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

Extraction of zinc(II) from model hydrochloric acid solutions was studied in Lewis cell mixing the bulks of both phases and keeping a stable interfacial surface. It was found that Lewis cell experiments, although dynamic in nature, support the extracting of $ZnCl_2 \cdot 2$ TBP chlorocomplex from model solutions containing 5 M Cl^- and 0,55 M H^+. 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 upon the mixing rates than the transfer of bulky zinc(II) chlorocomplex.

Key words: extraction, zinc(II), hot-dip galvanising, Lewis cell

INTRODUCTION

Hot-dip zinc galvanising 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 most often used method to process such solutions. However, the method can not be used 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.

Solvent extraction is one of different techniques which can be used to recover zinc(II) from such solutions [Schügerl et al., 1996; Bart, 2000]. Tributyl phosphate (TBP) is the most suitable reagent and enables both the effective extraction of zinc(II) from HCl solutions and subsequent stripping with water [Regel et al., 2001, Tórz et al., 2002]. However, iron(III) is strongly co-extracted and must be reduced to iron(II)

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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 published works was limited only to equilibrium studies [Navratil, 1987].

The aim of the work was to study the kinetics of zinc(II) extraction from model HCl solutions with TBP. A Lewis cell was used as a contractor. The intensive mixing of both phases enabled 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.

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 (Fig. 1) elaborated by Plucinski and Nitsch [1992]. The volumes of each phase were equal to 95 cm³. The interfacial surface area was 16.56 cm². 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.
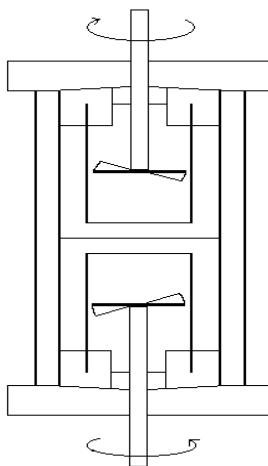

Fig. 1. Scheme of Lewis cell

One cm³ samples of the organic phase were taken at appropriate periods of time and stripped with 10 cm³ water. Samples of fresh TBP solution (1 cm³) 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 contents 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 reflecting the presence of zinc chlorocomplexes considered as 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 previous work [Cierpieszewski et al., 2002, Kirschling et al., 2001]. All experiments were carried out at room temperature.

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

RESULTS AND DISCUSSION

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. The composition of the aqueous phase does not change significantly in the Lewis cell experiments. However, the effect must be taken into account in classical counter-current extraction.

The precision of considered species determination is good. The confidence limits at significance level of 0.05 calculated from 10 independent measurements are equal to ±0.026 mg/dm^3, ±0.003 M; ±0.003 M, ±0.004 M, ±0.053% for zinc(II), HCl, Cl$^-$, chloride present in the complex and water, respectively.

In equilibrium TBP extracts better Zn(II) than HCl (Table 1). However, at least 80% TBP must be used to obtain an effective extraction of zinc(II).

Table 1. Distribution coefficients for the extraction of Zn(II), HCl and Cl$^-$ and the conten t of water in TBP phase in equilibrium

TBP concentration	Zn(II)	HCl	Cl$^-$	H$_2$O [%]
% vol	-	-	-	-
50	0.56	0.17	0.07	1.88
60	0.95	0.21	0.09	2.43
70	1.08	0.26	0.10	3.09
80	1.74	0.40	0.12	3.88
90	2.33	0.48	0.13	5.03
100	3.33	0.58	0.15	5.29

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 to TBP also increases in the same order and amounts 0.56, 0.60, 0.65, 0.72, 0.83, 0.78 for 50, 60, 70, 80, 90 and 100% TBP, respectively.

