous to fulfil the conditions of an ideal mixer. Mass transfer in this investigated extraction/re-extraction system did not influence the change of the volume of phases. For the extraction process the conditions of negligible axial diffusion and the formation of an axial concentration profile as a consequence of mass transfer could be considered as presumably fulfilled. Moreover, the surface reaction between zinc and DEHPA carrier is sufficiently rapid [7, 8] and only mass transfer resistances were considered. It was not possible to determine the volume of the organic phase accurately because the organic phase did not flow entirely out from the shell side of the contactor after completion of the experiment. After finishing the experiment the organic phase was drained and then pushed out by blowing air. A part of the organic phase remained in the module and some quantity of it penetrated through the wall of fibres into the inside of lumens. The whole volume of the organic phase was divided into two parts. The first part was held in the lumens, the second in the space between lumens. At the start of a new experiment the first part of the solvent held in the lumens of HFC was pushed out by the aqueous phase from the inside of fibres and by-passed the feed/raffinate reservoir. The second part of the solute held in the space between lumens increased the primary volume of the organic phase. At the beginning of the experiment there was a short period, when hydrodynamic conditions were

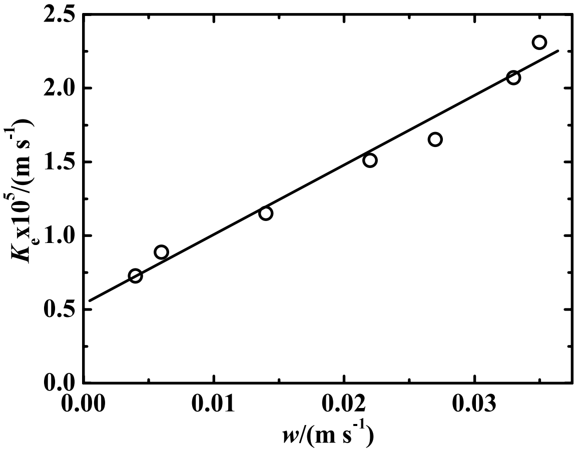

Fig. 6. Dependence of the extraction mass transfer coefficient on average velocity in fibres of the contactor.

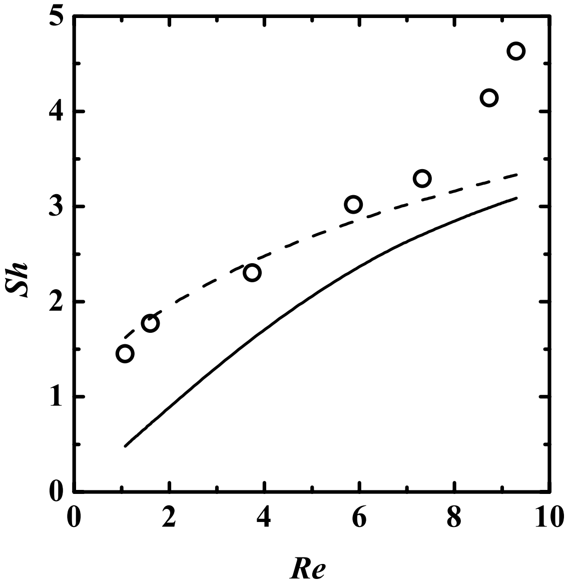

Fig. 7. Estimation of Sherwood number in fibres of the extraction contactor in a batch experiment of simultaneous extraction and stripping: ○ – calculated values from experimental data; solid line – correlation according to *Skelland* [23]; dashed line – correlation according to *Dahuron* and *Cussler* [10].

not stable (less than 1 % of the duration of the experiment). During experiments the feed/raffinate phase gradually got turbid (usually after 0.5—1 h from the start of the experiment).

The assumption of overall resistance against mass transfer in the aqueous phase is justified to consider an individual mass transfer coefficient, k_e, equal to the overall mass transfer coefficient, K_e. Correlation of the overall mass transfer coefficient, K_e *vs.* average velocity of the aqueous phase in fibres is shown in Fig. 6. The experimental values of mass transfer coefficients were compared with those calculated according to the correlation used by *Dahuron* and *Cussler* [10] and according to the correlation introduced by *Skelland* [23].

Above-mentioned correlations using original experimental data show better fit for *Dahuron* and *Cussler* [10] correlation (Fig. 7). For a more complex evaluation of the agreement between used correlations and experimental data it would be necessary to have more experimental data in a broader range of Reynolds numbers.

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SYMBOLS

A	interfacial area	m^2
c	molar concentration	kmol m^{-3}
c_{F0}	initial concentration of the extracted component in the feed	kmol m^{-3}
D	diffusion coefficient	m^2 s^{-1}
D_i	distribution coefficient, i = F or R	
d	diameter of fibre	m
E_F	quantity defined by eqn (*13*)	
E_S	quantity defined by eqn (*17*)	
K	overall mass transfer coefficient	m s^{-1}
k	individual mass transfer coefficient	m s^{-1}
L	length of the fibres of the module	m
m	mass of component	g
$\dot{m}$	mass flow of component	g s^{-1}
N	number of fibres in the module	
N_F	number of transfer units for the extraction process	
N_S	number of transfer units for the stripping process	
P	quantity defined by eqn (*24*)	
Q	quantity defined by eqn (*26*)	
t	time	s
V	volume of the reservoir	m^3
$\dot{V}$	flow rate of the liquid	m^3 s^{-1}
w	average velocity of fluid	m s^{-1}
τ_i	space-time defined by eqns (*19*—*21*)	s
τ	tortuosity	
δ	thickness of the wall of fibres	m
ρ	mass concentration	g m^{-3}

Indices

e	extraction
F	feed phase
i	inner
m	membrane
EC	extraction contactor
SC	stripping contactor
R	stripping phase
s	stripping
S	solvent (organic phase)
t	time-dependent

tot	total
1	marking of the place
2	marking of the place

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