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DIBUTYLBUTYL PHOSPHONATE AS AN EXTRACTANT OF ZINC(II) FROM HYDROCHLORIC ACID SOLUTIONS

The extraction of zinc(II) and iron(II) with solutions of dibutylbutyl phosphonate (DBBP) from hydrochloric acid solutions is studied. Iron(II) is slightly extracted by the considered extractant. The isotherms of zinc(II) extraction with DBBP are compared with those for TBP. They indicate that extraction effectiveness of DBBP as an extractant is higher than for tributyl phosphate (TBP). It is found that the extraction ability of zinc(II) chlorocomplexes from hydrochloric acid solutions decreases with decreasing DBBP content. Addition of kerosene increases hydrophobicity of DBBP at the same time slightly decreasing the efficiency of zinc(II) extraction. 80 vol% DBBP is applied successfully to separate zinc(II) from iron(II) in the following stages: extraction with excess of DBBP (o/w = 5:1), scrubbing of loaded extractant with small amount of water (w/o = 1:5) to remove iron(II), stripping with water to remove zinc(II) from loaded DBBP (w/o = 1:1).

Key words: extraction, zinc(II), dibutylbutyl phosphonate, tributyl phosphate.

INTRODUCTION

Spent pickling solutions are an important environmental problem of hot-dip galvanizing plants. There are over 50 such plants in Poland. Prior to hot-dip galvanizing of steel goods in 96-99% zinc, they are pickled with 20% hydrochloric acid to remove rust and purify the surface. During this stage, hydrochloric acid is consumed, however chloride ion concentration does not change because chlorides of zinc(II) and iron accumulate in the solution.

Some pickling solutions are used to remove poor zinc coatings. Thus, zinc(II) concentration in such a spent pickling solution is very high. Generally, the concentration of hydrochloric acid decreases by 75-85%, and the metal content increases up to 150-250 g/L (Maass et al. 1998).

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Removal of zinc(II) is essential because of both protection of the environment and technological problems caused in pyrometallurgical processes. Metallic zinc evaporates and glues to the walls of installation at high temperatures used in Ruthner process (800°C).

Zinc(II) extraction from chloride solution with basic, acidic and neutral reagents was studied in our previous works (Regel et al. 2001, Wojtaszak et al. 2000, Kirschling et al. 2001, Cierpiszewski et al. 2002, Regel-Rosocka et al. 2002). Tributyl phosphate (TBP) was chosen as the most effective for zinc(II) extraction and stripping from the loaded organic phase. However, the main drawback of TBP is transfer of high amounts of water to the organic phase. As a consequence, hydrolysis of TBP is observed (Kertes et al. 1961). Another neutral extractant, dibutylbutyl phosphonate (DBBP) is considered as an effective zinc(II) extractant from chloride solutions (Lin 1993, Alguacil et al. 1999).

It is the aim of the work was to study zinc(II) extraction from hydrochloric acid solutions in the presence of iron ions with dibutylbutyl phosphonate. Performance of DBBP is compared with TBP.

EXPERIMENTAL

Dibutylbutyl phosphonate (Rhodia, USA) was used as an extractant and low-aromatic kerosene (aromatic content: 0.05 wt%, distillation range 222-234°C) Exxsol D 220/230 (Exxon Mobil Chemical, Germany) as a diluent. It was used as delivered without any purification.

Extraction was carried out in a small scale using 10 ml volumes of phases at the volume ratio o/w equal 1:1, 8:1 or 9:1 . Phases were mechanically shaken for 15 minutes and left for phase separation. The aqueous feed used for the determination of extraction isotherms contained Zn(II) or Fe(II) or Fe(III) in the range from 0.01 to 50 g/L and 0.58 M (1.8 wt%) HCl. Contents of the model aqueous feed, used for extraction in o/w 8:1 and 9:1, was near to a real solution from "Belos" galvanizing plant in Bielsko-Biala and contained 100 g/L Zn(II), 29 g/L Fe(II), 1 g/L Fe(III), 2.5 M HCl, 6.5 M Cl⁻. Stripping from loaded DBBP was carried out with deionized water at volume ratio 1:1. Scrubbing of loaded DBBP was carried out with deionized water at w/o ratio 1:5 and 1:10.

Zn(II) concentration in the aqueous phase was determined by amperometric titration with 0.05 M $K_4[Fe(CN)_6]$. HCl content in aqueous phase was determined by potentiometric titration (702 SM Titrino, Metrohm, Switzerland) with 0.1 M NaOH. The content of Fe(II) and Fe(III) was determined by titration with $K_2Cr_2O_7$ (Fe(III) was reduced to Fe(II) with 5% solution of $SnCl_2$).