The concentration of zinc(II) in the TBP phase increases with time and with an increased mixing rate (Fig. 2). A strong blocking of the interface connected with the stop of zinc(II) transfer is not observed in the Lewis cell, even when in some cases the system is near equilibrium after 2 hours of experiments (Table 2). As a result, the period of 20 minutes was arbitrary chosen to determine the "initial fluxes" *j* defined as

$$j = \left(\frac{V}{A}\right) * \left(\frac{\Delta c}{\Delta t}\right), \tag{1}$$

where *V* denotes the volume of the organic phase, *A* stands for the interfacial surface area and Δc denotes the change of concentration in the organic phase for $\Delta t = 20$ minutes (c=0 for t=0). After 20 minutes of the process the transfer of zinc(II) is in the range usually below 20% of the equilibrium value, for low mixing rates (80 rpm). However, the process of zinc(II) extraction increases with MR increase even up to 50% for 200 rpm. The conclusion is also valid for the transfer of HCl and water to the TBP phase (Table 2). The transfer was decreased below 30% for Δt= 10 minutes.
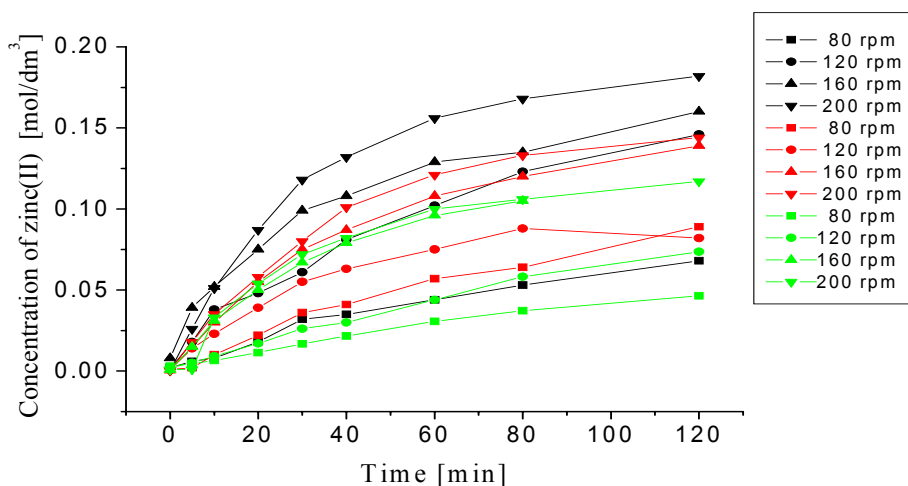

Fig. 2. Change of zinc(II) concentration in the organic phase for the constant rate mixing in the aqueous phase (MR$_w$=120 rpm) and different mixing rates in the organic phase (■ 80 rpm, ● 120 rpm, ▲ 160 rpm,▼ 200 rpm) and various contents of TBP (– – – 60 %, – – – 80 %, ——— 100%)

Table 2. Progress of zinc(II) extraction in the Lewis cell after 10, 20 and 120 minutes in respect with equilibrium (EP_{10}, EP_{20} and EP_{120}, respectively)

TBP concentration	Constant rate mixing (120 rpm) in							
	Aqueous phase				TBP phase			
	MR_O	EP_{10}	EP_{20}	EP_{120}	MR_W	EP_{10}	EP_{20}	EP_{120}
% vol	rpm	%	%	%	rpm	%	%	%
60	80	4.49	7.81	29.83	80	12.04	13.41	68.81
	120	6.26	20.93	63.54	120	6.26	20.93	63.54
	160	21.50	32.60	69.94	160	21.59	40.98	79.27
	200	22.89	38.12	79.49	200	28.07	45.05	71.59
80	80	5.01	12.00	47.40	80	8.69	16.76	71.78
	120	12.07	20.94	43.77	120	12.07	20.94	43.77
	160	15.87	29.37	74.46	160	23.94	41.67	93.34
	200	18.78	30.75	77.01	200	23.15	39.79	85.64
100	80	3.47	7.86	31.98	80	6.26	21.78	68.69
	120	16.64	11.78	50.74	120	16.64	11.78	50.74
	160	22.78	34.40	-	160	17.42	35.82	76.06
	200	22.18	36.99	80.78	200	22.53	48.91	78.93

Subscript ''o'' and ''w'' denote the organic and aqueous phase, respectively.

