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SHORT COMMUNICATION

THE EXTRACTION OF Zn(II) FROM ACID-CHLORIDE SOLUTION WITH TRI-n-OCTYL PHOSPHINE OXIDE

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ABSTRACT. The suitability of tri-n-octyl phosphine oxide/toluene as a solvent extraction system for Zn^{2+} recovery from acid chloride solutions was investigated. The effects of the aqueous Zn^{2+} and Cl^- concentrations, organic phase concentration of tri-n-octyl phosphine oxide (TOPO), aqueous pH and temperature on the degree of extraction of zinc were studied. The loading of zinc from the aqueous phase into the organic phase was pH dependent; a pH value between 5 and 6 appeared to be most favourable. While increased aqueous [Cl^-], [Zn^{2+}] and organic phase [TOPO] favoured Zn^{2+} extraction, temperature had little effect. The experimental data suggested that aqueous Zn^{2+}/Cl^- solutions contacted with organic TOPO/toluene might be a feasible hydrometallurgical route for zinc extraction.

INTRODUCTION

In recent times, the search for organic based metal extractants with low aqueous solubility, and for optimum conditions for metal recovery from leached liquors and industrial effluents have continued to receive serious attention from both the commercial and environmental points of view [1,2]. Many organophosphoric acid derivatives have been used as industrial extractants for metals [1,3,4]. For example, the solvating tri-alkyl phosphate, tri-n-butyl phosphate (TBP) is well known for its role in nuclear fuel processing [4-7]. These phosphate esters have been noticed to be quite compatible with a variety of water-insoluble organic diluents, and to show acceptable stability under ordinary processing conditions [4]. Moreover, the solubility of this group of extractants could be made adequately low by the use of sufficiently long alkyl chains, thus minimizing both extractant loss and possible environmental contamination.

Although the understanding of both the process equilibria and kinetics are essential for any process development in hydrometallurgy; these are subject to many variables with regard to the composition of the aqueous and organic phases. The possibility of controlling these process variables, however, makes solvent extraction a powerful separation technique that is now known to play a major role in metal processing [1,2,8]. The success of a solvent extraction process is also known to be strongly dependent on the selection of the most appropriate solvent [9].

Some of the parameters that could influence the extraction of Zn^{2+} by TBP had been previously investigated, and an optimum operating condition proposed [10]. The replacement of the electron--

withdrawing RO- chains of the tri-alkyl phosphate esters with the electron-releasing R- chains provides us with the tri-alkyl phosphine oxides which constitute a more powerful group of metal extractants as the ability of the phosphoryl oxygen for coordination is enhanced. It has been established for example, that TOPO extracts uranium with coefficients which are five orders of magnitude higher than those of TBP [2,3]; yet TOPO has not found much favour in industrial applications [1].

The extraction of Zn^{2+} from aqueous acid chloride solutions using TOPO has been studied under various conditions and the results are discussed in this paper.

EXPERIMENTAL

The organic extractant, TOPO was obtained from HOKKO Chemical Company Ltd, Japan; Erichrome Black T indicator from East Anglia Chemicals; EDTA from May and Baker; ammonia from Paul Hill Ltd; toluene, HCl and $ZnCl_2$ were from BDH. Except for EDTA which was of Analar grade, all the chemicals were of laboratory grade and they were used as supplied.

Zn^{2+} in the aqueous phase was determined by EDTA titration [11] while zinc in the organic phase was first stripped back into the aqueous phase with 2 M H_2SO_4 before titration. Since good mass balance was obtained for zinc concentrations in both the aqueous and organic phases, most organic phase zinc concentrations were calculated from their corresponding aqueous values by difference. pH was measured with a KENT EIL 7020 pH meter after adjusting the aqueous phase with dilute HCl and NaOH when necessary.

To extract Zn^{2+} into the organic phase, 25 ml of the aqueous zinc solution was pipetted into a clean 250 ml separatory funnel, 25 ml of TOPO solution in toluene was then carefully run into it from another pipette. The mixture was manually shaken for two minutes while opening the stop cock intermittently to vent any pressurized air. The mixture was then shaken vigorously for five min. on a mechanical shaker (Griffins) and allowed to stand for 1-2 min. for the two phases to separate. About 20 ml of the aqueous layer was then run into a clean 250 ml beaker from which 10 ml was pipetted for EDTA titration. After running out extra 20 ml from the separatory funnel, 10 ml was pipetted from the organic layer and contacted vigorously with 20 ml 2 M HCl in another separatory funnel. After running the aqueous layer into a beaker, the organic phase was contacted with a fresh 20 ml 2M HCl. The combined aqueous extract was then titrated with EDTA. All experiments were carried out at room temperature $(28 \pm 2)°$ except when the effect of temperature was being investigated and some experiments were subsequently carried out after thermostating the aqueous and organic phases for 1 hr and their mixture for 30 min. in a water bath at temperatures ranging between 25 and 50°.

