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Magdalena BARTKOWSKA, Magdalena REGEL-ROSOCKA, Jan SZYMANOWSKI*

EXTRACTION OF ZINC(II), IRON(III) AND IRON(II) WITH BINARY MIXTURES CONTAINING TRIBUTYL PHOSPHATE AND DI(2-ETHYLHEXYL)PHOSPHORIC ACID OR CYANEX 302

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The extraction of zinc(II), iron(III) and iron(II) with TBP and its binary mixtures with DEHPA and CYANEX 302 from hydrochloric acid solutions was studied. It was found that the extraction ability of zinc(II) chlorocomplexes from hydrochloric acid solutions decreased in the order: TBP > TBP:HL=3:1 vol/vol > TBP:HL=1:1 vol/vol. Iron(III) was strongly extracted by TBP and its binary mixtures with DEHPA and CYANEX 302, and the extraction fell in the order: binary mixtures with DEHPA or CYANEX 302> TBP> DEHPA >> CYANEX 302. Iron(II) was not extracted by the considered extractants. Zinc(II) could not be selectively extracted in the presence of iron(III). Contrary, iron(III) could be selectively extracted, especially with the binary 1:1 vol/vol mixtures of TBP with DEHPA or CYANEX 302. The stripping of zinc(II) could be accomplished in three successive stages using water and 0.1 M H_2SO_4. Iron(III) could be stripped in three stages with 0.1 M H_2SO_4.

Key words: extraction, zinc(II), iron(III), iron(II), tributyl phosphate, di(2ethylhexyl)phosphoric acid, CYANEX 302.

INTRODUCTION

Metallic coating (mainly with zinc) is nowadays a principal technique used to improve the corrosion resistance of various types of steel. Typically more than 50% of common automobile body sheets are metallically coated today.

Hot-dip galvanizing in 96.5-99% purity zinc, carried out at 445-465°C (Maass, 1998), needs the pure surface of iron goods. The rust is removed by the pickling with 20% HCl carried out at room temperature. As a result, the concentration of

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[*]Poznan University of Technology, Institute of Chemical Technology and Engineering
Pl. M. Sklodowskiej-Curie 2, 60-965 Poznan, Poland, e-mail: jan.szymanowski@put.poznan.pl

hydrochloric acid decreases and accumulation of iron ions (90% as Fe(II)) occurs. When pickled goods are housed on recycled hooks, i.e., covered in previous process with zinc, an accumulation of zinc(II) in the pickling solution is also observed.

The presence of zinc(II) causes technological problems in the Ruthner process (OSKO, Austria) used to regenerate the spent pickling solutions (Winkel, 1986). Metallic zinc evaporates and glues to the walls of installation at high temperatures used in the process (800°C).

We found in our recent work (Regel et al. 2001, Wojtaszak et al. 2000, Kirschling et al. 2001, Cierpiszewski et al. 2002, Regel-Rosocka et al. 2002) that zinc(II) can be recovered by extraction with various solvating and basic extractants, including tributyl phosphate (TBP), trialkylphosphine oxides and alkylamines. However, the effective stripping was only possible when TBP was used.

The main drawback of the extraction with TBP is the strong extraction of iron(III). The aim of this work was to study the effect of acidic extractants (di(2-ethylhexyl)phosphoric acid – DEHPA and bis(2, 4, 4-trimethylpentyl)monotio-phosphinic acid – CYANEX 302) on extraction of zinc(II) from 10% HCl with TBP. Both these acidic extractants are used for zinc(II) recovery from acidic sulfate solutions (Bart, 2000, Alguacil et al. 1992). CYANEX 302 shows good selectivity of zinc(II) extraction with respect to iron(III) at pH below 1. However, it is impossible to predict a priori the extraction of zinc(II) from hydrochloric acid solutions with binary mixtures containing TBP and DEHPA or CYANEX 302.

EXPERIMENTAL

Tributyl phosphate (Merck, Germany), di(2-ethylhexyl)phosphoric acid (Merck, Germany) and CYANEX 302 (Cytec, Canada) were used as extractants. All these reagents were used as delivered without any purification and without dilution with any solvent. Undiluted TBP and binary mixtures of TBP with DEHPA or CYANEX 302 (3:1 or 1:1 vol/vol) were used.

