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Stoichiometry and structural studies of Fe(III) and Zn(II) solvent extraction using D2EHPA/TBP

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The extraction equilibrium of Zn(II) and Fe(III) from chloride solution by the mixture of TBP (tri-n-butyl phosphate) and D2EHPA (di(2-ethylhexyl) phosphoric acid), diluted in kerosene was studied. The results show that in TBP to D2EHPA volume ratio of 3:1 (0.55 M TBP:0.15 M D2EHPA) $\Delta pH_{0.5}$ increased to about 2.5 and Fe(III) and Zn(II) extracted separately with the percentage extraction of 99% and 80%, respectively. The Fourier transform infrared (FTIR) measurements were used in order to find the possible structural functionalities of extracted species in the organic phase. Moreover, the FTIR measurements indicated that there was a hydrogen bond between TBP and D2EHPA molecules. According to FTIR studies and slope analysis method, the reaction between TBP, D2EHPA and zinc was determined and the FTIR-ATR (attenuated total reflectance) method was also employed to verify the stoichiometry of Zn(II) - organic complexes in the organic phase. Both FTIR-ATR and slope analysis methods provided the same results that the $ZnA_2AH{\cdot}TBP$ was probably the extracted specie in the organic phase.

1. Introduction

Zinc is one of the important base metals that has applications in metallurgical industries such as in galvanizing of metal sheets and steelmaking [1–3]. A major portion of zinc is wasted through hot dip galvanizing plants, electric arc furnace in the forms of flue dusts, zinc ash, zinc dross, etc. [1]. Leaching of zinc from some of these secondary materials is carried out with certain concentration of hydrochloric acid. Thus, this kind of waste liquor containing different concentration of heavy metal species like Pb, Ni, Cu and Mn [4,5] in chloride media causes significant environmental and economic issues [6]. Although zinc in the secondary materials contains several different metals based on the sources, it is invariably associated with iron [1,7]. Both zinc and iron have been considered as valuable and useful metals in several applications [1–3]; thus, recycling of them has resulted in consuming less energy compared with primary metals production and also in conserving raw materials [1]. Several pyrometallurgical and hydrometallurgical techniques have been used to extract zinc and iron separately from waste liquors [3]. The pyrometallurgical processes such as Waelse [10] suffer from drawbacks such as high energy consumption and large amount of residue production. For these reasons, hydrometallurgical processing comes to prominence [1].

Selective extraction of zinc and iron has been considered by several authors recently [8–10], and the solvent extraction (SX) has been known as a widely used clean hydrometallurgical separation technique [11,12]. Authors have previously employed several extracting agents in order to recover both zinc and iron from chloride solutions [1-3-8-10]. The main extracting agent used in zinc and iron extraction is di(2-ethylhexyl) phosphoric acid (D2EHPA) [13–16]. Regardless of advantages associated with using D2EHPA, it comprises some problems which the poor selectivity for zinc (II) over Fe(III) is the most important of them [17]. Due to the fact that a high concentration of hydrochloric acid is required, the stripping of Fe(III) from D2EHPA has some difficulties like dissolving heavy metals [18,19] and financial problems in macro scale [12,13]. It has been reported that tri-n-butyl phosphate (TBP) is the most effective extracting agent one for Zn(II) extraction and stripping [9–20]. However, a considerable amount of TBP (from 80 to 100 vol.%) is needed to show a high percentage extraction which is not economically comparable with D2EHPA [18]. It should be mentioned that the major disadvantage of using TBP is its hydrophilicity which leads to the transfer of a considerable amount of water to the organic phase [20,21].

To boost the efficiency of selective extraction and decrease the co-extraction of Fe(III), synergistic effect of D2EHPA and TBP has

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been studied [10,17]. Adding TBP to D2EHPA as a second component has resulted in synergistic shifts in Zn(II) and Fe(III) isotherms enhancing their separation [17]. Darvishi et al. [15] found out the isotherms shifting in metals (Zn, Cd, Mn, Cu, Co and Ni) extraction by adding TBP to D2EHPA resulted from the interaction between TBP and D2EHPA by investigating the solvent extraction mechanism. In order to select proper extracting agent(s), it is highly beneficial to find out the mechanism of solvent extraction including stoichiometry of extracting agent species, identification of newly formed bonds (interaction between metal ions and extracting agent or interaction between extracting agents in synergistic studies), etc.

Previously, researchers have focused on stoichiometry of extracting agent species explaining the mechanism of SX [15,22–24]. The equilibrium slope [22,23] and the numerical analysis [13] are two widely known methods for determining the stoichiometry of metal-organic complexes in the organic phase. Utilizing these methods, the stoichiometry of extraction equation has only been explained and the explanation of newly formed bonds and their properties in the organic phase have been neglected. Fourier Transform Infrared (FT-IR) was developed in order to overcome the limitations encountered with previous methods. It provides a method for identifying chemical bonds (functional group and covalent bonds) in an organic or inorganic molecule [13,25]. Saniz-Diaz et al. proposed quantitative FT-IR for finding the number of D2EHPA molecules that are required for extracting one zinc atom, by considering the height of peaks, especially the highly polar bond in the organic phase which is P═O in the phosphoric acid extracting agents like D2EHPA [25]. Chang et al. also used the similar way with higher accuracy, in which he used FTIR-ATR method for clarifying the stoichiometry of Cu extracted specie by D2EHPA [13].

