



Insights into the extraction of various vanadium species by primary amine



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ABSTRACT

For the purpose of the recovery of the high-purity vanadium product in leaching solution, solvent extraction has been considered as a promising approach. However, the vanadium species varied in different concentrations and pH values in aqueous solution, thus affecting the extraction yield or the reaction product in the process. In this paper, the main species of vanadium in solutions were determined with the equilibrium constants. The extraction reactions were determined based on determined species, then the hydrogen bond association mechanism of the reaction as well as the possible structures of the vanadium complexes were proposed and discussed in detail. This study established a systematic methodology for understanding the transition metal speciation in aqueous solutions as well as the extraction reactions, and envisaged the insights into the mechanism of the transition metal solvent extraction by primary amines.

1. Introduction

Vanadium, which is the 22nd most abundant element in the earth's crust (Moskalyk and Alfantazi, 2003), has a constantly increase in industrial applications, especially in high-tech fields such as photocatalysis (Li et al., 2015), electrochemical and fuel cells (Tong et al., 2017; Yin et al., 2015). However, vanadium and its compounds can accumulate in the body through many routes and thus are harmful to animals and humans, sometimes even fatal (Mutlu et al., 2016). Therefore, it is significant to recover vanadium cleanly, purely, efficiently and economically from the low grade minerals as well as wastewater.

Currently, several efforts have been devoted to the recovery of vanadium in aqueous solution (Sporeen et al., 2016; Weinhardt and Hixson, 1951; Zhao et al., 2015), such as ion exchange and solvent extraction. The ion exchange method, despite of its wide application, still suffers from the less purity of vanadium product and the generation of much waste water (Zeng and Cheng, 2009). Solvent extraction, with the advantages of larger capacity, higher selectivity and wider operation scope, has been proposed as a more effective approach to recover vanadium from the aqueous solution. Primary amine, as an extractant owning two active H atoms and one active N atom, can extract vanadium selectively in priority from the wastewater containing vanadium and chromium simultaneously (Jing et al., 2017a; Lozano and Godí, 2003; Ning et al., 2014; Ning et al., 2016), and the high-performance

recovery of vanadium in leaching solution by primary amine N1519 has been investigated before (Jing et al., 2017b).

However, detailed probing on the reaction mechanism and industrial feasibility still remains a big issue. The chemistry of vanadium is complex due to the existence of many polynuclear species. Meanwhile, the species of vanadium varied with the concentrations and pH values in aqueous solution, thus affecting the extraction yield as well as the reaction product. Therefore, the species in the aqueous solution of vanadium, need to be confirmed accurately, otherwise it will mislead the determination of extraction complexes.

In this work, we systematically investigated the extraction of vanadium in (NaVO₃ + H₂SO₄ + H₂O) system by primary amine N1923. Based on the experimental data affected by concentrations and pH values in the system, we determined the main species of vanadium in each condition with the use of the phase diagram and its chemical equilibrium constants of V, then the data were divided into three regions according to the main species. The extraction reactions in different regions of vanadium species were determined by slope method. The hydrogen bond association mechanism for the extraction was clarified while the possible structures of the complex reaction products were proposed. The outline of this work was expressed in Fig. 1.

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Fig. 1. Our research outline for the vanadium extractions.

2. Experimental

2.1. Materials and instruments

2.1.1. Materials

The source and mass purity of all the reagents were listed in Table 1.

2.1.2. Instruments

The instruments and inaccuracies in the experiment were listed in Table 2.

2.2. The extraction and measurement methods

The experimental setup was similar in our previous work (Liu et al., 2015). The aqueous solution (0.001–0.01 mol/kg) was prepared with sodium metavanadate (NaVO_3) dissolved in distilled water, the initial pH of the aqueous solution was adjusted to the desired value using dilute sulfuric acid and measured with a pH meter, while the organic phase was obtained by N1923 diluted in toluene to the concentration ranges of 0.004–0.03 mol/kg. Then 10 mL of each aqueous and organic phase were added to the vessel, which was kept at constant temperature of 298.15 K controlled by a thermostat, and under agitation by a magnetic stirrer for 0.5 h. After that, the solution was transferred into separating funnels and kept standing for 0.5 h. The metal concentration in the aqueous solution was analyzed by inductively coupled plasma-optical emission spectrometer (ICP-OES) with the correlation accuracy of 99.99% for standard curve.

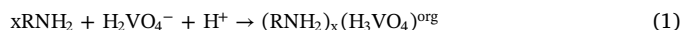
2.3. The determination of vanadium species in aqueous solution

There exist several vanadium species in aqueous solution, such as H_2VO_4^- , HVO_4^{2-} , $\text{V}_3\text{O}_9^{3-}$, $\text{V}_4\text{O}_{12}^{4-}$, $\text{V}_{10}\text{O}_{28}^{6-}$ and $\text{V}_{10}\text{O}_{27}\text{OH}^{5-}$, which will influence the extraction reaction. Baes and Mesmer (1976) had discussed the species and equilibria in vanadium system. The regions of predominant vanadium species were showed in Fig. 2. The solid lines represented the predominant species in adjacent regions with the same elemental V concentrations. It can be found that both the equilibrium pH and the equilibrium concentration can influence the species of vanadium in aqueous solution. The chemical equilibria for these species were listed in Table 3. Here, the species in vanadium system at different conditions can be confirmed with the equilibrium constants listed in Table 3.