Extraction was carried out in a small scale using 10 ml volumes of phases at the volume ratio equal to 1. Phases were mechanically shaken for 10 minutes and left for phase separation. The aqueous feed used for the determination of extraction isotherms contained 56.88 g/L Zn(II), or 50 g/L Fe(II) or 30 g/L Fe(III) and 3.26 M (10%) HCl. The chloride concentration adjusted with NaCl (POCh, Poland) was equal to 5 M in the initial aqueous feed. The separated aqueous phase (raffinate) was extracted with a new portion of extractants, always at the volume ratio equal to 1. The extractions were repeated several times.

Concentrations of zinc(II) in the aqueous phase were determined by titration with 0.05 M EDTA using PAN as an indicator. Iron concentrations were determined by titration with 0.1 M K_2CrO_7 in the presence of diphenylamine-4-sulphonic acid.

RESULTS AND DISCUSSION

In the considered system of high chloride concentration, metal ions were mainly in the form of chlorocomplexes:

$$M^{n+} + i\ Cl^{-} = MCl_i^{n-i} \qquad (1)$$

where i = 1, 2, 3 and 4. Knowing the chlorocomplex formation constants, it was possible to calculate the content of each species present in the aqueous phase. However, β values were very sensitive for ionic strength and the constants were mainly determined for diluted solutions of relatively low ionic strength.

The computer program Medusa (Puigdomenech) was used to estimate roughly the distribution of various chlorocomplexes. The computing showed that in the initial aqueous feed iron(II) was present in comparable amounts in the form of Fe^{2+} and $FeCl^{+}$ (Table 1). Iron(III) was distributed between $FeCl_2^{+}$, $FeCl_3$, $FeCl^{2+}$ and Fe^{3+} given in the order of decreasing content. However, in spectra of aqueous ferric chloride solutions in hydrochloric acid, the absorption at 335 nm appears in 2-4 M HCl, and then the absorption bands at 245, 316 and 364 nm appear gradually with increasing acid concentration. These absorptions are due to $FeCl_4^{-}$ (Cotton and Wilkins, 1988, Sato et al 2002.). Over 80% of zinc was in the form of $ZnCl_4^{2-}$, and only few percents existed as $ZnCl_3^{-}$. However, the concentration of chloride ions and ionic strength were lower in each successive extraction step, especially in extraction of Zn(II) and Fe(III). Thus, the equilibrium was shifted towards lower chlorocomplexes.

Table 1. Estimated distribution of metal species in the aqueous phase

[M^{n+}] M	[Cl^{-}] M	Ionic strength M	Mole fraction				
Zn(II)			Zn^{2+}	$ZnCl^{+}$	$ZnCl_2$	$ZnCl_3^{-}$	$ZnCl_4^{2-}$
0.84	5	5.84	0.03	-	0.05	0.09	0.81
0.65	4	4.69	0.06	0.03	0.06	0.11	0.73
0.40	3	3.40	0.11	0.07	0.05	0.13	0.64
0.15	2	2.00	0.19	0.09	0.08	0.14	0.49
Fe(III)			Fe^{3+}	$FeCl^{2+}$	$FeCl_2^{+}$	$FeCl_3$	$FeCl_4^{-}$
0.54	5	6.72	0.06	0.20	0.46	0.27	-
0.39	4	5.21	0.1	0.27	0.42	0.16	-
0.24	3.3	4.01	0.13	0.31	0.45	0.10	-
0.09	2.5	2.76	0.17	0.36	0.41	0.06	-
Fe(II)			Fe^{2+}	$FeCl^{+}$	-	-	-
0.90	5	5.93	0.56	0.44			

It was impossible to predict precisely the composition of the successive aqueous phases because the composition of the extracted complexes could change. If zinc(II) and iron(III) were extracted with TBP (S) according to the following equations (Morris and Short, 1962):

$$2H^{+}_{w} + ZnCl_4{}^{2-}{}_{w} + 2S_o = H_2ZnCl_4{\cdot}2S_o \tag{2}$$

$$H^{+}_{w} + Cl^{-}_{w} + FeCl_{3w} + 2S_o = HFeCl_4{\cdot}2S_o \tag{3}$$

then the total recovery of zinc(II) or iron(III) would give a decrease of chloride concentration equal to 3.36 and 2.16 M, respectively. The extraction of hydrochloric acid was relatively low and the concentration of hydrochloric acid in the organic phase did not exceed 0.1 M. The total decrease of HCl concentration would be 2.2 and 1 M for the extraction of zinc(II) and iron(III), respectively (e.g. 1.68 M with $H_2ZnCl_4{\cdot}2S$ and 0.5 M of free HCl in 5 successive extraction steps).