The effect of the mixing rate upon the "initial" fluxes of zinc(II), HCl, chloride present in the complex and water are shown in Figs 3-6. The results indicate that the transfer of considered components increases generally with an increase of TBP concentration. An atypical change of flux is only observed for zinc(II) and for low mixing rate. It can be caused by an experimental error but it can also reflect some blocking of the interface by the bulky chlorocomplex $ZnCl_2·2TBP$, which is probably formed at the aqueous side of the interface or near its venicity

$$ZnCl_4^{2-} + 2TBP = ZnCl_2·2TBP + 2Cl^- \qquad (2)$$
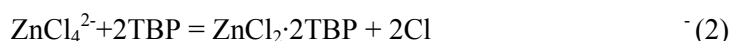
and then slowly transferred to the organic phase. By analogy to the formation of $ZnCl_2·2TBP$ complex given by Morris and Short [1962] and interfacial reactions of Cu(II) with hydroxyoximes [Szymanowski, 1993] the reaction can be described according to the scheme given in Fig. 7. The alternative version should take into account the protonation of TBP with HCl, i. e. the formation of intermediate $(BuO)_3P=O ••• HCl$.

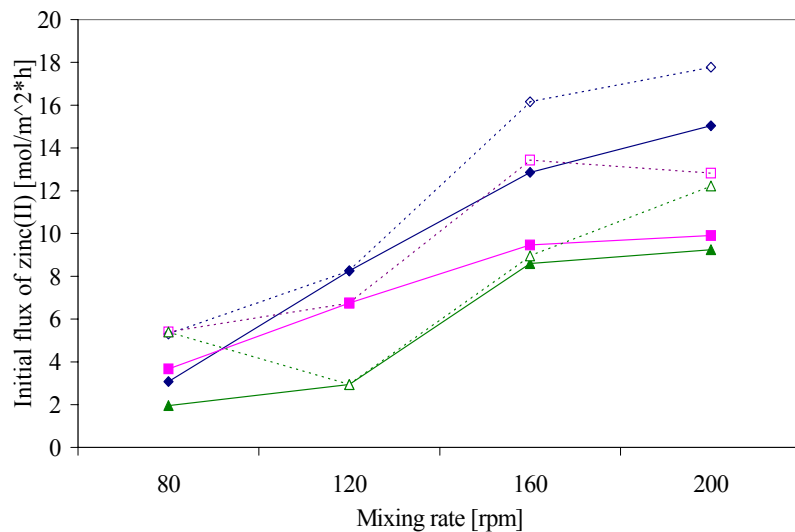*J. Niemczewska, R. Cierpiszewski, J. Szymanowski*

Fig. 3. Effect of mixing rate and TBP concentration upon the "initial flux" of zinc(II) (▲,△, 60% TBP; ■,▢, 80% TBP; ♦,◇, 100% TBP; full points, RM_w = 120 rpm; empty points RM_o= 120 rpm)
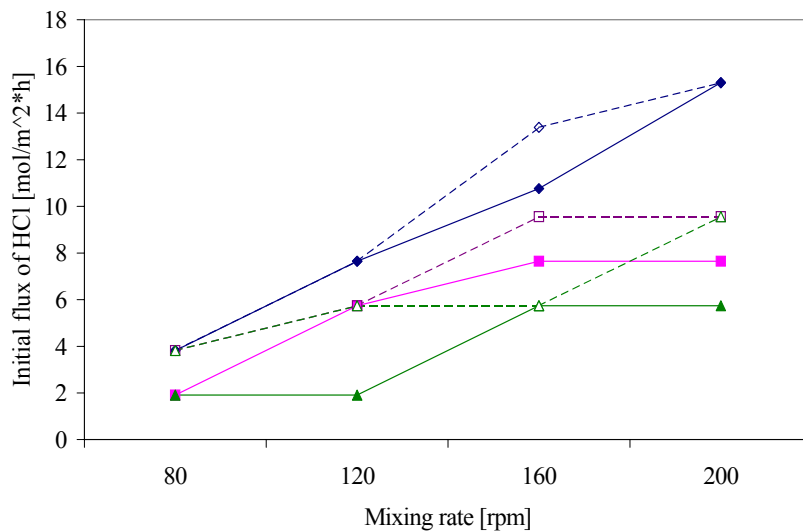