2.4. Determination of the extraction reactions with the slope method

Extraction reactions were decided by typical slope method (Ning et al., 2009). Taking H_2VO_4^- as dominant species for example, we supposed that extraction reaction was expressed as reaction (1), so the K , which referred to equilibrium constant of reaction, can be defined as Eq. (2). The m_i and γ_i referred to molality concentration and activity

coefficient, respectively. RNH_2 stands for primary amine N1923 in this paper, and a_{H^+} was the activity of H^+ .



$$K = \frac{m_{(\text{RNH}_2)_x\text{-HV}}^{\text{org}} \gamma_{(\text{RNH}_2)_x\text{-HV}}^{\text{org}}}{(m_{\text{RNH}_2}^{\text{org}} \gamma_{\text{RNH}_2}^{\text{org}})^x m_{\text{H}_2\text{VO}_4^-} m_{\text{H}^+} a_{\text{H}^+}} \quad (2)$$

The distribution coefficient of vanadium (D_v) between aqueous and organic solutions can be defined as Eq. (3). Then the equation was simplified from Eqs. (2) and (3), neglecting the activity coefficient ($\gamma_i \approx 1$), as shown in Eq. (4). The K_m was the extraction equilibrium constant without the consideration of activity coefficient. Thus, a plot of $\lg D_v + \text{pH}_e$ versus $\lg(m_{\text{RNH}_2}^{\text{org}})_e$ should be linear, and the slope which was represented as x was a stoichiometric ratio of the reaction.

$$D_v = \frac{m_{(\text{RNH}_2)_x\text{-HV}}^{\text{org}}}{m_{\text{H}_2\text{VO}_4^-}} \quad (3)$$

$$\lg D_v = x \lg(m_{\text{RNH}_2}^{\text{org}})_e + \lg K_m - \text{pH}_e \quad (4)$$

3. Results and discussion

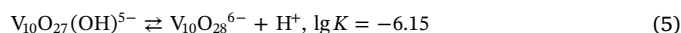
3.1. The experimental LLE data

All our experimental LLE data (15 sets) were listed in Table 4. From Table 4, it can be found in our LLE data, the ranges of equilibrated element V concentration in aqueous phase and pH_e values were in 0.00005–0.053 mol/kg and in 5.4–7.5, respectively. The first step was to decide the vanadium species in equilibrated aqueous phase with the use of the equilibrium constants from Table 3. The predominant V species in the aqueous solution were H_2VO_4^- , $\text{V}_3\text{O}_9^{3-}$, $\text{V}_{10}\text{O}_{28}^{6-}$ and $\text{V}_{10}\text{O}_{27}\text{OH}^{5-}$. The example of how to calculate and part of the results were discussed in Section 3.2, and then we classified our LLE data into three parts (Table 4). In Table 4, the regions of V and V_{10} species were determined using the data (Nos. 1–4, 11–15) from our previous work, however, the new data (Nos. 5–10) were obtained for the V_3 species.

$m_{v,0}$ and $m_{e,0}$ represented the initial concentration of element vanadium in aqueous phase and N1923 in organic phase; $m_{v,e}$ represented the concentration of element vanadium in the equilibrium aqueous phase; D_v and E represented the distribution coefficient and extraction yield of vanadium.

3.2. The determination of vanadium species in aqueous solution

By using the equilibrium constant from Table 3, every concentration near the solid line (represented a reaction) in Fig. 2 was calculated to decide the species accurately. Eqs. (5)–(7) were an example of the calculation process for V_{10} species with definite total concentration of vanadium and pH value.



$$K = \frac{a_{\text{H}^+} m_{\text{V}_{10}\text{O}_{28}^{6-}}}{a_{\text{V}_{10}\text{O}_{27}(\text{OH})^{5-}}} = \frac{a_{\text{H}^+} m_{\text{V}_{10}\text{O}_{28}^{6-}} \gamma_{\text{V}_{10}\text{O}_{28}^{6-}}}{m_{\text{V}_{10}\text{O}_{27}(\text{OH})^{5-}} \gamma_{\text{V}_{10}\text{O}_{27}(\text{OH})^{5-}}} = 7.079 \times 10^7 \quad (6)$$

Table 1

Source and purity of chemicals used in the experiment.

Chemicals		Molecular mass	Sources	Mass purity
Feed solution	NaVO_3	121.93	SIGMA-ALDRICH Inc. (USA)	≥ 0.99
	H_2O	18.02	Homemade from Milli-Q Direct 8 (Merck Millipore)	
pH modifier	H_2SO_4	98.08	Sinopharm Chemical Reagent Co., Ltd. (China)	0.95–0.98
	N1923	310.30	Shanghai Institute of Organic Chemistry (China)	≥ 0.98
Extractant	$(\text{C}_{10}\text{H}_{21})_2\text{CHNH}_2$			
	C_7H_8	92.14	Beijing Chemical Works	≥ 0.995

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