Hydrometallurgy 100 (2010) 116–121

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Solvent extraction of zinc from ammoniacal/ammonium chloride solutions by a sterically hindered β-diketone and its mixture with tri-n-octylphosphine oxide

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A R T I C L E I N F O

Article history:
Received 5 August 2009
Received in revised form 28 October 2009
Accepted 28 October 2009
Available online 5 November 2009

Keywords:
Solvent extraction
Zinc
Ammonia
Ammonium chloride
Sterically hindered β-diketones
TOPO
Synergism

A B S T R A C T

The extraction of zinc from ammoniacal/ammonium chloride solutions using a sterically hindered β-diketone, 4-ethyl-1-phenyl-1,3-octadione (XI-55, HA) as the extractant has been investigated in the presence or absence of tri-n-octylphosphine oxide (TOPO, B). The results indicate that the mixture of XI-55 and TOPO shows evident synergistic effects on zinc extraction. Zinc is extracted as ZnA_2B by the mixture and the stability constant of ZnA_2B is 2.08. Thermodynamic parameters ΔH, ΔS and ΔG are determined, which shows that the extractions of zinc by both XI-55 extraction system and the XI-55–TOPO synergistic extraction system are exothermic driven. The concentration of total ammonia has great influence on the extraction constants and distribution ratio for both extraction systems. FT-IR studies on zinc loaded organic phases confirm the non-extractability of zinc ammine complexes.

1. Introduction

In the last 50 years, there has been an upsurge of interest in the ammonia leaching process as a means of recovering zinc from difficult or intractable feedstocks such as feeds having basic gangues with high acid consumption (Wang et al., 2008); low-grade feeds or tailings where flotation and other means of separation have had limited success (Buckett et al., 1998); zinc-containing waste from galvanizing operations (Kasai et al., 1987; Lozano Blanco et al., 1999); and zinc-containing dust that is given off during steelmaking (Dreisinger et al., 1990; Nyirenda and Lugtmeijer, 1993). Ammonia is an attractive lixiviant due to its high complexation characteristics with zinc, low toxicity, low cost and ease of regeneration by evaporation. Furthermore, the major waste components in ores, such as Fe_2O_3, SiO_2, CaO and MgO are insoluble in ammoniacal solutions which allow selective zinc extraction (Meng and Kenneth, 1996).

Solvent extraction is useful for the recovery of zinc from the leaching solutions (Akash and de Carvalho, 2008) and organo-phosphorus extractants are definitely the widely recognized Zn(II) extractants. Some of the reagents of this category, namely DEHPA, PC-88A, CYANEX 272, and CYANEX 301, offer strong extraction of Zn(II) from acidic media. However, there is no available information concerning the extraction of zinc from ammoniacal solutions ($pH>7$) using organo-phosphorus extractants, because of their low p*K*a values (2.85–3.73), which increases their aqueous solubility in alkaline media.

β-diketones are a versatile class of chelating agents employed for the analytical separation of metal ions. In particular, a commercial reagent (LIX 54) extracts copper from ammoniacal leaching solutions and offers some advantages including low loading of ammonia and ease of stripping and faster kinetics (Gameiro et al., 2008). Alguacil and Alonso (1999) have studied the extraction of zinc from ammonium sulphate solutions using LIX 54 whilst Rao et al. (1992) carried out a similar investigation with Hostarex DK-16 (a commercial reagent similar to LIX 54). Unexpectedly, it has recently been found at the Escondida plant that LIX 54 reacts with ammonia to give surface active molecules which appear to increase the entrainment of aqueous in the loaded organic (with the resulting carryover of ammonia to the wash stage) and to decrease the copper stripping kinetics (Kordosky et al., 1999). To overcome this problem, Cognis designed several sterically hindered extractant molecules, called XI-55 and XI-57, which do not react with ammonia in the manner of LIX 54 (Kordosky et al., 2002). However, compared with copper, zinc is very difficult to recover from its ammoniacal solutions using β-diketone extractants (Przeszlakowskia and Wydr, 1982).

In many extraction systems of zinc β-diketone chelates, the presence of some neutral organic Lewis bases significantly enhances the extractability (Jerome and O'Brien, 1975; Sekine et al., 1974). Such phenomena, called “synergistic effect” can be explained by adduct formation between the zinc chelates and the Lewis bases. Shigematsu et al. (1970) have found that the stability of zinc adducts with oxygen-containing Lewis bases increases in the order, n-hexyl alcohol<TBP

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doi:10.1016/j.hydromet.2009.10.013

(tributylphosphate) < TBPO (tri-n-butylphosphine oxide) ≈ TOPO (tri-n-octylphosphine oxide), which is the same with that of the basicity of the Lewis bases. Therefore, TOPO especially gives rise to a large synergism in comparison with other oxygen-containing Lewis bases.

In the present work, the extraction behavior of zinc with 4-ethyl-1-phenyl-1, 3-octadione (XI-55 and HA) from ammoniacal chloride media was studied in the presence or absence of TOPO, contrary to the majority of research in ammoniacal sulphate systems. It was chosen because concentrated ammonium chloride is an effective leaching agent for recovery of zinc from secondary materials (Allan, 1995; Olper et al., 1993) and complex sulfide ores (Amer et al., 1995). The extracted complexes and their extraction constants were obtained together with the effects of the ratio of the synergist (TOPO), the aqueous acidity, experimental temperature and the concentration of total ammonia.

