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Extraction of Zinc (II) by Triphenylphosphite (TPP) in Hydrochloric acid: kinetics and mechanism

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The extraction of Zinc (II) in chloride medium with triphenyl phosphite (TPP) in kerosene has been investigated under different experimental conditions in order to have a better understanding of the extraction mechanism. The extraction yield was found to depend on the concentrations of Zinc (II) and TPP, and pH. The extraction yield can easily be predicted based on an established linear expression. The effect of salting-out agents: LiCl, NaCl and NH_4Cl were also studied and they ranked $NaCl < NH_4Cl < LiCl$ in increasing order of the extraction yield. This study suggests that Zn (II) forms a binuclear complex with TPP, according to the equation:
$$2Zn^{2+} + 2Cl^- + 2\overline{L} \rightleftharpoons (\overline{ZnClL})_2, \quad L = TPP$$
. On the other hand, the stripping study showed that 0.5M HCl was satisfactory for the stripping of about 79.42% of zinc from the organic phase in a single stage. Finally, the findings on the possible re-use of TPP in kerosene showed that the TPP continuously losses its extraction ability with successive re-use. This has been attributed to its gradual degradation or transformations, and decrease in the number of co-ordination sites available for the divalent metal ion.

Key words: Zinc (II) extraction, triphenylphosphite, mechanism.

INTRODUCTION

Zinc occurs in the nature mainly as the Sulphide ZnS, which is mineralogically known as sphalerite. In the commercial flowsheet for the production of Zinc metal, the sphalerite concentrate is roasted, leached in Sulphuric acid and electrolyzed (Alguacial and Martinez, 2001). The treatment of sphalerite and complex sulphide concentrates has also been carried out using various leaching reagents such as HCl, iron (III) sulphate or chloride (Gupta and Mukherjee, 2000).

The recovery of metals from aqueous chloride solutions has attracted much attention. This is due to the high efficiency of the chloride leaching processes, which are now recognized as a logical choice for treating complex ore concentrates which cannot be easily or economically treated by other means. Among the separation methods allowing the recovery and purification of metals from chloride solutions, solvent extraction is highly attractive (Szymanowski, 1993).

In recent years, the use of organo-phosphorus compounds in the liquid-liquid extraction of metals has been steadily increasing because of their excellent selective nature in forming complexes under different conditions. Besides dialkyl phosphoric acid, the introduction of dialkyl phosphinic and phosphinic acids has brought about a vast change in the separation technology (Preston, 1982; Preston and Aupreez, 1986).

In the case of solvent extraction of Zn (II) by either dialkyl phosphoric acid (Sastre and Muhammed, 1984; Aparicio and Muhammed, 1989) or phosphinic acid (Sastre et al., 1990) diluted in liquid hydrocarbon, different authors have reported the formation of different Zn(II) species, such as: $\overline{ZnL_2}$, $\overline{ZnL_2(HL)}$ and $\overline{ZnL_2(HL)_2}$, especially the last two species (Kunungo and Muhapatra, 1995). The predominant formation of $\overline{ZnL_2}$ in di(2-ethylhexyl) phosphoric acid-heptane system using the rotating diffusion cell technique has also been reported (Dreisinger and Cooper, 1989).

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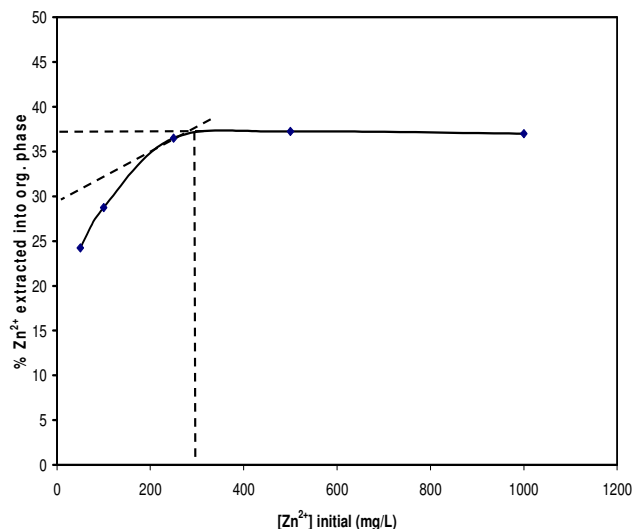
Figure 1. Percentage of Zinc extracted into organic phase as a function of the initial Zinc concentration.