The aim of our research is to provide an explanation of SX mechanism of synergistic extraction and separation of Fe(III) and Zn(II) using TBP and D2EHPA. Therefore, both qualitative and quantitative analyses have been used. For qualitative analysis, FT-IR measurement was used on each individual extracting agent, diluent and their mixture in order to anticipate new bonds in organic phase and their structures of the resultant species. Regarding the quantitative analysis, both slope analysis and FTIR-ATR methods were used and their results were compared, for more accuracy. The stoichiometry and the structures of Zn(II) and Fe (III)-organic complexes were also determined.

2. Experimental

2.1. Materials

Iron (III) chloride hexa-hydrate (99% pure) and zinc chloride (98% pure) were obtained from Merck, Germany. The organic solvents used in this work were industrial-grade D2EHPA (97% pure) from Bayer, Germany, and TBP (99% pure), from Merck, Germany. The extracting agents were used without further purification. Kerosene, from Tehran Oil Refinery Co., was used as diluent. Hydrochloric acid (37% pure) and sodium hydroxide pellets, from Merck, Germany, were used as pH modifiers.

2.2. Equipment

A magnetic stirrer (IKA, RH basic 2) was used to mix the aqueous and organic phases while a pH meter (Sartorius, PY-11) was applied to monitor the pH of aqueous solution during the experiments. The metals concentration in aqueous phases were analyzed by atomic absorption spectrometer (AAS) (Varian, AA240) and the concentration of zinc ions in the organic phase was calculated from the difference between concentrations in the aqueous phase by mass balance before and after extraction. In order to examine functional groups in organic phases before and after solvent extraction, FT-IR spectrometer (Perkin-Elmer, spectrum two) with KBr optical windows was used. FT-IR spectra were recorded at 0.5 $\mathrm{cm^{-1}}$ resolution. For identifying the stoichiometry of the SX reactions, the intensity of highly polar band in the organic phases were recorded on 4 $\mathrm{cm^{-1}}$ resolution by an attenuated total reflectance - Fourier transform infrared (FTIR - ATR) spectroscopy (Bruker, equinox 55).

2.3. Experimental procedure

Synthetic aqueous solution of Zn(II) and Fe(III) with a concentration of 2 $\mathrm{g\,L^{-1}}$ each [15] was prepared by dissolving sufficient amount of Fe(III) chloride and zinc chloride in distilled water. The organic phase composition comprises 20 vol.% of the extracting agent (either D2EHPA or the mixture of D2EHPA and TBP) and 80 vol.% kerosene. This aqueous to organic phase ratio (A/O) of 1:1 was used in all the tests. All the SX tests were conducted at ambient temperature. The pH was adjusted by adding either hydrochloric acid or sodium hydroxide solution. Then, phases were mechanically shaken at stable pH and temperature. The shaking time was found to be sufficient to reach equilibration at 10 min for extraction [19]. Phases were separated by settling down the solution mixtures.

2.4. Treatment of extraction data

The percentage extraction (%E) of Zn(II) and Fe(III) ions were given by:

$$\%E = \frac{[C]_{i,aq} - [C]_{f,aq}}{[C]_{i,aq}} \times 100\% \tag{1}$$

where $[C]_{i,aq}$ and $[C]_{f,aq}$ indicate the initial and final concentration of metal ions in the aqueous phase, respectively. The distribution ratio (D) was calculated by:

$$D = \frac{[C]_{org}}{[C]_{aq}} \tag{2}$$

where $[C]_{org}$ and $[C]_{aq}$ are the concentration of metal ions in organic and aqueous phase, respectively.

3. Results and discussion

3.1. Extraction studies

Investigations were carried out to determine the optimum condition for the selective extraction of Zn(II) and Fe(III) with proper extracting agent. The extraction isotherms for Zn(II) and Fe(III) in D2EHPA, TBP and their mixtures are shown in Fig. 1. It is obvious that D2EHPA (0.6 M) illustrates poor selectivity for Zn(II) over Fe (III) in the pH range of 1.5–2.5. On the other hand, TBP (0.73 M) has extracted less metal ions compared with D2EHPA. As can be seen in this figure, the mixture of D2EHPA and TBP at ratio of 1:3 (0.15 M D2EHPA:0.55 M TBP) resulted in a selective extraction of Zn(II) over Fe(III). The $\Delta pH_{0.5}$ (difference between $pH_{0.5}$ for iron and zinc) in this volume ratio is about 2.5. Furthermore, iron was extracted over 99% and zinc was extracted about 80%. Adding a neutral extracting agent such as TBP which have extra coordination sites can boost solvent extraction of metal chelates [18,19]. TBP has a lone electron pair and can form adduct complexes with acidic extracting agents such as D2EHPA, in the organic phase [18,19]. It should be mentioned that addition of TBP resulted in a decrease in the concentration of D2EHPA required for Fe(III) and Zn(II) extraction as mentioned by Darvishi et al. [15].