The chloride concentration adjusted with NaCl (POCh, Poland) was equal to 5 M in the initial aqueous feed. The content of chloride ions after extraction was determined by potentiometric titration with 0.05 M $AgNO_3$ solution. The content of water in the organic phase was determined by the Karl – Fischer titration.

RESULTS AND DISCUSSION

DBBP has been studied as an extractant of zinc(II) from chloride media, however no data for more concentrated solutions (above 10 g/L) and on the transfer of water to the organic phase are available (Lin 1993, Alguacil et al. 1999). Moreover, the effect of iron ion presence on zinc(II) extraction with DBBP has not been studied either.
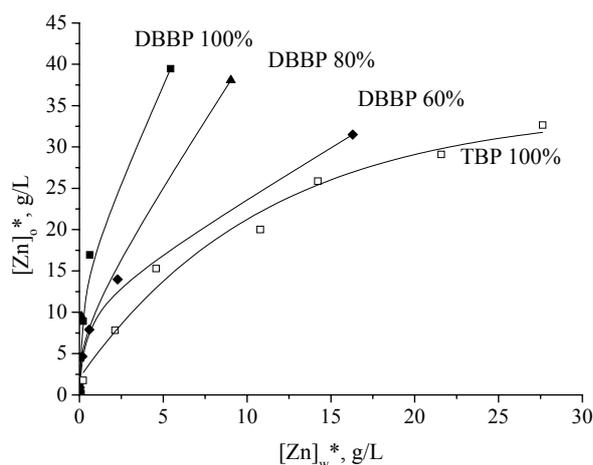

Fig. 1. Isotherms of zinc(II) extraction (■ – 100 vol% DBBP; ▲ – 80 vol% DBBP; ◆ - 60 vol% DBBP, □ - 100 vol% TBP; Feed: 0.1 – 50 g/L, 0.58 M HCl, 5 M Cl⁻)

The isotherms of zinc(II) extraction from 0.58 M HCl (1.8 wt%), presented in Fig. 1, indicate that zinc(II) is very well extracted with both diluted and undiluted DBBP. The isotherms are very steep and loading capacity exceeds 40 g/L and 30 g/L Zn(II) for 100 and 60 vol% DBBP, respectively. Slight extraction of iron(II) is observed (Fig. 2). However, for high initial concentration of iron(II) about 10 g/L of iron(II) occurs in the organic phase. Iron(II) transfer to the organic phase is higher than in case of TBP.

The extraction effectiveness of neutral organophosphorus compounds depends upon the polarity of P=O bond and increases significantly with increasing number of C-P bonds in the following order: $(RO)_3PO < (RO)_2RPO < (RO)R_2PO < R_3PO$ (Marcus and Kertes, 1969). Comparison of the isotherms for DBBP and TBP (Figs 1 and 2) is consistent with the theory. Loading capacity for 60 vol% DBBP is higher than for 80 vol% TBP. For that reason, the substitution of TBP with DBBP, as a zinc(II) extractant from hydrochloric acid solutions containing iron(II) ions, seems to be justified. The only disadvantage of DBBP could be its solubility in water, which is higher than for TBP because of higher polarity of phosphoryl group in the phosphonate molecule. However, addition of kerosene (20-40 vol%) increases the hydrophobicity of DBBP without significant reduction of its extraction power.
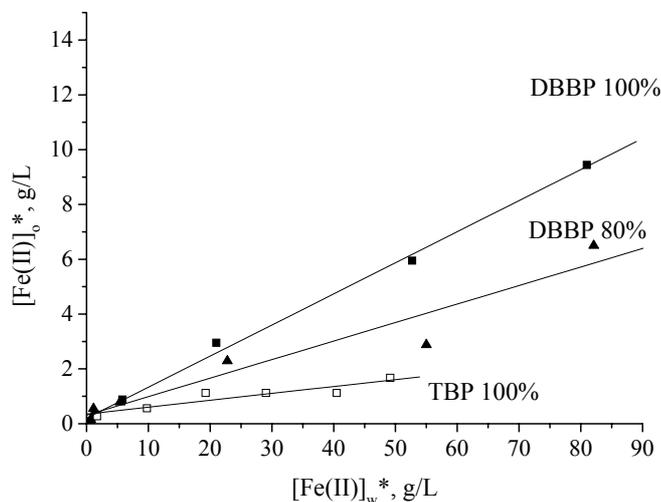
Fig. 2. Isotherms of iron(III) extraction (■ – 100 vol% DBBP; ▲ – 80 vol% DBBP; □ - 100 vol% TBP; Feed: 0.1 – 50 g/L, 0.58 M HCl, 5 M Cl⁻)