The recovery of Zinc (II) from chloride leach solution is also of particular interest and the use of various extractants such as tributyl phosphate (TBP), (Keshavarz et al., 2002; Ritcey et al., 1982; Bartkowska et al., 2002), dibutylbutylphosphonate (DBBP) (Regel-Rosocka et al., 2005; Regel-Rosocka and Grzeszczyk, 2007), di-n-pentyl pentaphosphonate (DPPP) (Nogueira and Cosmen, 1983), Kelex-100 (Mellah and Benachour, 2006), tri-n-octylphosphine oxide (Sato and Nakamura, 1980), Cyanex 272 (Flett, 2005; Ali et al., 2006) and Alamine 336-m-xylene systems (Sayar et al., 2007) have been investigated. There are, however, a number of disadvantages with these reagents. For instance, there is the inconvenience of co-extracting Iron (III) along with Zinc by most of the phosphate-type extractants. Therefore, this work aims at unravel the extraction mechanism of zinc with triphenylphosphite (TPP) in aqueous chloride medium. To the best of our knowledge, the use of TPP in solvent extraction of Zinc has not been given proper attention. The only recent work on TPP concerned its use for the diasteroselective synthesis of phosphonate esters (Maghsoodlu et al, 2006). Recently, we reported results of our preliminary investigation on the solvent extraction of Zinc with Triphenyl phosphite (Baba et al., 2004). Then, the mechanism was not understood. The main aim of the present work was therefore to investigate fully the mechanism of extraction of Zinc by TPP. The influence of ionic strength and kinetics, on the extraction, as well as the stripping and possibility of regeneration of TPP after successive stages of re-use were also studied.

MATERIALS AND METHODS

Reagents

Triphenylphosphite (BDH chemicals, Poole England; Purity 97%,

FW 310.29, n=1.59-1.592, d=1.182-1.188g/ml); zinc chloride (BDH chemicals, Poole England); benzene (BDH chemicals, Poole England); lithium chloride (Baker chemical Co., N. J.); sodium chloride (BDH chemicals England) and ammonium chloride (AnalaR Chem, Poole England) were used as delivered without any further purification. Commercial kerosene, a product of a Nigerian petroleum refinery used as a diluent for the extractant was re-distilled before use. Doubly distilled water was also used in the preparation of all aqueous solutions.

Experimental procedures

Extraction

Extraction was carried out in a small scale using 25 ml volumes of phases at the volume ratio equal to 1. Phases were shaken vigorously in plastic containers on a shaker (Burrel Wrist Action Shaker – Model 75) at room temperature (25 ± 2^{0}C) for a period of 40 min. This time was sufficient for equilibrium to be achieved (Baba et al., 2004). Phase separation required up to one minute. The two phases were separated with 100 ml Quick fit separating funnel and concentration of Zinc (II) in the aqueous phase was determined by titration against 0.1M EDTA using solochrome T-black indicator (Regel- Rosocka and Grzeszczyk, 2007; Baba et al., 2004). The amount extracted into the organic phase was obtained by difference. The pH of the aqueous solution was measured with a HANA pH meter, serial number HI98106.

Stripping studies

The stripping investigation was carried out to determine the optimum concentration of HCl for the stripping of Zinc from 0.2 M TPP after extraction.

Study on the re-use of TPP

This study concerns the determination of the recovered organic phase (TPP in kerosene) after stripping can be re-used for effective extraction of Zinc from a fresh aqueous solution.

RESULTS AND DISCUSSION

Kinetic studies

Influence of concentration on Zn^{2+} extraction

For each concentrations and at 40 min contact time, the results of the percentage of the Zn^{2+} extracted into organic phase as a function of Zn^{2+} concentration were presented in Figure 1. From Figure 1, a concentration of 300 mg/L was kept for use for subsequent experiments.

