



## Synergistic extraction of vanadium(IV) in sulfuric acid media using a mixture of D2EHPA and EHEHPA



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### ARTICLE INFO

#### Article history:

Received 3 April 2016

Received in revised form 27 July 2016

Accepted 9 September 2016

Available online 24 September 2016

#### Keywords:

Vanadium

Synergistic extraction

Stripping

Sulfuric acid

### ABSTRACT

In the present study, the mechanisms and thermodynamics of vanadium extraction by a mixture of bis-2-ethylhexyl phosphorous acid (D2EHPA) and 2-ethylhexyl phosphorous acid mono-2-ethylhexyl ester (EHEHPA) from sulfate medium were investigated. It was found that the maximum synergistic factors obtained at  $X_{D2EHPA} = 0.2$  and the reaction of the synergistic extraction is exothermic. Results showed that the mixture system in the presence of complexing agents exhibit a higher extraction efficiency and require a lower acid consumption during the stripping process of vanadium. Fourier transform infrared (FT-IR) spectroscopy showed that P–O–H and P=O of the extractants are responsible for the synergistic extraction of  $VO^{2+}$  species by cation exchange mechanism and some hydrogen bonds between EHEHPA and D2EHPA formed in the synergistic extraction system. With the slope analysis method, the reaction of the synergistic extraction was mainly predicted.

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### 1. Introduction

Vanadium is a rare metal having strategic and industrial importance due to its wide applications in ferrous metallurgy, nonferrous metal metallurgy, aerospace, nuclear and chemical industry and other technological fields (Moskalyk and Alfantazi, 2003; Biswas and Mondal, 2003). Vanadium belongs to the VB group of the periodic table, it almost co-exists with various minerals and with low-grade under 1% (Rehder, 2003). China has the third largest vanadium reserves in the world while most of the vanadium exists as vanadium–titanium magnetite ores which would be oxidized and enriched into vanadium slag during the steel-making process in oxygen blowing converter (Yang et al., 2014). A common way to extract vanadium from vanadium slag is to roast the vanadium slag with sodium salts followed by water leaching, but it suffered from high-energy consumption, poor operation condition and hazardous gases (HCl, SO<sub>2</sub>, Cl<sub>2</sub>) emission which corrode equipment and contaminate the environment severely (Ju et al., 2015). Another applicable way is calcium roasting followed by sulfuric acid or alkaline leaching, during which vanadium slag is roasted with lime or limestone instead of sodium salts to produce calcium vanadates. This process avoid harmful gas generation with an environment-friendly roasting, but it always brings problems of low recovery rate in subsequent leaching and low purity of vanadium products due to the existence of phosphorus (Ju et al., 2015; Li et al., 2016). As an innovative hydrometallurgical trend, direct atmospheric or pressure acid leaching process to extract vanadium from vanadium slag has attracted conspicuous

attention due to high recovery rate of V and low environment pollution, in which sulfuric acid act as a commonly used leaching agent (Wang et al., 2014; Mirazimi et al., 2015; Zhang et al., 2015; Tavakoli et al., 2014) and dominant valences of V are +4 (VO<sub>2</sub><sup>+</sup>) and +5 (VO<sub>2</sub><sup>3+</sup>) in the solutions.

Since vanadium spinel is broken and extracted into the leach solution as well as other different elements in the slag during the direct leaching process, the purification step in sulfuric acid medium is always a challenging part of the production process (Tavakoli and Dreisinger, 2014). Several methods such as coprecipitation, adsorption with activated carbon, ion exchange and solvent extraction have been used to separate and purify vanadium contained solution (Chen et al., 2007; Park et al., 2006; Henry and Van Lierde, 1998). Solvent extraction is widely used to extract vanadium effectively (Jiang et al., 2015), organophosphorus extractants are the popular choices for solvent extraction of cation vanadium in sulfuric acid solution. Among them, D2EHPA seems to be the most economic and effective reagent for extracting vanadium (IV) from acid media (Remya et al., 2003). However, it suffers from a high acid consumption in stripping process as well as its poor performance in elimination of emulsion. EHEHPA as another kind of commonly used extraction agent has better stripping properties and phase-separate performance as well as excellent selectivity over some metals like molybdenum (VI), aluminium (III) and iron (II), but it has a relatively lower extraction efficiency. Compared with the properties and defects of D2EHPA and EHEHPA in the purification process of vanadium leach solution, it is a promising method to use the mixture of D2EHPA and EHEHPA as the extractant for vanadium extraction and stripping in order to eliminate the defect of each extractant. Cheraghi et al. investigated the thermodynamics and mechanisms of vanadium extraction