RESULTS AND DISCUSSION

The major results for the extraction of Zn^{2+} into TOPO are illustrated by Figures 1-5 and partly by Tables 1. For brevity, the data from which the percentage metal extraction (E%) and the distribution coefficient (D) were calculated are presented in Table 1.

Table 1: Effect of aqueous ph on the degree of extraction of Z^{2+} with TOPO.

pH	$[Zn]_a$ mmol/dm^3	$[Zn]_b$ mmol/dm^3	D	E (%)
2.00	6.00	4.50	0.75	42.86
3.00	4.90	5.60	1.14	53.33
4.00	2.05	8.45	4.12	80.48
5.00	1.03	9.47	9.19	90.19
7.00	1.06	9.44	8.91	89.81

$[Zn^{2+}] = 0.01$ M, $[TOPO]_0 = 0.10$ M, $[Cl^-]_a = 0.10$ M, T = 28°

From Table 1, it is observed that E% increased with increase in pH and appeared to reach a maximum between the pH values of 5 and 6 (see Figure 1). The tendency for the degree of metal extraction to fall at high pH has been noticed by several workers [1] and this observation has invariably been attributed to the possibility of the metal cation getting hydrolysed at high pH. Zinc being amphoteric, the possibility of forming non-extractable negative zincate ions would be more pronounced at high pH. At low pH, TOPO can also solvate protons to give rise to the extraction of acids [1, 2].

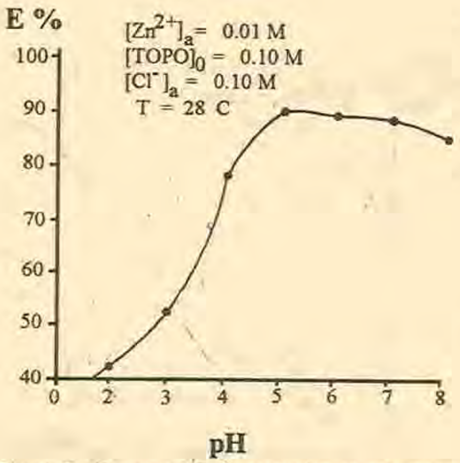

Figure 1. Degree of Zn^{2+} extraction as a function of pH.

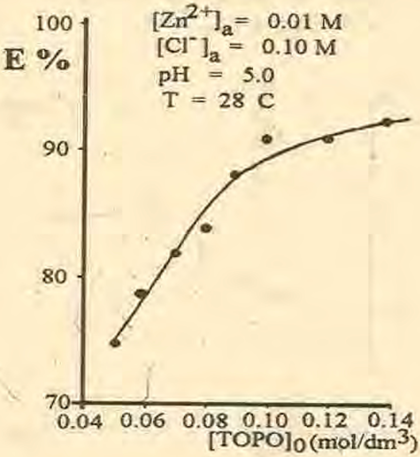

Figure 2. Degree of Zn^{2+} extraction as a function of organic phase TOPO concentration

Figure 2 shows that the extraction coefficient of zinc increased with increase in the extractant concentration in the organic phase, This trend has also been observed for some other metal solvent extraction systems [1,2]. Apart from the extractant being more available for metal complexing at high concentration, a relatively large concentration of the extractant could also lead to further solvation of the metal-extractant complex by the extractant molecules and this would enhance the solubility of the complex in the organic phase and thus prevent third phase formation. The non-linear increase in the degree of zinc extraction with increase in TOPO concentration might also be due to dimerization or polymerisation of the extractant in the inert solvent, toluene, at high concentration as previously observed by many workers [1].

