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KINETICS OF ZINC(II) EXTRACTION FROM MODEL HYDROCHLORIC ACID SOLUTIONS IN THE LEWIS CELL

Extraction of zinc(II) from model hydrochloric acid solutions was studied in the Lewis cell mixing the bulks of both phases and keeping a stable interfacial surface. Equilibrium extraction data were obtained in a classical way described in previous papers. All experiments were carried out at room temperature. MEDUSA program was used to estimate the distribution of zinc(II) chlorocomplexes in the aqueous feed. In the aqueous feed, zinc(II) is mainly in the form of $ZnCl_4^{2-}$ (92 mole %). The contents of $ZnCl_3^-$ and $ZnCl_2$ are estimated as equal to 8 and 0 mole %, respectively. It was found that the Lewis cell experiments, although dynamic in nature, support the extraction of $ZnCl_2 \cdot 2TBP$ chlorocomplex from model solutions containing 5 M Cl^- and 0.55 M H^+. The fluxes and mass transfer coefficients were estimated using two-layer model of mass transfer. The initial fluxes of zinc(II), HCl, Cl^-, chloride present in the zinc(II) complex and water depend upon the concentration of tributyl phosphate and the mixing rates. The diffusion step in the organic phase gives a higher resistance to the mass transfer than the diffusion step in the aqueous phase. The physical transfer of small water molecules is less sensitive to the mixing rates than the transfer of bulky zinc(II) chlorocomplex.

Keywords: *mass transfer, the Lewis cell, zinc extraction*

1. INTRODUCTION

Hot-dip zinc galvanizing is the most common method of protecting steel from corrosion. The method generates spent pickling solutions containing iron(II), iron(III) and zinc(II) in hydrochloric acid. Hydropyrolysis is the method most often used to process such solutions. However, the method cannot be employed when the content of zinc(II) exceeds 0.5 g/dm^3. Such solutions are obtained when the spent pickling liquor is used for depleting the bad-quality zinc protective layers.

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Solvent extraction is one of different techniques, which allow recovery of zinc(II) from such solutions [1]–[3]. Tributyl phosphate (TBP) is the most suitable reagent and enables both an effective extraction of zinc(II) from HCl solutions and its subsequent stripping with water [4]–[7]. However, iron(III) is strongly co-extracted and must be reduced to iron(II) prior the extraction of zinc(II). Up to now, the kinetics of zinc(II) extraction from HCl solutions with TBP was not studied, and the scope of the works published was limited mainly to equilibrium studies [8].

Zinc(II) can be also recovered in membrane processes carried out in two parallel hollow fiber modules [9], [10]. The process is limited by the transfer at the membrane/strip interface. This phenomenon seems to be responsible for the slow stripping also in other membrane systems, probably due to the blocking of the interface by the surfaces-active molecules of the carriers. To verify the hypothesis it was decided to study separately the transfer of zinc(II) from the model feed to the membrane and then from the membrane to the strip phase. The Lewis cell was used, and the effect of mixing rate and tributyl phosphate concentration upon the transfer of zinc(II), zinc chlorocomplex, chloride, hydrochloric acid and water was studied. Thus, the aim of the work was to study the kinetics of zinc(II) extraction from model HCl solutions with TBP in the Lewis cell used as a contractor. The intensive mixing of both phases enabled us to decrease substantially the effects of diffusion steps upon the transfer of zinc(II) to the TBP phase. The fluxes and mass transfer coefficient could be easily estimated when experiments were performed with a stable interfacial surface. First, simplified approach to the kinetics description was presented in [11]. In this paper, a mathematical model is developed and discussed.

2. EXPERIMENTAL

The composition of model aqueous solutions was as follows: [Zn(II)] = 0.31 M; $[H^+]$ = 0.55 M; $[Cl^-]$ = 5 M (adjusted with NaCl). All reagents ($ZnCl_2$, NaCl and HCl from P.O.Ch. Gliwice) were pure grade. Deionised water from reverse osmosis was used. Pure tributyl phosphate (Fluka) was diluted with aliphatic kerosene Exxsol D 220/230 (Deutsche Exxon Chemical GmbH).