All these meant that in extraction with extractant binary mixtures (S and HL) the role of the acidic extractant (DEHPA and CYANEX 302) could increase in each successive step. Both these acidic reagents extracted cations of zinc according to the reaction (Alguacil et al. 1992):

$$(2+n)\ (HL)_{2\,o} + 2Zn^{2+}{}_{w} = (ZnL_2)_2\ .n(HL)_{2\,o} + 4H^{+}_{w} \tag{4}$$

where n=1 or 2.

When mixtures of two extractants were used then the mixed complexes could be formed. As a result, the ability and selectivity of extraction could be changed.

The isotherms of zinc(II) extraction presented in Fig. 1 indicated that an addition of acidic extractants to TBP decreased the extraction of zinc(II), especially strongly in the first four extraction steps in which the concentration of chloride in the aqueous feeds was high. The extraction ability decreased in the order: TBP > TBP:HL=3:1 vol/vol > TBP:HL=1:1 vol/vol. Both acidic extractants had similar effects and there was no statistical difference when 1:1 vol/vol mixtures of DEHPA or CYANEX 302 with TBP were used. A better performance of DEHPA was observed when the mixture of TBP:DEHPA=3:1 was used.

Iron(III) (Fig. 2) was better extracted than zinc(II). The isotherms were very steep and the concentration of iron(III) in the organic phase increased rapidly in the region of low equilibrium concentrations in the aqueous phase. An addition of acidic extractants to TBP had a significant effect on extraction of iron(III). The extraction ability of extractants changed in the order: binary mixtures with DEHPA or CYANEX 302> TBP> DEHPA >> CYANEX 302. The high extraction of iron(III) with acidic extractants, especially DEHPA, was in a good agreement with the computing results (Table 1) demonstrating high molar contribution of iron(III) cationic species extracted by the acidic extractants.

It is worth to mention here that the shapes of extraction isotherms given in this work (Figs. 1 and 2) were different in comparison to those presented in our previous works (Regel et al. 2001, Wojtaszak et al. 2000). The shape of isotherms depended upon the concentrations of Cl^- and HCl in aqueous feeds. In previous works these concentrations were kept constant, while in this work they changed in each successive step. The approach used in this work is more justified in design of the multistage counter-current process in which the concentrations also decrease in each successive step.

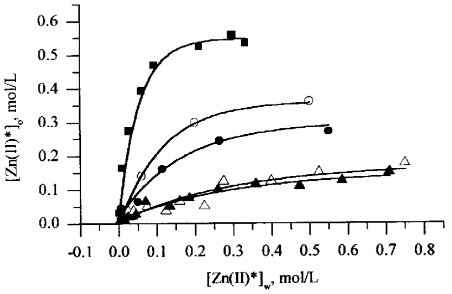

Fig. 1. Isotherms of zinc(II) extraction (■ – TBP; ○ – TBP:DEHPA=3:1 vol/vol; ● - TBP:Cyanex 302=3:1 vol/vol; Δ - TBP:DEHPA=1:1 vol/vol and ▲ - TBP:Cyanex 302=1:1 vol/vol).

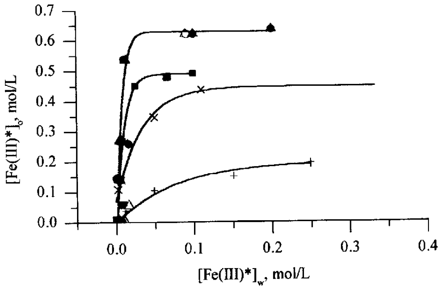

Fig. 2. Isotherms of iron(III) extraction (■ – TBP; ○ – TBP:DEHPA=3:1 vol/vol; ● - TBP:Cyanex 302=3:1 vol/vol; Δ - TBP:DEHPA=1:1 vol/vol; ▲ - TBP:Cyanex 302=1:1 vol/vol – each mixture gives approximately the same extraction of iron(III); x – DEHPA and + - Cyanex 302).

Iron(II) was only slightly extracted (Table 2). The concentration of iron(II) in the organic phase was below 0.6 g/L with the distribution coefficient equal to 0.01-0.03. The comparison of the distribution coefficients given in Table 2 could be only quantitative because they were determined at different locations on the extraction isotherms. However, it was obvious that iron(II) did not disturb the extraction of zinc(II). Thus, prior to extraction iron(III) must be reduced to iron(II). Selectivity of extraction can be characterized by the ratio of distribution coefficients:

$$S_{Zn(II)/Fe(III)} = \frac{D_{Zn(II)}}{D_{Fe(III)}} \tag{5}$$

Extraction isotherms were not linear and the distribution ratios depended upon the loading of the organic phase or the equilibrium concentrations of metal ions in the aqueous phase. Thus, the selectivity $S_{Zn(II)/Fe(III)}$ depended also on the equilibrium contents of metal species (Fig. 3). The obtained results indicated that $S_{Zn(II)/Fe(III)}$ decreased in the same order as the extraction of zinc(II). Iron(III) could be extracted with the binary mixtures of extractants from solutions containing similar molar concentrations of zinc(II) and iron(III). The use of 1:1 vol/vol mixture was preferred.