Fig. 4. Effect of mixing rate and TBP concentration upon the "initial flux" of HCl (▲,Δ, 60% TBP; ■,□, 80% TBP; ♦,◇, 100% TBP; full points, RM_w = 120 rpm; empty points, RM_o= 120 rpm)
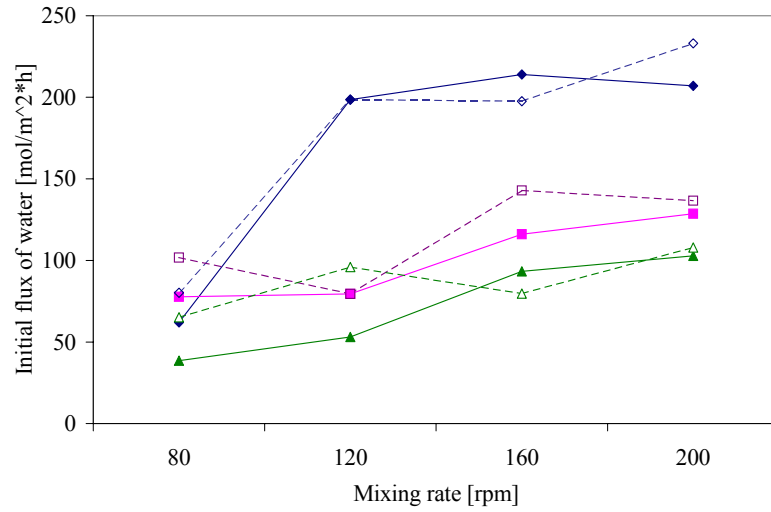
Fig. 5. Effect of mixing rate and TBP concentration upon the "initial flux" of water (▲,Δ, 60% TBP; ■,□, 80% TBP; ♦,◊, 100% TBP; full points, RM_w = 120 rpm; empty points, RM_o= 120 rpm)
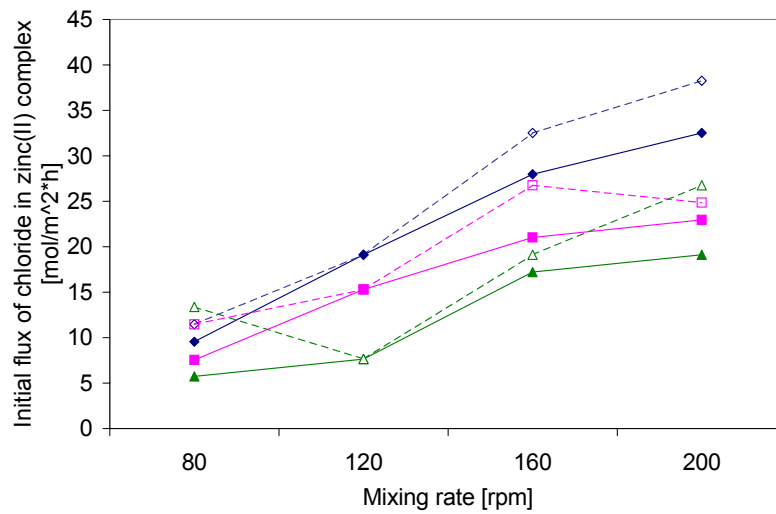

Fig. 6. Effect of mixing rate and TBP concentration upon the initial flux of chloride present in zinc(II) complex (▲,Δ, 60% TBP; ■,□, 80% TBP; ♦,◊, 100% TBP; full points, RM_w = 120 rpm; empty points, RM_o = 120 rpm)

$ZnCl_2 \cdot 2TBP$ Organic phase

BuO   OBu OBu   BuO   OBu OBu   Organic interfacial
                                               layer