Extraction was carried out in a home-made Lewis cell (figure 1) designed by PLUCINSKI and NITSCH [12]. The volume of each phase was equal to 95 cm^3. The interfacial surface area was 16.56 cm^2. The phases were mixed by independent stirrers. The mixing rate (MR) of one phase was constant (120 rpm), while the mixing rate of the second phase was changed from 80 to 200 rpm.

1 cm^3 samples of the organic phase were taken in appropriate periods of time and stripped with 10 cm^3 water. Samples of fresh TBP solution (1 cm^3) were added to keep the constant volume of the organic phase. The content of zinc(II) in the stripping solution was determined by atomic absorption Spectr AA 800, Varian, Australia. The con-

tents of HCl and chloride ions were determined by potentiometric titration with 0.05 M NaOH and 0.05 M $AgNO_3$, respectively, using Titrino 702 SM, Metrohm, Switzerland. In titration with NaOH, the second equivalent point was observed at about pH 9. It testifies to the presence of zinc chlorocomplexes considered weak acid. The content of complexed chloride ions was determined in this way. The content of water in the organic phase was determined by Karl Fisher titration with Hydronal Composite 5 (Riedel de Haen).

Equilibrium extraction data were obtained in a classical way described in [5]. All experiments were carried out at room temperature.

MEDUSA program [13] was used to estimate the distribution of zinc(II) chlorocomplexes in the aqueous feed.

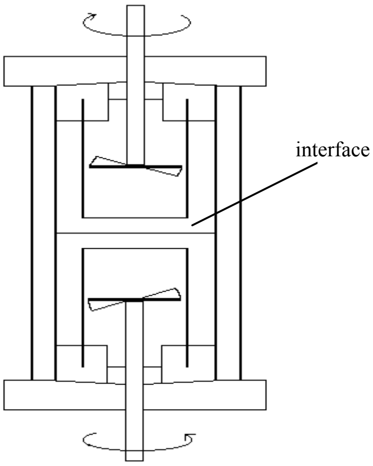

Fig. 1. Scheme of the Lewis cell

3. EQUILIBRIUM OF THE SYSTEM

Depending upon chloride concentration, zinc(II) forms chlorocomplexes according to the following reactions:

$$Zn(H_2O)_4^{2+} + Cl^- \leftrightarrow Zn(H_2O)_3Cl^+ + H_2O, \tag{1}$$

$$Zn(H_2O)_4^{2+} + 2Cl^- \leftrightarrow Zn(H_2O)_2Cl_2 + H_2O, \tag{2}$$

$$Zn(H_2O)_4^{2+} + 3Cl^- \leftrightarrow Zn(H_2O)Cl_3^{2-} + H_2O, \tag{3}$$

$$Zn(H_2O)_4^{2+} + 4Cl^- \leftrightarrow ZnCl_4^{2-} + H_2O. \tag{4}$$

The formation of metal chlorocomplexes depends not only upon chloride concentration in aqueous solutions, but also on the presence of other ions resulting in an increase in the ionic strength. An increase in the ionic strength causes an increase in the formation of higher zinc(II) chlorocomplexes. According to various authors the constants β_i of complex formation differ significantly. Thus, the composition of zinc(II) chlorocomplexes computed with MEDUSA program [13] (table 1) can be considered as rough estimation only. The computation shows that in the aqueous feed, zinc(II) is mainly in the form of $ZnCl_4^{2-}$ (92 mole %). The content of $ZnCl_3^-$ and $ZnCl_2$ is estimated to be equal to 8 and 0 mole %, respectively. The composition of the aqueous phase does not change significantly in the Lewis cell experiments because the concentration of chloride decreases from 5 M to 4.5 M only. However, the stripping with water carried out at the volume ratio equal to 1:1 gives solutions of low chloride content (below 0.5 M) and low ionic strength (below 0.8). As a result, cationic forms of zinc(II) are present which enables effective stripping of zinc(II) with water. However, neutral zinc(II) chlorocomplex is observed at the chloride content of about 0.5 M.