When the concentration of Zn^{2+} in the aqueous phase was varied, the degree of metal extraction increased gradually with increase in aqueous metal concentration until the aqueous Zn^{2+} concentration was between 0.008 and 0.01 M and subsequently went down very gradually (Figure 3). High aqueous metal concentration did not appear to lead to corresponding high degree of metal extraction. Raman spectra have shown [12] that depending on the concentration, the species in aqueous solution of $ZnCl_2$ are $(Zn(H_2O)_6)^{2+}$, $ZnCl^+$, $ZnCl_2$ and $(ZnCl_4(H_2O)_2)^{2-}$. Except $ZnCl_2$, other complexes cannot be readily extracted into TOPO because of their charges.

It was noticed that the higher the aqueous Cl^- concentration the better the degree of Zn^{2+} extraction as shown by Figure 4. The hydrated Zn^{2+} ion in the aqueous medium would normally have little or no tendency to transfer into the organic phase. However, high concentration of Cl^- would convert the metal ion into an extractable species by having the charges on zinc neutralised and at the same time replacing some of the water of hydration, thus making the zinc complex more hydrophobic. This explanation is, however, limited by the fact that when the concentration of Cl^- becomes too high, inextractable negatively charged complexes could also be formed and this would tend to lower the degree of extraction. Since TOPO also extracts mineral acids independently [2], this could be another contributing factor why high concentration of Cl^- might be necessary during zinc extraction with TOPO.

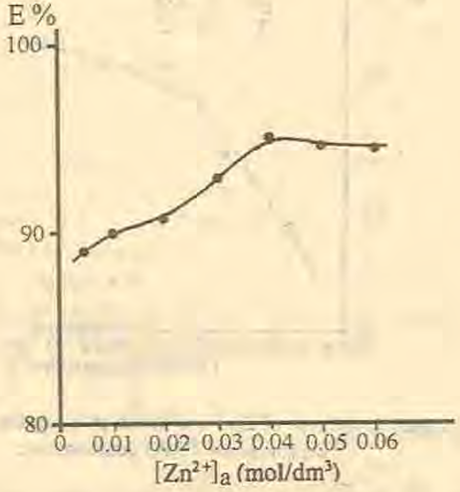

Figure 3. Degree of Zn^{2+} extraction as a function of aqueous zinc concentration.

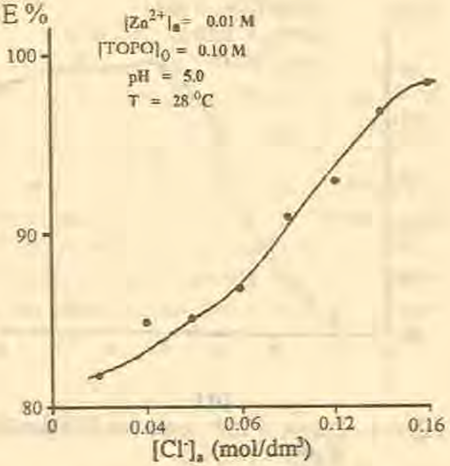

Figure 4. Degree of zinc extraction as function of aqueous chloride concentration.

The effect of temperature on the equilibrium extraction of Zn^{2+} was minimal. It appears that a process plant for Zn^{2+} extraction based on TOPO might be run at room temperature. This would save energy and consequently lower the production cost. However, detailed kinetic study would be necessary before a definite conclusion on the effect of temperature can be pronounced.

In general, the distribution coefficients at various operating conditions are higher for zinc extraction using TOPO rather than TBP [10]. TOPO might therefore be a more competitive extractant for Zn^{2+} than TBP if the kinetics of the process is also more favourable. TOPO, unlike TBP which is a liquid, has the additional advantage of being a solid, thus making packaging and transportation easier.

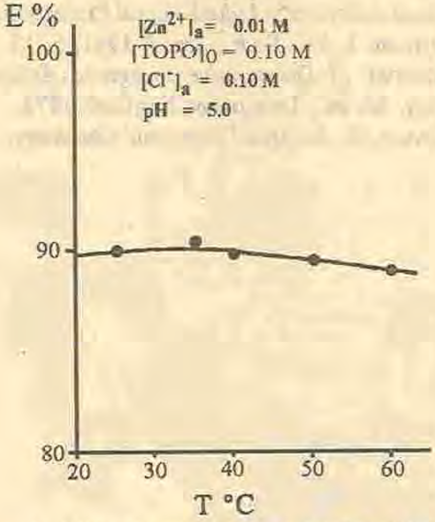

Figure 5. Effect of temperature as a function of the degree of zinc extraction.

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