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by a mixture of D2EHPA and tri-*n* butyl phosphate (TBP) from sulfate medium (Cheraghi et al., 2015). Noori studied the recovery and separation of nickel and vanadium in sulfate media by solvent extraction using D2EHPA, Cyanex 272 and their mixtures in various proportions (Noori et al., 2014). But no report studied the synergistic extraction of vanadium with mixture system of D2EHPA and EHEHPA in sulfate media. Since the separation between V(IV) and Fe(III) is very important for V extraction and the extraction selectivity order of organophosphorus extractants is  $\text{Fe}^{3+} > \text{VO}^{2+} > \text{VO}^{2+} \gg \text{Fe}^{2+}$  in sulfate media, it is necessary to use a reducing agent to reduce ferric iron to iron as well as to reduce pentavalent vanadium to tetravalent vanadium in order to increase the separation performance between vanadium and iron. Considering that the valence state of vanadium has always been vanadium (IV) after the reduction treatment in sulfate media, the synergistic extraction behaviors of vanadium (IV) with mixture systems of EHEHPA and D2EHPA were intensively investigated in this article. The synergistic effect, the extraction mechanism of vanadium (IV), Fourier transform infrared (FT-IR) spectroscopy and the thermodynamic parameters of the synergistic extraction were investigated.

## 2. Experimental

### 2.1. Materials

D2EHPA and EHEHPA were kindly supplied by Kopper Chemical Industry Co., Ltd. (CN). All the extractants were used without further purification and dissolved in sulfonated kerosene provided by Hubei Seven Eight Nine Chemical Co., Ltd., China to the required concentrations. The stock solutions were prepared by dissolving  $\text{VO}_2\text{SO}_4$  (Aladdin, Shanghai) in sulfuric acid ( $\text{H}_2\text{SO}_4$ ) to required concentration, pH of the aqueous phase was adjusted by the addition of  $\text{H}_2\text{SO}_4$  or sodium hydroxide (NaOH) solutions. The initial V (IV) concentrations were maintained at 0.1 mol/L or 0.01 mol/L. A constant ionic strength (1.0 mol/L) adjusted by NaCl was used for all extraction experiments. All the other reagents and chemicals used were of analytical reagent grade.

### 2.2. Methods and apparatus

Solvent extraction and stripping tests were carried out in a 60 mL separatory glass funnel reactor fixed in a gas bath thermostatic oscillator ( $60 \pm 5^\circ\text{C}$ ) at a shaking speed of 130 rpm. Preliminary results showed that the extraction can reach equilibrium after mixing 30 min, so the synergistic extraction experiment was conducted by mechanically shaking for 60 min at  $25^\circ\text{C}$  with equal volumes of aqueous and organic solutions (20 mL) unless otherwise stated. After extraction of V (IV) by the extractants, the loaded organic phase was equilibrated with  $\text{H}_2\text{SO}_4$  solutions of different concentrations for 10 min with equal volumes of aqueous and organic solutions. After the phases were separated by gravity, the concentration of V (IV) in the aqueous phase was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) and the concentration in the organic phase was obtained by mass balance, the distribution ratio  $D$  and stripping rate  $S$  were calculated by Eqs. (1)–(2). A PHS-3F digital pH meter was used to measure the pH of the aqueous solutions. The Fourier transform infrared (FT-IR) spectra of the organic system were obtained with an FT-IR spectrometer (Nicolet 6700, USA) and all measurements were done with a cell equipped with KBr windows. Their spectra were recorded with a resolution of  $2\text{ cm}^{-1}$  with 32 scans in the wave number range of  $4000\text{--}400\text{ cm}^{-1}$ .

$$D = \frac{C_{\text{Org}}}{C_{\text{Aqu}}} \quad (1)$$

$$\%S = \left(1 - \frac{C_{\text{Org}}}{\bar{C}_{\text{Org}}}\right) \quad (2)$$

where  $C_{\text{Org}}$  and  $C_{\text{Aqu}}$  are the concentration of metal in equilibrated organic phase and equilibrated aqueous phase, respectively, g/L;  $\bar{C}_{\text{Org}}$  is the concentrations of metal in original organic phase in the stripping process.