Table 1

Distribution of zinc(II) chlorocomplexes in the aqueous feed and the aqueous phase after zinc(II) stripping with water ($V_o/V_w = 1:1$, V_o – volume of organic phase, V_w – volume of aqueous phase)

Solution	Concentration		Ionic strength	Complexes of zinc(II)				
	Zinc(II) [mM]	Chloride [mM]		Zn^{2+} [%]	$ZnCl^+$ [%]	$ZnCl_2$ [%]	$ZnCl_3^-$ [%]	$ZnCl_4^{2-}$ [%]
Aqueous feed	310	5000	5.310	0	0	0	8	92
	90	4540	4.560	0	0	0	8	92
Aqueous strip	1	0	0.002	100	0	0	0	0
	25	78	0.100	94	6	0	0	0
	40	122	0.158	91	9	0	0	0
	94	278	0.366	85	15	0	0	0
	121	378	0.487	82	16	0	0	0
	135	422	0.542	81	19	0	0	0
	159	511	0.646	78	21	1	0	0
	166	533	0.677	78	21	1	0	0
	182	556	0.720	78	21	1	0	0

In equilibrium, TBP is a better extractant of Zn(II) than HCl (table 2). However, at least 80% TBP must be used to obtain an effective extraction of zinc(II). Low values of the distribution coefficients obtained for chloride ions are the result of great Cl^- excess in the aqueous feed (5 M). The equilibrium transfer of water increases with an increased concentration of TBP, i.e. from 0.92 M for 50% TBP to 2.86 M for 100% TBP. The mole ratio of transferred water in TBP also increases in the same order and ranged from 0.56 to 0.85 for 50 to 100% TBP, respectively.

Table 2

Distribution coefficients for the extraction of Zn(II), HCl and Cl^- and the content of water in TBP phase in equilibrium

TBP concentration	Distribution coefficients			Water content	Equilibrium transfer of water	Mole ratio of water/TBP
% vol	Zn(II)	HCl	Cl^-	[%vol]	[M]	–
50	0.56	0.17	0.07	1.88	0.92	0.56
60	0.95	0.21	0.09	2.43	1.22	0.60
70	1.08	0.26	0.10	3.09	1.63	0.65
80	1.74	0.40	0.12	3.88	2.11	0.72
90	2.33	0.48	0.13	5.03	2.65	0.83
100	3.33	0.58	0.15	5.29	2.86	0.85

Depending upon the content of chlorides and acidity of the aqueous feed, TBP can transfer the following complexes to the organic phase:

$$\mathrm{ZnCl_{2w} + 2TBP_o = ZnCl_2 \cdot 2TBP_o}\,, \tag{5}$$

$$\mathrm{HZnCl_{3w} + 3TBP_o = HZnCl_3 \cdot 3TBP_o}\,, \tag{6}$$

$$\mathrm{H_2ZnCl_{4w} + 2TBP_o = H_2ZnCl_4 \cdot 2TBP_o} \tag{7}$$

in which indexes “o” and “w” denote organic and aqueous phase, respectively. An increase in acidity and chloride content shift the equilibrium towards the transfer of $H_2ZnCl_4 \cdot 2TBP$.

4. MATHEMATICAL MODEL

Transfer of zinc(II) and HCl from water to organic phase in the Lewis cell can be described by the following set of differential equations with initial conditions:

Concentration of zinc(II) in aqueous phase

$$V_\mathrm{w}\frac{dC_\mathrm{Zn,w}(t)}{dt} = -k_\mathrm{Zn}F\left(C_\mathrm{Zn,w}(t) - \frac{C_\mathrm{Zn,o}(t)}{D_\mathrm{Zn}(C_\mathrm{Zn,w}, C_\mathrm{HCl,w})}\right). \tag{8}$$

Concentration of zinc(II) in organic phase

$$V_\mathrm{o}\frac{dC_\mathrm{Zn,o}(t)}{dt} = k_\mathrm{Zn}F\left(C_\mathrm{Zn,w}(t) - \frac{C_\mathrm{Zn,o}(t)}{D_\mathrm{Zn}(C_\mathrm{Zn,w}, C_\mathrm{HCl,w})}\right). \tag{9}$$