The separation of iron(III) could be quantitative with an excess of the aqueous feed due to the crowd effect, i.e. when the organic phase was saturated with metal species and weaker complexes were replaced by the stronger ones. This selective extraction of iron(III) could be explained by the formation of mixed complexes composed from iron(III) di(2-ethylhexyl)phosphates solvated with TBP molecules.

Table 2. Distribution coefficients (56.88 g/L Zn(II), 50 g/L Fe(II) or 30 g/L Fe(III), 3.26 M HCl (10%) and $[Cl^-]$=5 M in the aqueous feed)

Extractant	$D_{Zn(II)}$	$D_{Fe(II)}$	$D_{Fe(III)}$
TBP	2.65	0.029	2.45
TBP:DEHPA = 3:1 vol/vol	1.50	0.014	3.16
TBP:DEHPA = 1:1 vol/vol	0.43	0.016	3.16
TBP:Cyanex 302 = 3:1 vol/vol	1.08	0.015	3.16
TBP:Cyanex 302 = 1:1 vol/vol	0.38	0.009	3.16

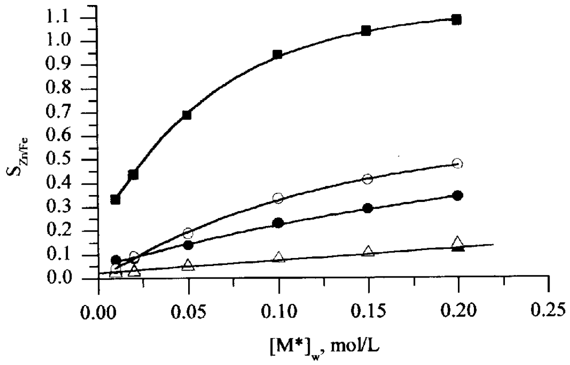

Fig. 3. Selectivity of extraction for various equilibrium concentrations of metal ions (equimolar quantities of zinc(II) and iron(III)) in the aqueous phase (■ – TBP; ○ – TBP:DEHPA=3:1 vol/vol; ● - TBP:Cyanex 302=3:1 vol/vol; Δ - TBP:DEHPA=1:1 vol/vol and ▲ - TBP:Cyanex 302=1:1 vol/vol)

Although iron(II) was not extracted, its presence in the aqueous feed caused a positive increase of zinc(II) extraction with TBP and TBP-DEHPA mixtures (Table 3). The effect could be explained by an increase of the ionic strength. Such a positive effect was not observed for TBP-CYANEX 302 mixture.

TBP formed easily complexes with water, especially in the presence of HCl (Kertes and Halpern 1961). As a result, a significant transfer of water to TBP phase (4-6%) was observed. An addition of acidic extractants caused a decrease of water in the extractant phase to about 3% and 1-3% for TBP-DEHPA and TBP-CYANEX 302 mixtures, respectively.

Table 3. Effect of iron(II) presence upon zinc(II) extraction. Aqueous feed: FI – 5 g/L Zn(II), 10% HCl, $[Cl^-]$=5 M or FII – 5 g/L Zn(II), 50 g/L Fe(II), 10% HCl, $[Cl^-]$=5 M

Extractant	FI			FII		
	Ionic strength [M]	%	$D_{Zn(II)}$	Ionic strength [M]	%	$D_{Zn(II)}$
TBP	5.08	96.3	23.7	6.17	97.9	39.5
TBP:DEHPA = 3:1 vol/vol	5.08	68.8	2.21	6.17	81.3	4.34
TBP:DEHPA = 1:1 vol/vol	5.08	20.0	0.25	6.17	31.2	0.45
TBP:Cyanex 302 = 3:1 vol/vol	5.08	80.0	4.00	6.17	75.2	3.03
TBP:Cyanex 302 = 1:1 vol/vol	5.08	37.5	0.60	6.17	30.6	0.44