Influence of pH on zinc extraction

The pH of the initial aqueous solution of Zinc was varied between 1 and 6 at a contact time of 40 min. The initial liquor solution of Zinc was 300 mg/L while the concentration of TPP was maintained at 0.2 M.

Figure 2 illustrates the percentage of Zn^{2+} extracted as a function of pH of the initial liquor solution. From Figure 2, it is evident that there was a very slight increase between the pH of 1 - 3, and a sudden jump when the pH
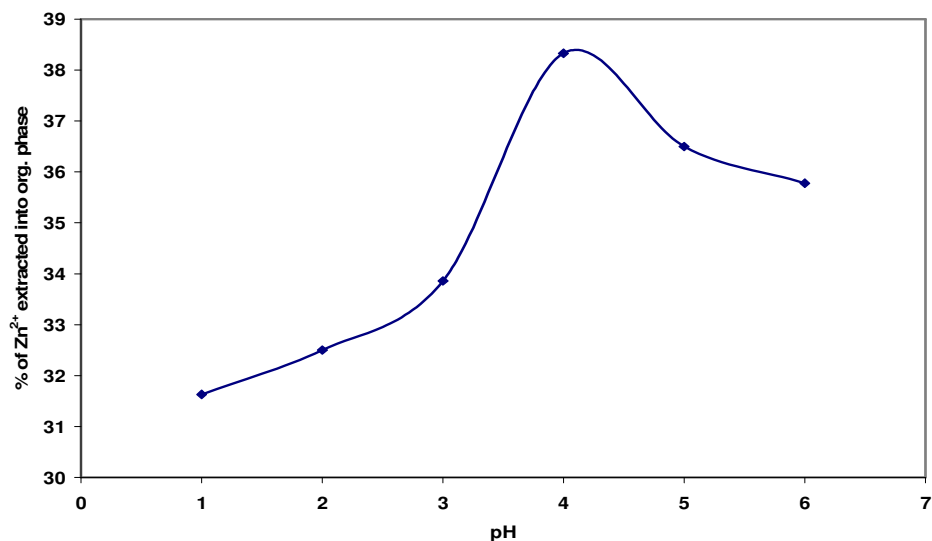
Figure 2. Percentage of Zn^{2+} extracted versus pH.
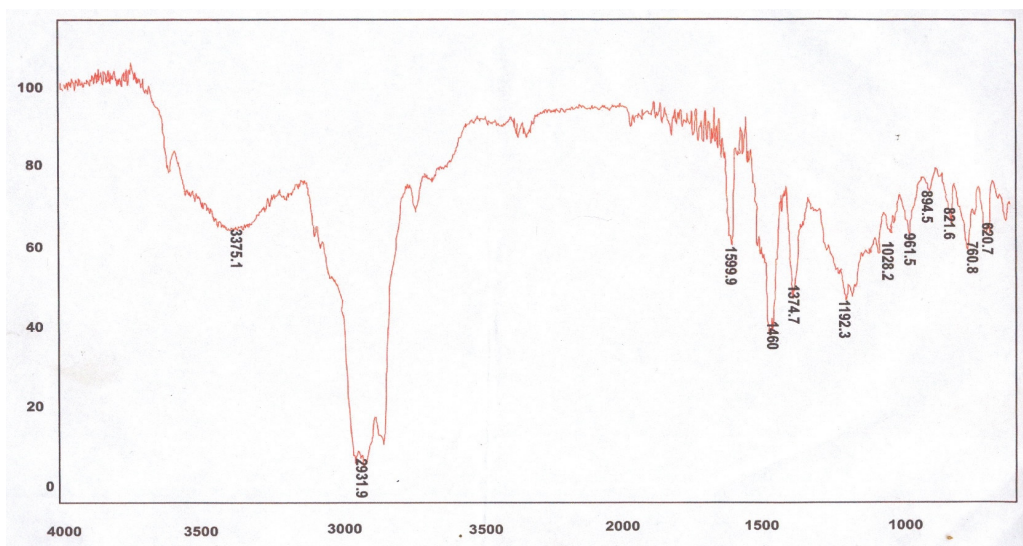