Concentration of HCl in aqueous phase

$$V_{\mathrm{w}}\frac{dC_{\mathrm{HCl,w}}(t)}{dt}=-k_{\mathrm{HCl}}F\left(C_{\mathrm{HCl,w}}(t)-\frac{C_{\mathrm{HCl,o}}(t)}{D_{\mathrm{HCl}}(C_{\mathrm{Zn,w}},C_{\mathrm{HCl,w}})}\right). \tag{10}$$

Concentration of HCl in organic phase

$$V_{\mathrm{o}}\frac{dC_{\mathrm{HCl,o}}(t)}{dt}=k_{\mathrm{HCl}}F\left(C_{\mathrm{HCl,w}}(t)-\frac{C_{\mathrm{HCl,o}}(t)}{D_{\mathrm{HCl}}(C_{\mathrm{Zn,w}},C_{\mathrm{HCl,w}})}\right). \tag{11}$$

Initial conditions

$$C_{\mathrm{Zn,w}}(0)=C^{0}_{\mathrm{Zn,w}},\quad C_{\mathrm{Zn,o}}(0)=C^{0}_{\mathrm{Zn,o}},\quad C_{\mathrm{HCl,w}}(0)=C^{0}_{\mathrm{HCl,w}},\quad C_{\mathrm{HCl,w}}(0)=C^{0}_{\mathrm{HCl,w}},$$

where C denotes the concentrations, D – the distribution coefficient, F – the mass transfer area, k – the mass transfer coefficient, V – the phase volume and t – the time. Subscripts "o" and "w" denote organic and aqueous phases, respectively. Superscript "0" denotes an initial value. The same relationship can be written for other compounds. The above equations are coupled with parts concerning mass transfer between phases and also with distribution coefficients depending on the concentrations of zinc(II) and hydrochloride. In general, they cannot be solved analytically and numerical methods have to be used. However, assuming small changes of concentration during experiments, constant distribution coefficients can be used in calculations. In this case, analytical solution can be found:

$$C_{\mathrm{Zn,w}}(t)=\frac{C^{0}_{\mathrm{Zn,o}}V_{\mathrm{o}}+C^{0}_{\mathrm{Zn,w}}V_{\mathrm{w}}}{D_{\mathrm{Zn}}V_{\mathrm{o}}+V_{\mathrm{w}}}+\frac{V_{\mathrm{o}}(D_{\mathrm{Zn}}C^{0}_{\mathrm{Zn,w}}-C^{0}_{\mathrm{Zn,o}})}{D_{\mathrm{Zn}}V_{\mathrm{o}}+V_{\mathrm{w}}}\exp\left(-\frac{k_{\mathrm{Zn}}F(D_{\mathrm{Zn}}V_{\mathrm{o}}+V_{\mathrm{w}})}{D_{\mathrm{Zn}}V_{\mathrm{o}}V_{\mathrm{w}}}t\right), \tag{12}$$

$$C_{\mathrm{Zn,o}}(t)=\frac{D_{\mathrm{Zn}}(C^{0}_{\mathrm{Zn,o}}V_{\mathrm{o}}+C^{0}_{\mathrm{Zn,w}}V_{\mathrm{w}})}{D_{\mathrm{Zn}}V_{\mathrm{o}}+V_{\mathrm{w}}}-\frac{V_{\mathrm{w}}(D_{\mathrm{Zn}}C^{0}_{\mathrm{Zn,w}}-C^{0}_{\mathrm{Zn,o}})}{D_{\mathrm{Zn}}V_{\mathrm{o}}+V_{\mathrm{w}}}\exp\left(-\frac{k_{\mathrm{Zn}}F(D_{\mathrm{Zn}}V_{\mathrm{o}}+V_{\mathrm{w}})}{D_{\mathrm{Zn}}V_{\mathrm{o}}V_{\mathrm{w}}}t\right), \tag{13}$$