2. Experimental

2.1. Reagents

The 4-ethyl-1-phenyl-1,3-octadione (XI-55) was made by Claisen condensation of acetophenone and methyl 2-ethylhexanoate in the presence of sodium hydride (Swamer and Hauser, 1950). The crude product was acidified with sulfuric acid, washed with water and brine and dried by passing through anhydrous sodium sulphate. Vacuum distillation (11.84 mm Hg) yielded the product in the middle cut (97.8% pure; 58% yield; and bp:152–155 °C). The extraction diluent was a type of sulphonated kerosene purchased from Shanghai Rare-Earth Chemical Co, Ltd, having the following specifications: aromatics 4%; density 0.810 g/cm^3 (20 °C); boiling range 198–247 °C and flash point 65 °C. Tri-n-octylphosphine (TOPO) was purchased from J&K Chemical Ltd. All the other reagents used in this work were of A.R. grade, obtained from Sinopharm Chemical Reagent Co, Ltd.

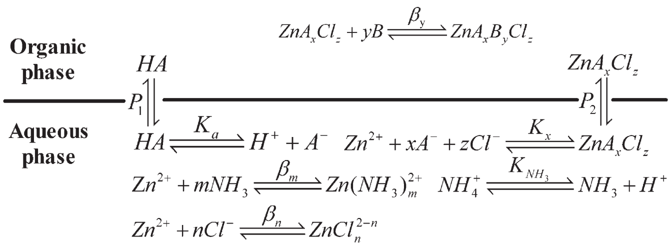
2.2. Extraction and analytical procedures

The extractions were performed using a batch technique in thermostat vessels at 298 ± 0.5 K. Equal volumes (10 mL) of aqueous and organic phases were equilibrated over 30 min and pH adjustment of the aqueous phase was performed by adding NaOH solution (pHs-3C digital pH meter, Shanghai Rex Instrument Factory, China). The zinc content of the aqueous phases was analyzed by ICP (inductively coupled plasma) (Perkin-Elmer Optima 5300) and the metal concentration in the organic phase was calculated by mass balance. FT-IR spectra were recorded on a Thermo Scientific Nicolet 6700 spectrometer using KBr windows.

3. Theory

When zinc ion in ammoniacal/ammonium chloride solution reacts with 4-ethyl-1-phenyl-1,3-octadione (XI-55 and HA), it is extracted as the neutral chelate, ZnA_xCl_z and forms the synergistic adduct compounds, $ZnA_xB_yCl_z$, with an organic base, tri-n-octylphosphine (TOPO, B), the overall extraction processes can be written as shown in Scheme 1.

In this scheme, β_y, P_1, P_2, K_a, K_x, K_{NH3}, β_m and β_n represent respectively the stability constant of the adduct, the partition coefficient of HA, the partition coefficient of the zinc complex, the acid dissociation constant of HA, the complex formation constant of a zinc ion with ligand anions, the disassociation constant of ammonium ions, the formation constant of the zinc ammine complexes and the formation constant of the zinc chloride complexes. The last two formation constants of zinc complexes were presented in Table 1 (Smith and Matell, 1976).



Scheme 1. The overall extraction processes.

3.1. XI-55 extraction system

The distribution ratio in the absence of TOPO is described as:

$$D_{ex} = \frac{[ZnA_xCl_z]_{org}}{[Zn^{2+}]_T + [ZnA_xCl_z]_{aq}} \tag{1}$$

$$\begin{aligned}\left[Zn^{2+}\right]_T &= \left[Zn^{2+}\right] + \sum_{m=1}^{4}\left[Zn(NH_3)_m^{2+}\right] + \sum_{n=1}^{4}\left[Zn(Cl)_n^{2-n}\right]\\ &= \left[Zn^{2+}\right]\cdot\left(1+\sum_{m=1}^{4}\beta_m\left(\frac{[NH_3]_{total}\cdot K_{NH_3}}{[H^+]+K_{NH_3}}\right)^m + \sum_{n=1}^{4}\beta_n[Cl^-]^n\right)\\ &= \left[Zn^{2+}\right]\cdot f\end{aligned} \tag{2}$$

Where $[NH_3]_{total} = [NH_3] + [NH_4^+]$,

$$f = 1 + \sum_{m=1}^{4}\beta_m\left(\frac{[NH_3]_{total}\cdot K_{NH_3}}{[H^+]+K_{NH_3}}\right)^m + \sum_{n=1}^{4}\beta_n[Cl^-]^n;$$

By introducing P_1, P_2, K_a, K_x and Eqs. (2) and (1) can be rewritten as:

$$D_{ex} = \frac{K_x\cdot K_a^x\cdot P_2}{P_1^x}\cdot\frac{[Cl^-]^z\cdot[HA]_{org}^x}{f\cdot[H^+]^x} \tag{3}$$

Taking logarithms in Eq. (3):

$$\log D_{ex} = \log\left(\frac{K_x\cdot K_a^x\cdot P_2}{P_1^x}\right) + z\log[Cl^-] + x\log[HA]_{org} + xpH - \log f \tag{4}$$

The extraction constant, K_{ex} is described as:

$$Zn^{2+} + xHA_{(org)} + zCl^- \rightleftharpoons ZnA_xCl_{z(org)} + xH^+$$

for which

$$K_{ex} = \frac{[ZnA_xCl_z]_{org}\cdot[H^+]^x}{[Zn^{2+}]\cdot[HA]_{org}^x\cdot[Cl^-]^z} = \frac{K_x\cdot K_a^x\cdot P_2}{P_1^x} \tag{5}$$

Table 1
Critical stability constants of zinc complexes at $T = 298$ K.

Species	Logβ_m	Species	Logβ_n
$Zn(NH_3)^{2+}$	2.38	$ZnCl^+$	0.10
$Zn(NH_3)_2^{2+}$	4.88	$ZnCl_2$	0.06
$Zn(NH_3)_3^{2+}$	7.43	$ZnCl_3^-$	0.10
$Zn(NH_3)_4^{2+}$	9.65	$ZnCl_4^{2-}$	0.30