**Figure 3.** Result of IR measurement

was increased from 3 - 4. While a gradual but slow decrease as the pH was increased between pH 4 - 6. The optimum pH for the extraction is 4.0, above which shows a progressive decrease in the percentage of Zn extracted. This trend has also been observed by Oki and Terada, (1972) in a separate study on the extraction of zinc with oxine. These results also showed that both TPP and H$^+$ ions are active participants in the extraction. On the other hand, the constancy of the zinc extraction at this optimum pH, giving an "S" shape conforms to the general extraction behaviour already reported for some acidic extractants (Yuen et al, 1988; Yao et al., 1996). The decrease in %Zn extracted after the optimum pH ≈4 could be attributed to the formation of hydroxylated spe-

cies of Zinc (II).

The results of infrared spectroscopic measurement at pH 4 with 0.2M TPP also lent support to this (Figure 3). Here, broad and strong vibrations are observed at 3375.1 cm^{-1} due to γ_{O-H}; 1192.3, 1374.7 cm^{-1} due to $\gamma_{P=O}$ and 2931.9 cm^{-1} assigned to γ_{C-H} are evidence of hydrolysis (Maghsoodlu et al., 2006).

Study on the successive extraction of Zinc with TPP

A study on the successive extraction of Zinc with TPP has been undertaken in order to establish the efficiency of successive extraction on the extraction yield. The plot
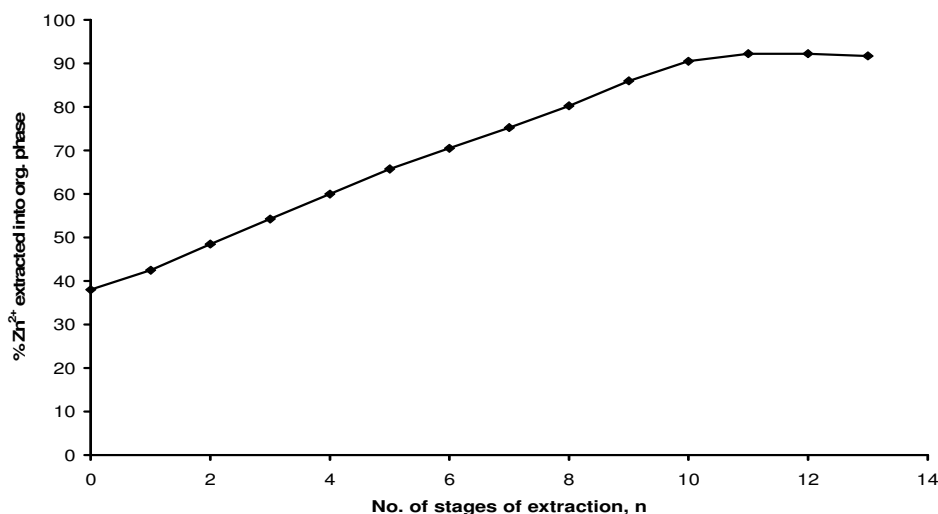
Figure 4. Effect of number of stages, n, on the extraction of Zinc by TPP in kerosene from aqueous solution of pH 3.5 at 25^{0}C. Other experimental conditions: concentration of Zn^{2+} = 300 mg/L in 0.1 M HCl at constant ionic strength of 0.4 MLiCl.
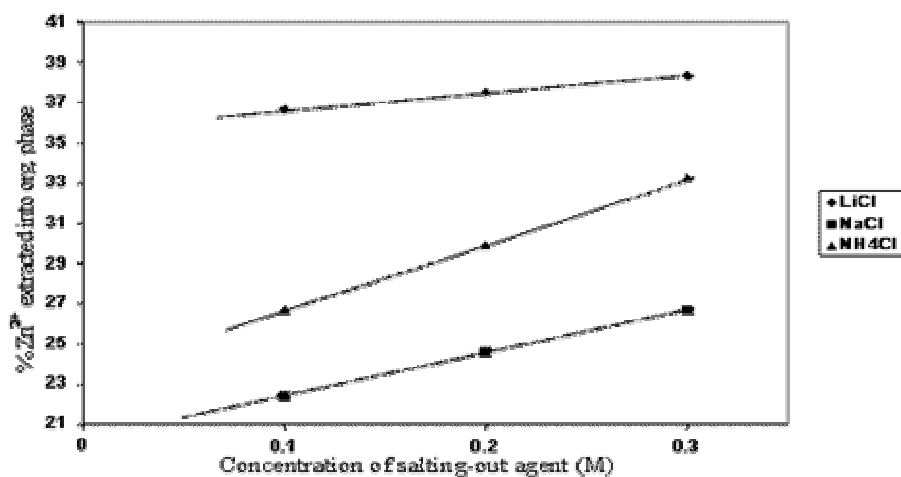
Figure 5. Percentage Zn^{2+} extracted as a function of salting-out agent Concentration.