$$C_{\mathrm{HCl,w}}(t)=\frac{C^{0}_{\mathrm{HCl,o}}V_{\mathrm{o}}+C^{0}_{\mathrm{HCl,w}}V_{\mathrm{w}}}{D_{\mathrm{HCl}}V_{\mathrm{o}}+V_{\mathrm{w}}}+\frac{V_{\mathrm{o}}(D_{\mathrm{HCl}}C^{0}_{\mathrm{HCl,w}}-C^{0}_{\mathrm{HCl,o}})}{D_{\mathrm{HCl}}V_{\mathrm{o}}+V_{\mathrm{w}}}\exp\left(-\frac{k_{\mathrm{HCl}}F(D_{\mathrm{HCl}}V_{\mathrm{o}}+V_{\mathrm{w}})}{D_{\mathrm{HCl}}V_{\mathrm{o}}V_{\mathrm{w}}}t\right), \tag{14}$$

$$C_{\mathrm{HCl,o}}(t)=\frac{D_{\mathrm{HCl}}(C^{0}_{\mathrm{HCl,o}}V_{\mathrm{o}}+C^{0}_{\mathrm{HCl,w}}V_{\mathrm{w}})}{D_{\mathrm{HCl}}V_{\mathrm{o}}+V_{\mathrm{w}}}-\frac{V_{\mathrm{w}}(D_{\mathrm{HCl}}C^{0}_{\mathrm{HCl,w}}-C^{0}_{\mathrm{HCl,o}})}{D_{\mathrm{HCl}}V_{\mathrm{o}}+V_{\mathrm{w}}}\exp\left(-\frac{k_{\mathrm{HCl}}F(D_{\mathrm{HCl}}V_{\mathrm{o}}+V_{\mathrm{w}})}{D_{\mathrm{HCl}}V_{\mathrm{o}}V_{\mathrm{w}}}t\right). \tag{15}$$

In the case of equal volumes of phases ($V_{\mathrm{w}}=V_{\mathrm{o}}$) and initial concentrations in organic phase equal zero ($C_{\mathrm{Zn,o}}(0)=0$, $C_{\mathrm{HCl,o}}(0)=0$), equations (12)–(15) can be simplified as follows:

$$C_{\mathrm{Zn,w}}(t)=\frac{C^0_{\mathrm{Zn,w}}}{D_{\mathrm{Zn}}+1}+\frac{D_{\mathrm{Zn}}C^0_{\mathrm{Zn,w}}}{D_{\mathrm{Zn}}+1}\exp\left(-\frac{k_{\mathrm{Zn}}F(D_{\mathrm{Zn}}+1)}{D_{\mathrm{Zn}}V}t\right), \tag{16}$$

$$C_{\mathrm{Zn,o}}(t)=\frac{D_{\mathrm{Zn}}C^0_{\mathrm{Zn,w}}}{D_{\mathrm{Zn}}+1}-\frac{D_{\mathrm{Zn}}C^0_{\mathrm{Zn,w}}}{D_{\mathrm{Zn}}+1}\exp\left(-\frac{k_{\mathrm{Zn}}F(D_{\mathrm{Zn}}+1)}{D_{\mathrm{Zn}}V}t\right), \tag{17}$$

$$C_{\mathrm{HCl,w}}(t)=\frac{C^0_{\mathrm{HCl,w}}}{D_{\mathrm{HCl}}+1}+\frac{D_{\mathrm{HCl}}C^0_{\mathrm{HCl,w}}}{D_{\mathrm{HCl}}+1}\exp\left(-\frac{k_{\mathrm{HCl}}F(D_{\mathrm{HCl}}+1)}{D_{\mathrm{HCl}}V}t\right), \tag{18}$$

$$C_{\mathrm{HCl,o}}(t)=\frac{D_{\mathrm{HCl}}C^0_{\mathrm{HCl,w}}}{D_{\mathrm{HCl}}+1}-\frac{D_{\mathrm{HCl}}C^0_{\mathrm{HCl,w}}}{D_{\mathrm{HCl}}+1}\exp\left(-\frac{k_{\mathrm{HCl}}F(D_{\mathrm{HCl}}+1)}{D_{\mathrm{HCl}}V}t\right). \tag{19}$$

The solutions obtained are the basis for calculation of mass transfer coefficients by fitting the theoretical predictions to experimental data. The method of least square roots was used in calculations.