P   P   Interface

O   O   Aqueous interfacial
                                       layer

$ZnCl_4^{2-}$

2Cl$^-$ Aquoeus phase
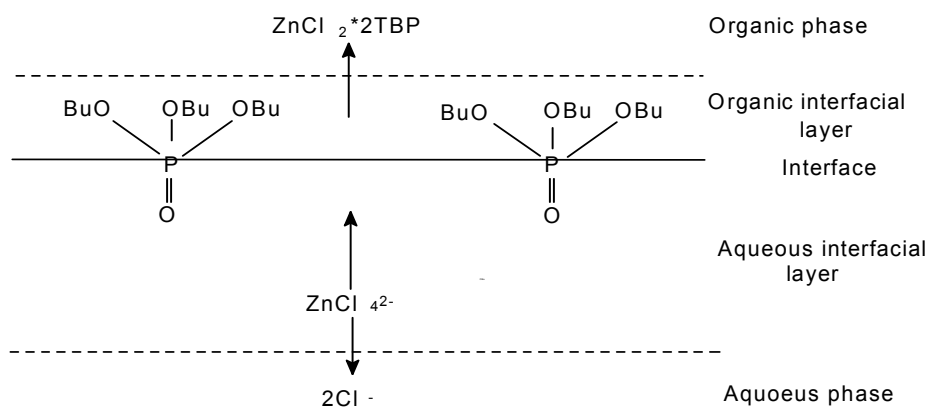
Fig. 7. Complexation of zinc(II) in the interfacial region

The extraction of $ZnCl_2 \cdot 2TBP$ complex is supported by the ratio of initial fluxes R_{20} determined for the transport of zinc(II) and chlorides present in zinc(II) complex considered as a weak acid and characterised by the equivalent point in potentiometric titration at pH about 9 (Table 3). The ratio is near to the theoretical value (0.5 mol/mol) for $ZnCl_2 \cdot 2TBP$ complex, having the values of confidence limits equal to 0.43 ± 0.03 and 0.46 ± 0.02 for the constant mixing rates (120 rpm) in the aqueous and organic phase, respectively. A similar ratio (0.45 mol/mol) was obtained from equilibrium extraction data. Thus, the Lewis cell kinetic experiments give additional support for the extraction of the complex $ZnCl_2 \cdot 2TBP$, although zinc(II) is almost qualitatively present in the aqueous phase in the form of anion chlorocomplexes.

Generally, an increase of the mixing rate causes an increase of the fluxes. However, the character of this relationship is different for considered components and TBP concentrations.

Approximately constant fluxes for zinc(II), HCl and chloride ions present in extracted chlorocomplexes are obtained for high mixing rates, i.e. 170-200 rpm, suggesting the elimination of the diffusion resistance in the mixed phase upon the mass transfer of the total process. The plateau region increases for the transport of water and approximately constant fluxes are obtained for the mixing rates changed from 110 to 200 rpm. In the used Lewis cell it is impossible to increase the rate of mixing above 200 rpm because the interface becomes unstable and/or vertex is formed. As a result, a sharp increase of the flux calculated with assumption of the constant interfacial surface area is observed.

Table 3. Ratios of initial fluxes (R_{20}) of zinc(II) determined by atomic absorption and chlorides complexed with zinc(II) determined by potentiometric titration

TBP concentration	MR_W = 120 rpm		MR_O = 120 rpm	
	MR_O	R_{20}	MR_W	R_{20}
% vol	rpm	mole Zn(II)/mole Cl$^-$	rpm	mole Zn(II)/mole Cl$^-$
60	80	0.34	80	0.40
	120	0.39	120	0.39
	160	0.50	160	0.47
	200	0.48	200	0.46
80	80	0.51	80	0.47
	120	0.44	120	0.43
	160	0.45	160	0.50
	200	0.43	200	0.52
100	80	0.32	80	0.46
	120	0.43	120	0.43
	160	0.46	160	0.50
	200	0.46	200	0.46
Confidence limits (α=0,05)		0.43±0.03		0.46±0.02
		0.46±0.02*		

* - after rejection of ratios below 0.40

The observed effects are in a good agreement with the discussed extraction mechanism. The transfer of the zinc(II) complex can depend not only upon the both diffusion steps but also upon the chemical reaction giving an addition interfacial resistance. Contrary, the transfer of water can be considered as physical extraction. Moreover, the water transfer should be rather limited by the diffusion step in the organic phase. One can also expect a higher diffusion resistance in the organic phase in comparison to the aqueous phase for the transfer of bulky zinc(II) chlorocomplex. The hypothesis finds support in experimental data presented in Table 4. An increase of the mixing rate in the organic phase has always a stronger positive effect than MR increase in the aqueous phase.