As it was presented in a previous paper (Bartkowska et al., 2002), in the system containing 6 M Cl⁻, over 80% of zinc(II) is in the form of $ZnCl_4^{2-}$, iron(II) ions are mainly in the form of cationic chlorocomplexes. Thus, the extraction of zinc(II) with DBBP can be described with the following equation:

$$2H^+_w + ZnCl_4^{2-}{}_w + 2DBBP_o = (H_2ZnCl_4 \cdot 2DBBP)_o \tag{1}$$
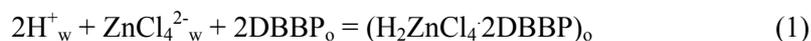
The extraction of Fe(II) to the organic phase can be explained by transport of metal cations in the water pool of reverse micelles as in case of TBP (Regel-Rosocka et al. 2005).

Extraction of chloride ions (determined by titration), observed in the system of 0.6 M HCl, corresponds to an amount of chlorides calculated from HCl and Zn(II) transferred to the organic phase, assuming the extraction of $ZnCl_4^{2-}$ (Fig. 3). The extraction of hydrochloric acid is constant and does not exceed 0.3 M. Chloride extraction increases with increasing initial concentration of zinc(II).

Only in case of high initial Zn(II) concentration (50 g/L) the determined amount of chloride is not consistent with the calculated. It suggests that, in this case, zinc(II) forms $ZnCl_2$ complex with DBBP. Then a sum of chlorides transferred to the organic phase with $ZnCl_2$ and HCl equals to 1.8 M, while the one determined by titration amounts 1.96 M. Thus, the extraction of zinc(II) can be well described with the equation proposed by Lin (Lin 1993):

$$Zn^{2+}_w + 2Cl^-_w + 2DBBP_o = (ZnCl_2 \cdot 2DBBP)_o \tag{2}$$
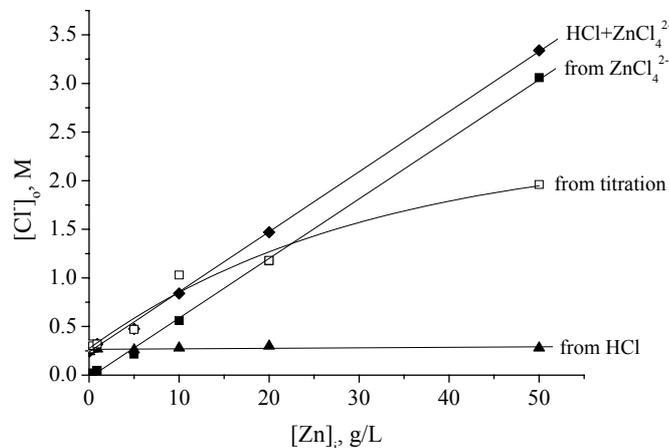
Fig. 3. Chloride balance in the organic phase after zinc(II) extraction ▲ - chlorides calculated in HCl, ■ - chlorides calculated in $ZnCl_4^{2-}$ complex, ◆ - sum of chlorides in HCl and $ZnCl_4^{2-}$ □ - chlorides determined by Volhard titration (Feed: 0.1 – 50 g/L Zn(II), 0.58 M HCl, 5 M Cl⁻).

Table 1. Percentage of zinc(II) extraction with DBBP and water content in the organic phase
(Feed: 1 or 40 g/L Zn(II), 0.58 M HCl, 5 M Cl⁻)

Zn_i, g/L	E_{Zn}, %	H_2O, % after extraction	H_2O, % after stripping
100% DBBP			
1	93.3	9.70	10.6
40	89.9	9.40	10.2
80% DBBP			
1	98.9	5.95	7.38
40	95.1	6.02	8.83
60% DBBP			
1	98.3	4.12	6.70
40	69.3	3.60	4.70

A significant transfer of water to DBBP phase (Table 1) is observed. Water content amounts about 6 and 9 vol% in 80 and 100 vol% DBBP, respectively. It increases after stripping with water up to 7 and almost 11 vol% in 80 and 100 vol% DBBP, respectively. However, it does not change in each successive step of stripping, which means that the organic phase is saturated with water. Although DBBP is diluted with kerosene, its hydrophobicity does not increase enough to inhibit the water transfer.

As a result of a good performance of DBBP as an extractant of zinc(II), some experiments on zinc(II) removal from solution containing iron ions were carried out. An excess of the organic phase was used to obtain high efficiency of zinc(II) extraction and to minimize iron ion transfer to DBBP.