Table 4. Percentage of zinc(II) and iron(III) stripping from loaded TBP:DEHPA = 3:1 vol/vol with different stripping phases in three successive steps (Aqueous feed: 10% HCl, [Cl$^-$] = 5 M and 5 g/L Zn(II) or 30 g/L Fe(III), o/w = 1:1 vol/vol)

Stripping phase	$\%S_{Zn(II)}$	$\%S_{Fe(III)}$
H_2O	71.7	37.7
0.1 M H_2SO_4	100.0	59.2
0.1 M H_2SO_4	100.0	60.8
H_2O	71.1	37.2
H_2O	77.0	55.5
H_2O	83.9	55.5
0.1 M H_2SO_4	75.2	41.4
0.1 M H_2SO_4	83.7	79.2
0.1 M H_2SO_4	83.7	100.0

Water could strip only zinc(II) and iron(III) from complexes with TBP. Zinc(II) was better stripped than iron(III), and about 71 and 38% of zinc(II) and iron(III) could be stripped in one stage (Table 4). Additional stripping with water caused an increase of the stripped metal ions to about 84 and 55% for zinc(II) and iron(III), respectively. The total stripping of zinc(II) was obtained when the stripping with water was followed by the stripping with sulphuric acid. The total stripping of iron(III) was achieved in three stages using 0.1 M H_2SO_4. The necessity of using two different stripping solutions had to be considered as an important technological disadvantage.

CONCLUSIONS

The extraction ability of zinc(II) chlorocomplexes from hydrochloric acid solutions decreased in the order: TBP > TBP:HL=3:1 vol/vol > TBP:HL=1:1 vol/vol. Iron(III) was strongly extracted by TBP and its binary mixtures with DEHPA and CYANEX 302, and the extraction fell in the order: binary mixtures with DEHPA or CYANEX 302> TBP> DEHPA >> CYANEX 302. Iron(II) was not extracted by the considered extractants.

Zinc(II) could not be selectively extracted in the presence of iron(III). Contrary, iron(III) could be selectively extracted especially with the binary 1:1 vol/vol mixtures of TBP with DEHPA or CYANEX 302.

The stripping of zinc(II) could be accomplished in three successive stages using water and 0.1 M H_2SO_4. Iron(III) could be stripped in three stages with 0.1 M H_2SO_4.

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Bartkowska M, Regel-Rosocka M., Szymanowski J., *Ekstrakcja cynku(ii), żelaza(iii) i żelaza(ii) za pomocą mieszanin dwuskładnikowych zawierających fosforan tributylu i kwas di(2-etyloheksylo)fosforowy lub cyanex 302*, Fizykochemiczne Problemy Mineralurgii, 36 (2002), 217-224, (w jęz. ang.)

Badano ekstrakcję cynku(II), żelaza(III) oraz żelaza(II) za pomocą fosforanu tributylu (TBP) i jego mieszanin dwuskładnikowych z kwasem di(2-etyloheksylo)fosforowym (DEHPA) oraz tlenkiem trialkilofosfiny (CYANEX 302) z roztworów kwasu solnego. W wyniku przeprowadzonych badań stwierdzono, że zdolność ekstrakcji chlorokompleksów cynku z roztworów kwasu solnego maleje w następującej kolejności: TBP > TBP:HL=3:1 vol/vol > TBP:HL=1:1 vol/vol. Żelazo(III) jest silnie ekstrahowane przez TBP i jego mieszaniny dwuskładnikowe z DEHPA i CYANEX 302. Zdolność ekstrakcyjna maleje w kolejności: mieszaniny dwuskładnikowe TBP:DEHPA lub TBP:CYANEX 302> TBP> DEHPA >> CYANEX 302. Żelazo(II) nie jest ekstrahowane przez badane reagenty organiczne.Cynku(II) nie można selektywnie wyekstrahować w obecności żelaza(III). Natomiast żelazo(III) można wyekstrahować przy użyciu mieszaniny dwuskładnikowej TBP:DEHPA=1:1 vol/vol lub TBP:CYANEX 302=1:1 vol/vol.Przebadano również reekstrakcję cynku(II) i żelaza(III) z naładowanej fazy organicznej TBP:DEHPA = 3:1 vol/vol. Uzyskane wyniki wskazują na to, że cynk można całkowicie wydzielić prowadząc trzystopniową reekstrakcję w pierwszym etapie wodą, a następnie 0.1 M H_2SO_4. Najskuteczniej można zreekstrahować żelazo(III) za pomocą trzystopniowej reekstrakcji 0.1 M H_2SO_4.