of the percentage of Zinc extracted into organic phase and and a function of extraction step, n, is illustrated in Figure 4

From Figure 4, the slope $\Delta Zn^{2+}/\Delta n$ is 5.28 and the intercept is 38. The multiple extractions can therefore be fitted with y = 5.28n + 38.

Influence of ionic strength on Zn^{2+} Extraction

Some salting-out agents, such as ammonium chloride, sodium chloride and lithium chloride were investigated for their effect on Zn^{2+} extraction in 0.2M TPP in 100% kerosene. The results are presented in Figure 5. Figure 5 shows that LiCl gave the best result. This was followed by NH$_4$Cl and NaCl in that order. With LiCl, and during the separation of the organic and aqueous products,

there exists formation of aquo-product in the aqueous phase. This might be due to the small size effect of lithium, compared to other metals in the group. As for LiCl, the % of Zn extracted did not vary appreciably between 0.1 and 0.3M (Yadav and Khopkar, 1971). Hence, all subsequent studies were carried out in 0.4 M LiCl.

DISCUSSIONS

Effect of distribution ratio of Zn^{2+} extraction with TPP

The values of distribution ratio D of Zn^{2+} corresponding to various concentration of TPP have been calculated. These are illustrated in Figure 6. These two different
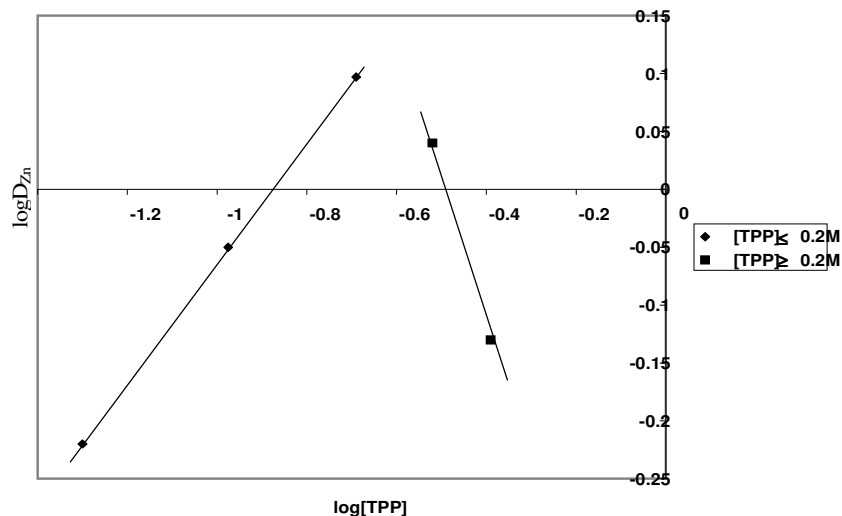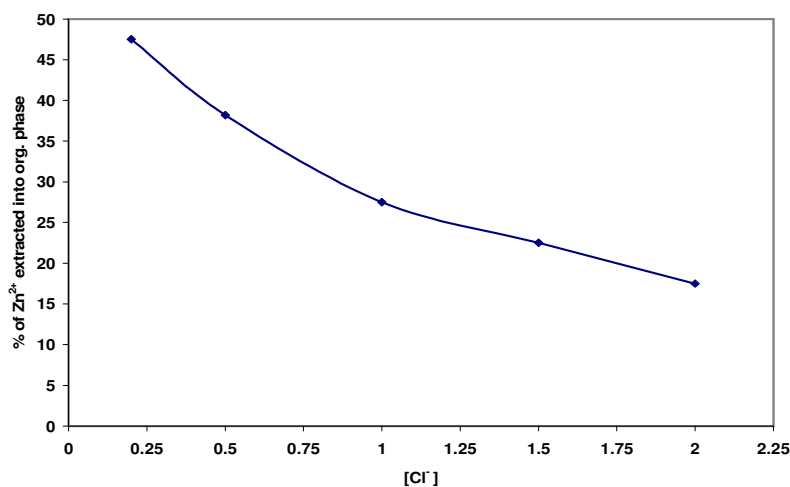
Figure 6. log D_{Zn} vs log [TPP].