Table 4. Effect of mixing rate from 80 to 200 rpm upon initial fluxes' ratios j_{200}/j_{80} at constant mixing rate in the second phase for Zn(II), complexed Cl^-, HCl and water

TBP concentration	MR_w or MR_w	Zn(II)	Cl^- in complex	HCl	H_2O
% vol	rpm	-	-	-	-
60	$MR_w =120$	4.71	3.33	3.00	2.67
	$MR_o =120$	2.25	1.99	2.45	1.65
80	$MR_w =120$	2.56	3.03	4.00	1.66
	$MR_o =120$	2.37	2.17	2.50	1.34
100	$MR_w =120$	4.88	3.40	4.00	3.34
	$MR_o =120$	3.35	3.33	4.00	2.91

REFERENCES

BART H. J. (2000), *Reactive Extraction*, Springer, Berlin.

CIERPISZEWSKI R., MIESIĄC I., REGEL-ROSOCKA M., SASTRE A. M., SZYMANOWSKI J. (2002), *Removal of Zinc(II) from Spent Hydrochloric Acid Solutions from Zinc Hot Galvanazing Plants,* Ind. Chem. Eng. Res., Vol. 41, pp 598-603.

KIRSCHLING P., NOWAK K.,MIESIĄC I., NITSH W., SZYMANOWSKI J. (2001), *Membrane Extraction-Stripping Process for Zinc(II) Recovery from HCl Solution,* Solvent Extr. Res. Dev.., Jpn, Vol. 8, pp. 135-143.

MORRIS D. C. F., SHORT E. L. (1962), *Zinc Chloride and Zinc Bromide Complexes. Part II. Solvent-Extraction Studies with Zinc – 65 as Tracer,* J. Chem. Soc., pp 2662-2671.

NAVRATIL J. M., Handbook *Science and Technology of Tributyl Phosphate,* CRC Press. Inc. Boca Raton, Florida 1987.

PLUCINSKI P., NITSCH W. (1992), *Two Phases Kinetics of the Solubilization in Reversed Micelles,* Solvent Extraction, pp. 847-852, Elsevier Science Publishers BV.

PUIGDOMENECH I., *Medusa,* Royal Institute of Technology, Sweden.

REGEL M., SASTRE A. M., SZYMANOWSKI J.(2001), *Recovery of Zinc(II) from HCl Spent Pickling Solutions by Solvent Extraction,* Environ. Sci. Technol., Vol. 35, pp. 630-635.

SCHÜGERL K., LARM A., GUDORF M. (1996), *Recovery of Zinc from Zinc Mordant Solutions of Dovetail Plants,* ISEC Melboune Australia, pp. 1543-1547.

SZYMANOWSKI J. (1993), *Hydroxyoximes and Copper Hydrometallurgy*, CRC Press, Boca Raton, USA.

TÓRZ M., ALEJSKI K., SZYMANOWSKI J.(2002), *Recovery of zinc(II) from model hydrochloric acid solutions in hollow fibre modules,* Phycochem. Prob. Mineral. Process., Vol. 36, pp 101-113.

Niemczewska J., Cierpiszewski R., Szymanowski J., *Ekstrakcja cynku(II) z modelowych roztworów HCl w komórce Lewisa,* Physicochemical Problems of Mineral Processing 37 (2003) 87-96 (w jęz. ang.).

W pracy badano ekstrakcję cynku(II) fosforanem tributylu (TBP) z modelowych roztworów HCl. Stosowano komórkę Lewisa z mieszaniem obu faz przy stabilnej granicy międzyfazowej. Stwierdzono, że eksperymenty w komórce Lewisa, chociaż dynamiczne w naturze, potwierdzają ekstrakcję chlorokompleksu $ZnCl_2·2TBP$ z roztworów modelowych zawierających 5 M Cl^- i 0,55 M H^+. Początkowe strumienie Zn(II), HCl, Cl^-, chlorków zawartych w kompleksie cynku oraz wody zależą od stężenia TBP oraz szybkości mieszania faz. Etap dyfuzji w fazie organicznej daje większy opór od etapu dyfuzji w fazie wodnej. Fizyczne przeniesienie małych cząsteczek wody jest mniej wrażliwe na szybkość mieszania od przeniesienia przestrzennego dużego chlorokompleksu cynku(II).