## 3. Results and discussions

### 3.1. Synergistic extraction effect of V (IV) with mixture of D2EHPA and EHEHPA

The synergistic factors ( $R$ ) of vanadium (IV) (0.01 mol/L, 0.1 mol/L) extraction at variant equilibrium pH and with different mole fractions of D2EHPA are shown in Tables 1 and 2, whereas the total concentration of D2EHPA and EHEHPA was fixed at 1 mol/L,  $X_{\text{D2EHPA}}$  represents the mole fraction of D2EHPA in the organic phase, and the synergistic factors,  $R$ , can be obtained according to Eq. (3) (Zhang et al., 2014).

$$R = \frac{D_{\text{mix}}}{D_A + D_B} \quad (3)$$

where  $D_A$ ,  $D_B$  and  $D_{\text{mix}}$  represents the distribution ratios when V (IV) is extracted by D2EHPA and EHEHPA, and their mixtures, respectively.

According to Table 1, with the decrease of  $X_{\text{D2EHPA}}$ , the synergistic factor increase under variant acidity conditions but decrease at the equilibrium pH = 1.8. It can be explained by that the vanadium (IV) of low concentration was almost fully extracted into the organic phase under the favorable extraction condition of low acidity, so the extraction enhancement effect disappear and the value of  $R$  obtained was less than 1. The synergistic factors in Table 2 increased with the decrease of  $X_{\text{D2EHPA}}$  under variant acidity conditions, which has the same variation tendency as that of Table 1. These above indicate that a higher synergistic factor value can be obtained when  $X_{\text{D2EHPA}} = 0.2$  and under a suitable acidity condition.

The distribution ratios of vanadium (IV) in given pH condition are shown in Fig. 1 ( $[\text{VO}^{2+}] = 0.01\text{ mol/L}$ ) and Fig. 2 ( $[\text{VO}^{2+}] = 0.1\text{ mol/L}$ ). Considering the  $\Delta D$  value (difference) between  $D_{\text{mix}}$  and ( $D_A + D_B$ ) represent the increase of  $D$  after mixing extractants in the extraction system, the  $\Delta D$  value can intuitively reflect the enhancement of the synergistic extraction on the other side. It can be seen from Fig. 1 that the  $\Delta D$  value reach maximum when  $X_{\text{D2EHPA}} = 0.2$ , then it decreases obviously with the increase of  $X_{\text{D2EHPA}}$ . As shown in Fig. 2 that  $\Delta D$  value reach the maximum when  $X_{\text{D2EHPA}} = 0.2$ , then it decreases slightly with the increase of  $X_{\text{D2EHPA}}$  and rise again when  $X_{\text{D2EHPA}} = 0.8$ . The  $\Delta D$  values in Fig. 2 are generally larger comparing to Fig. 1 with different  $X_{\text{D2EHPA}}$ , which indicated the extraction system has a better synergistic effect for stock solution with appropriate concentration.

### 3.2. Synergistic extraction mechanism of V (IV) with mixture of D2EHPA and EHEHPA

Organophosphorous-based acidic extractants exit as dimers in nonpolar organic diluents. The extraction of vanadium (IV) from aqueous sulfuric media by organophosphorous-based acidic

**Table 1**  
Synergistic factor of vanadium (IV) ( $[\text{VO}^{2+}] = 0.01\text{ mol/L}$ ) at different equilibrium pH and D2EHPA mole fraction.

$X_{\text{D2EHPA}}$ Equilibrium pH	0.2	0.4	0.6	0.8
1.2	1.55	1.38	1.12	1.08
1.4	1.32	1.13	1.03	1.03
1.6	1.25	1.10	1.02	0.99
1.8	0.62	0.70	0.82	0.93

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