Figure 7. Percentage Zn^{2+} extracted vs [Cl⁻].

slopes could be attributed to the formation of different zinc–TPP complexes. The first corresponding to the attainment of TPP saturation, can be linked the formation of 1:1 complex Zn and TPP, while the second would most likely to be an indication of the formation of polynuclear complex at concentration of TPP > 0.2M. (Cote and Jakubiak, 1996)

Influence of chloride concentration on Zinc extraction

The influence of chloride concentration on Zn^{2+} extraction was verified using $[Zn^{2+}]_{aq}$ = 300 mg/L in 0.2, 0.5, 1.0, 1.5 and 2.0 M HCl and in 0.4 M LiCl respectively, with 0.2 M TPP in 100% kerosene and contacted for 40 min at a temperature of 25^{0}C. The percentage of Zinc extracted versus chloride concentration is presented in Figure 7. Similarly, log D of Zn is plotted against log [Cl⁻] and this is represented in Figure 8. The calculated slope is 0.62, which could be approximated to 1. This shows that one mole of chloride ion is participating in extraction complex. From Figure 9 it is seen that the higher the concentration of chloride, the less the Zn^{2+} extraction. This shows that formation of higher Zinc-chloro complexes such as Zn Cl_3^-, $ZnCl_4^{2-}$ should not be envisaged. In fact, what we have resembles $ZnCl^+$ or $ZnCl_2$. With 1:1 slope, the extraction resembles $ZnCl^+$. Similarly, the salting out agent effect equally favours the extraction of Zn. These results are amenable to the suggestions earlier made (Cote and Jakubiak, 1996). Consequently, the expression leading to the formation of extraction complex by TPP is proposed as:
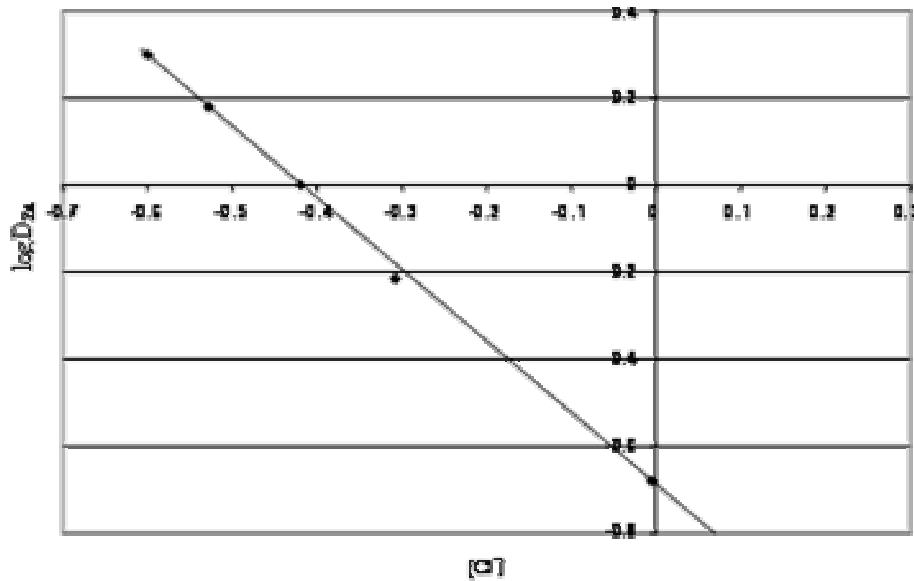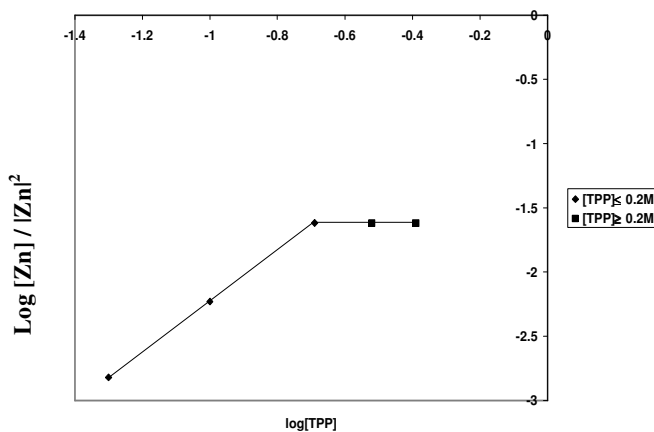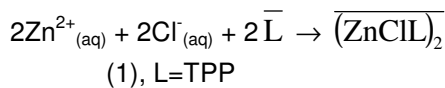
Figure 8. log D of Zn vs log [Cl⁻].