Table 2. Zinc(II) and iron(II) extraction for different volume ratios (Organic phase: 80 vol% DBBP or TBP; feed: 100 g/L Zn(II), 30 g/L Fe(II), 2.5 M HCl, 6.5 M Cl$^-$)

Extractant	o/w before extraction	$E_{Zn(II)}$ %	$E_{Fe(II)}$ %	$[Zn(II)]_o$ g/L	$[Fe(II)]_o$ g/L	o/w after extraction
80% DBBP	5:1	100	3.50	14.0	0.196	10:1
	8:1	100	43.7	8.62	1.52	37:1
	9:1	100	41.7	7.90	1.35	54:1
80% TBP	8:1	98.3	12.4	11.7	0.44	16:1
	9:1	99.0	14.9	10.9	0.49	20:1

Results presented in Table 2 exhibit very effective zinc(II) extraction (100%) in the presence of iron(II). On the other hand, iron(II) extraction increases significantly (over 40%) with increase of the organic phase ratio. Moreover, high water transfer to the organic phase is observed. It confirms possibility of physical transport of iron(II) in reverse micelles. The results are compared with the data obtained in the same aqueous system with TBP (Rozenblat et al. 2004). The best results are obtained for o/w ratio equal to 5. Zinc(II) is totally extracted from the aqueous feed, while only 3.5% of iron(II) is transferred to the organic phase. The extraction with TBP does not allow to obtain such low iron(II) content in the organic phase.

Small amounts of water (w/o = 1:5) are used to scrub iron(II) from DBBP loaded with zinc(II) and iron(II). The scrubbing enables the 100% removal of iron(II) with small amounts of zinc(II) only in case when 5 folded excess of 80 vol% DBBP was used to extraction (Table 3). For the rest o/w ratios the results of scrubbing are worse. The removal of iron(II) by scrubbing with water supports the idea of iron(II) transfer in the cores of reverse micelles.

Table 3. Zinc(II) and iron(II) scrubbing with water from loaded 80% DBBP at w:o = 1:5
(Sc stands for scrubbing, o1 and o2 denote organic phase before and after scrubbing, respectively)

o/w before extraction	$[Zn(II)]_{o1}$ g/L	$[Fe(II)]_{o1}$ g/L	$Sc_{Zn(II)}$ %	$Sc_{Fe(II)}$ %	$[Zn(II)]_{o2}$ g/L	$[Fe(II)]_{o2}$ g/L
5:1	14.0	0.196	2.26	100	18.8	0
8:1	8.62	1.52	3.14	24.6	13.9	1.92
9:1	7.90	1.35	4.89	20.4	14.3	2.61

Finally, DBBP loaded with zinc(II) is stripped with water. It enables to obtain an aqueous solution of 9 g/L Zn(II). The solution can be concentrated and added to the pickling bath.

CONCLUSIONS

DBBP is a very effective extractant of zinc(II) from hydrochloric acid solutions. It permits to remove 99% of zinc(II). It extracts iron(II) slightly, which is positive because enables to extract zinc(II) selectively from solutions containing iron ions.

Iron(III) must be reduced to iron(II). Comparing with TBP, DBBP has higher extraction effectiveness. It can be loaded more with zinc(II), even at lower extractant concentration. However, high water transport to the organic phase (even up to 11 vol%) is a main drawback of DBBP.

100% zinc(II) removal from solution containing iron(II) confirms a good performance of DBBP at o/w = 5. Diluted DBBP can replace TBP in extraction with an excess of the organic phase.

ACKNOWLEDGEMENT

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Badano ekstrakcję cynku(II) oraz żelaza(II) z roztworów kwasu solnego za pomocą fosfonianu dibutylobutylu (DBBP) o różnych stężeniach. Otrzymane izotermy ekstrakcji porównano z izotermami uzyskanymi wcześniej dla fosforanu tributylu (TBP). W wyniku przeprowadzonych badań stwierdzono, że zdolność ekstrakcyjna DBBP jest większa niż TBP. Dodatek rozpuszczalnika węglowodorowego powoduje wzrost hydrofobowości DBBP, a nie zmniejsza w znaczący sposób wydajności ekstrakcji cynku(II). 80% DBBP zastosowano z powodzeniem do oddzielenia cynku(II) od żelaza(II) w procesie składającym się z następujących etapów: ekstrakcja cynku(II) nadmiarem DBBP (o/w = 5:1), odmycie z naładowanej fazy organicznej żelaza(II) małą ilością wody (w/o = 1:5), reekstrakcja cynku(II) z DBBP wodą (w/o = 1:1).