The flux j of transferred compounds is expressed by:

$$j=\frac{V}{F}\frac{dC_0}{dt}. \tag{20}$$

For solutions obtained for organic phase (equations (17) and (19)) the flux of mass transfer is described by equation (21):

$$j=k\cdot C^0_{\mathrm{w}}\exp\left(-\frac{kF(D+1)}{DV}t\right) \tag{21}$$

and the ratio of fluxes of various compounds is equal to:

$$\frac{j_1}{j_2}=\frac{C^0_{\mathrm{w,1}}k_1}{C^0_{\mathrm{w,2}}k_2}\exp\left[\frac{F}{V}\left(k_2\frac{D_2+1}{D_2}-k_1\frac{D_1+1}{D_1}\right)t\right]. \tag{22}$$

The overall mass transfer coefficients calculated from experimental data for constant mixing rate in aqueous phase and variable mixing rate in organic phase are presented in table 3. The values obtained support the hypothesis that the main resistance to the transport of the bulky complex is in the organic phase. Some examples of zinc(II) concentration profiles versus time at various mixing rates and various TBP concentration are presented in figures 2 and 3, respectively. Good agreement was obtained between experimental and calculated concentrations. Figure 4 shows the ratio of the flux of zinc(II) to the flux of complexed chloride $j_{\mathrm{Zn}}/j_{\mathrm{Cl}}$ transferred to the organic phase versus time. The initial ratio ranges from 0.35 to 0.4 and its change with time depends on the mixing rate. The theoretical ratios of the fluxes equivalent to the transfer of the following complexes: $\mathrm{ZnCl_2\cdot 2TBP}$, $\mathrm{HZnCl_3\cdot 3TBP}$ and $\mathrm{H_2ZnCl_4\cdot 2TBP}$ amount to 0.5, 0.33 and

0.25, respectively. The results prove that two or more complexes are transferred to the organic phase. It is also possible that the mechanism of mass transfer changes during the process. In the initial period of the process, the most probable is the equimolar transfer of $ZnCl_2 \cdot 2TBP$ and $H_2ZnCl_4 \cdot 2TBP$.

Table 3

Mass transfer coefficient for zinc(II) extraction (mixing rate in aqueous phase equal to 120 rpm)

TBP concentration [%vol]	Mixing rate in the organic phase [rpm]	Mass transfer coefficients [m/s]$\cdot 10^3$
100	80	0.20
	120	0.47
	160	0.90
	200	0.99
80	80	0.19
	120	0.35
	160	0.61
	200	0.80
60	80	0.12
	120	0.19
	160	0.54
	200	0.61

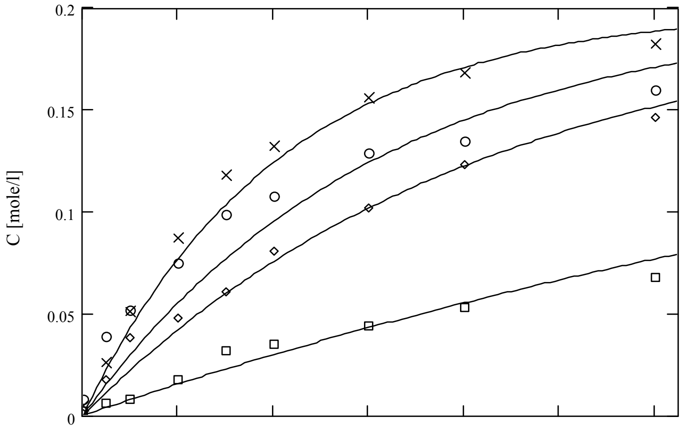

Fig. 2. Zinc(II) concentrations in an organic phase as a function of time for 100% TBP at a constant mixing rate in an aqueous phase (120 rpm) and different mixing rates in an organic phase (□ – 80 rpm, ◊ – 120 rpm, ○ – 160 rpm, × – 200 rpm, solid line – calculated values, symbols – experimental data)