Figure 9. log $\dfrac{\left|\overline{Zn}\right|}{\left|Zn\right|^2}$ vs. log [TPP].

$$2Zn^{2+}_{(aq)} + 2Cl^-_{(aq)} + 2\,\overline{L} \rightarrow \overline{(ZnClL)_2}$$
$$(1), L=TPP$$

For equation (1) to be valid and from what many authors including Cote and Jakubiak, proposed on the assumption that Zn (II) forms a binuclear complex with certain extractants. Consequently, the log $\dfrac{\left|\overline{Zn}\right|}{\left|Zn\right|^2}$ vs. log [TPP] is plotted in Figure 9. $\left|\overline{Zn}\right|$ = quantity of Zn extracted with organic phase and |Zn| is the quantity of Zn left in aqueous phase (unreacted).

The slope of Δ log $\dfrac{\left|\overline{Zn}\right|}{\left|Zn\right|^2}$ / Δlog [TPP], from Figure 9 is 2.08 ≈ 2. This result indicates that Zn (II) forms a binuclear complex with TPP.

Stripping investigations

The result of stripping experiments carried out with differrent concentration of HCl is illustrated in Figure 10. The optimum concentration of HCl for the stripping of Zinc from TPP was 0.5 M.

Experimental conditions

Conc. of Zn^{2+} = 300 mg/L in 0.4 M LiCl at pH 3.5; conc. of TPP = 0.2 M in 100% kerosene; Contact time = 40 min; Temperature = 27^0C; conc. of HCl = varied from 0–2.0 M.

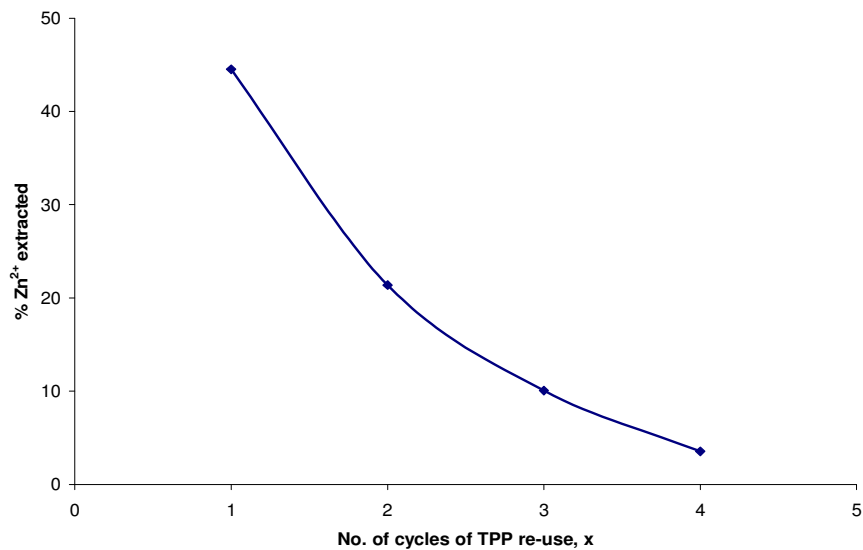### Investigations on the re-use of TPP

The results on the findings on the re-use of TPP in kerosene (Figure 11) showed that TPP continuously losses its extraction ability with successive re-use. This could be attributed to two phenomena. Firstly, there could be gradual degradation of TPP, while the other reason could be due to the decrease in the number of coordination sites available for the divalent metal ion. *Experimental conditions:* Conc. of Zn^{2+} = 300mg/L in 0.5M HCl in 0.4M LiCl at pH 3.5; conc. of TPP = 0.2M in 100% kerosene;

Conclusion

The extraction of Zinc (II) in chloride medium by Triphenyl phosphite in 100% kerosene is strongly dependent on the
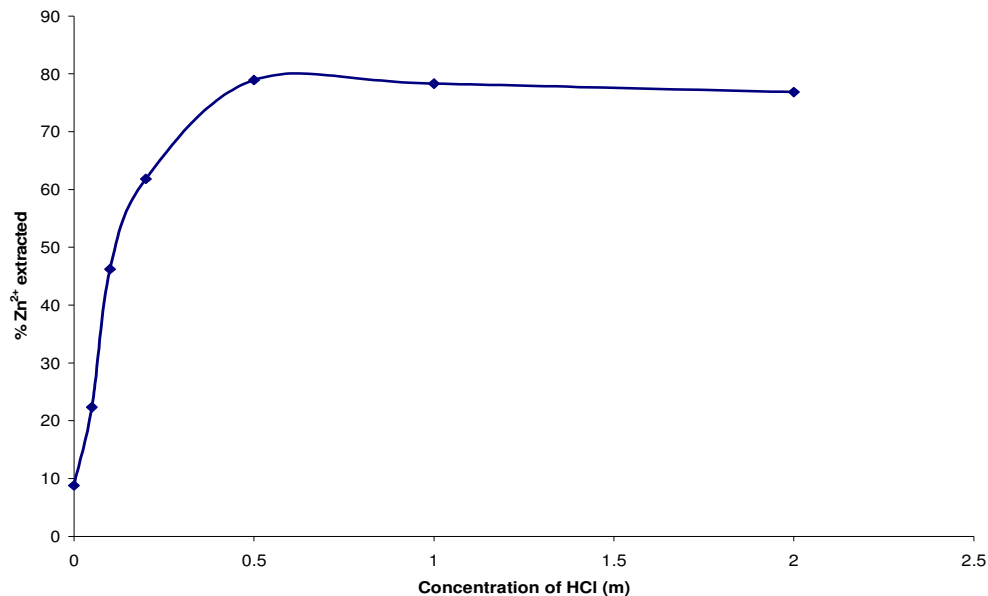
Figure 10. % of zinc extracted as a function of HCl concentration.

Figure 11. Amount of zinc extraction as a function of the number of cycles of TPP re-use

contact time = 40 min; Temperature = 27^0C. pH, chloride concentration, salting-out agent, Zinc concentration and TPP concentration. The results obtained showed that Zn (II) forms a binuclear complex with TPP. The stripping study showed that 0.5M HCl was satisfactory for the stripping of about 79.42% of zinc from the organic phase in a single stage. Finally, the findings on the possible re-use of TPP in kerosene showed that the TPP continuously losses its extraction ability with successive re-use. This has been attributed to its gradual degradation or transformations, with respect to decrease in the number of co-ordination sites available for the divalent metal ion.

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