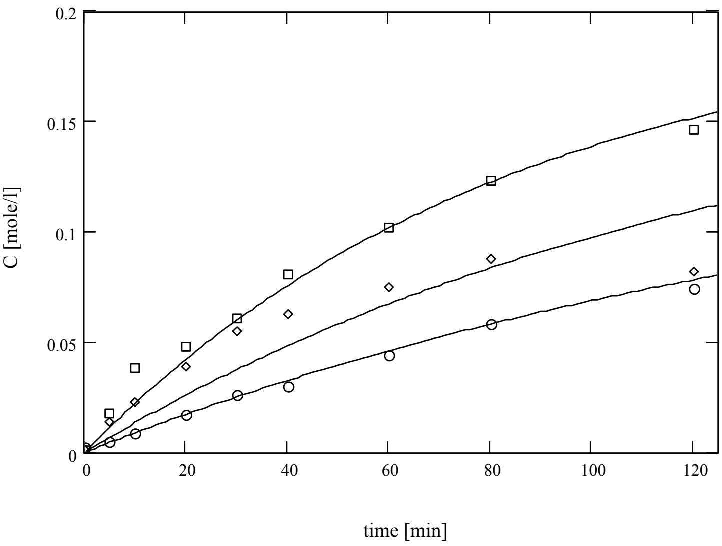

Fig. 3. Zinc(II) concentrations in an organic phase as a function of time at a constant mixing rate in an aqueous phase and organic phase (120 rpm) for different TBP concentrations (□ – 100%, ◊ – 80%, ○ – 60%, solid line – calculated values, symbols – experimental data)

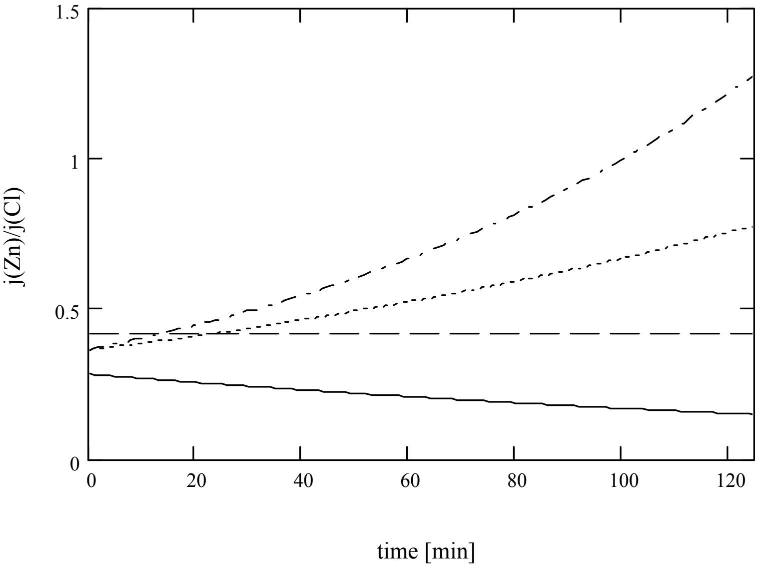

Fig. 4. Ratio of the flux of zinc(II) to the flux of complexed chloride transferred to an organic phase at different mixing rates (—— 80 rpm, ... 120 rpm, — — 160 rpm, — · — 200 rpm)

5. CONCLUSION

A mathematical model of extraction of zinc(II) with tributyl phosphate (TBP) in the Lewis cell was designed and discussed. Overall mass transfer coefficients calculated by fitting the model to experimental data suggest that the organic phase is strongly resistant to the mass transfer. An initial ratio of the flux of zinc(II) to the flux of complexed chloride transferred to the organic phase supports the hypothesis that in the first phase of the process the most probable is the equimolar transfer of $ZnCl_2 \cdot 2TBP$ and $H_2ZnCl_4 \cdot 2TBP$. For longer periods the situation is more complicated and requires further investigations.

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