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Measurement and modeling for vanadium extraction from the $(NaVO_3 + H_2SO_4 + H_2O)$ system by primary amine N1923

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ABSTRACT

In this work, the solvent extraction of vanadium by using the primary amine N1923 as extractant was studied. Within different vanadium concentration ranges, the extraction reactions were determined using the slope method at $T = 298.15$ K based on the vanadium phase diagram. The slopes (the stoichiometric ratio) were determined as 5/3, 1 and 11/3 for $(RNH_2)_{5/3}H_3VO_4$, $(RNH_2)H_3V_3O_9$ and $(RNH_2)_{11/3}H_6V_{10}O_{28}$, respectively. The thermodynamic model was established through regression of the experimental results with the Pitzer equation for both aqueous and organic phases by the General Algebraic Modelling System (GAMS). Three different sets of parameters and chemical equilibrium constants K were determined, which corresponded to the three extraction reactions. The orders of the lnK values are $V_{10} > V_3 > V_1$ (organic V species), and the distribution coefficients (D_V) are $D_{V_1} > D_{V_3} > D_{V_{10}}$. The new model was applied to predict the regularities of extraction yield along with different initial conditions, and the results agree well with the experimental values.

1. Introduction

Vanadium is one of the important national strategic resources, which is extensively used in metallurgy, catalysis in chemical industry [1], medical treatment [2], aerospace and other industry, due to its wonderful plasticity and malleability, high corrosion resistance and excellent oxidation–reduction characters. On the other hand, vanadium is also a noxious heavy metal, which can turn into hazardous solid waste stacked in the open air, resulting in significant pollution to the environment, and can accumulate in the body through a variety of routes such as water [3,4]. However, chromium, silicon, phosphorus and so on often exist together with vanadium in natural minerals and industry wastes, such as (vanadium + titanium magnetite) ore [5] and spent hydrodesulphurization catalysts [6]. Therefore, recovering vanadium cleanly and efficiently with low-cost from the natural minerals and secondary resources for the high-value products is requisite and particularly important to harmlessly dispose and utilize the resources.

Currently, several techniques have been used to separate and recover vanadium. Many investigations have been devoted to the chemical precipitation and ion exchange [7,8] to separate and recycle vanadium from solution. Despite the above methods applied to separate vanadium, the disadvantages that they cannot obtain high purity of vanadium or generate a large amount of waste water in industry still exist. For satisfying the requirement of high purity vanadium, the solvent extraction method is used to take the place of precipitation in metallurgical flow sheets [9], because of the advantages of larger capacity, wider operation scope, and the most important high selectivity. Thus, the study of efficiently separating vanadium from other elements by solvent extraction is the key point due to its extremely dispersed distribution in nature and multiple vanadium species existing in solution.

In recent years, many reports about the separation and recovery of vanadium with solvent extraction method have been published. The study from Chen *et al.* indicates that the efficiency order of the amine extractants by the hydrogen bond association mechanism is primary amine > secondary amine > tertiary amine [10]. On the basis of detailed study of the chemical composition and existing forms of the vanadium slag [5,11], the primary amine N1923 as the extractant has been applied to recover vanadium from the chromium-containing vanadium slag. Due to the complex in vanadium aqueous phase [12,13], this causes difficulties for establishing a thermodynamic model for vanadium extraction. Furthermore, although many extraction reactions of vanadium have been studied, the thermodynamic model and chemical equilibrium constants for vanadium extraction have not yet been reported.

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It has been reported that the mechanism of vanadium extraction is hydrogen bond association [10,14], and the vanadium species are extracted in the form of neutral molecules. Based on this mechanism, this study is to determine the extraction reaction in different vanadium concentration solutions with the slope method. And the Pitzer model was used both for aqueous and organic phases to calculate the activity coefficients. The new model parameters and chemical equilibrium constants K were obtained via the regression of our experimental results.

2. Experimental

2.1. Materials

The extractant primary amine N1923 was C_{19}–C_{23} secondary alkyl primary amine with a mass fraction purity of 0.98 and the average molar mass $310.30\ g \cdot mol^{-1}$, which was produced by Shanghai Institute of Organic Chemistry affiliated with the Chinese Academy of Science. According to the molar mass of N1923, the assumed total carbon number of RNH_2 is 21, the structure of which is shown in figure 1. The source and mass purity fraction of all the reagents used in this experiment are listed in table 1.

The extractant primary amine N1923 was prepared by mass using an analytical balance (Mettler ML104, ±0.0001 g), and was diluted by toluene without any other modifier added. The aqueous phase in the process of extraction was $NaVO_3$ solution prepared by dissolving sodium metavanadate ($NaVO_3$) in the doubly distilled water with specific conductivity less than $0.1 \mu S \cdot cm^{-1}$.

2.2. Experimental procedure

In our experiments, the following procedures were employed, and the experimental setup is shown in figure 2. The extraction experiments were made at normal atmospheric pressure. The aqueous solution of $NaVO_3$ was prepared and the pH was adjusted with sulfuric acid to the range of (2.0 to 5.0). A pH meter (Delta320, Mettler, Switzerland) with an uncertainty of 0.01 was used to measure the pH value of the aqueous phase. The extractant N1923 was diluted by toluene to the concentration range of (0.001 to 0.1) $mol \cdot L^{-1}$. Equal volumes (10 mL) of aqueous vanadium solution and organic extractant solution were added to the vessel. The facility was closed with ground glass stoppers, and was maintained at the temperature of 298.15 K using a thermostat within $T = \pm 0.1$ K. A magnetic stirrer was used to afford vigorous agitation to the solution in the vessel. Then the aqueous and organic phases were transferred into the separating funnel, and kept standing for stratification. After that, the aqueous phase was obtained and analyzed. The content of vanadium in the aqueous phase was analyzed using an OPTIMA 5300DV inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer, USA) at the wavelength of 309.311 nm with the correlation degree of standard curve ⩾99.99%. Before analysis, the aqueous phase was diluted by doubly distilled water to the required volume, and filtered by 0.22 μm cellulose membrane. All the experiments were carried out in duplicate at least, and the values listed in table 2 are the average of the replicates. In table 2, the LLE results were classified with their different extraction reactions in system.

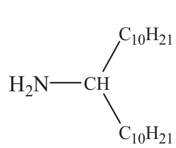

FIGURE 1. Assumed molecular structure of N1923.

TABLE 1
Source and purity of chemicals used in this work.

Chemicals	Source	Mass fraction purity
$NaVO_3$	SIGMA–ALDRICH Inc (USA)	⩾0.99
N1923	Shanghai Institute of Organic Chemistry (China)	⩾0.98
Toluene	Beijing Chemical Works (China)	⩾0.995
Sulfuric acid	Sinopharm Chemical Reagent Co., Ltd. (China)	0.95 to 0.98

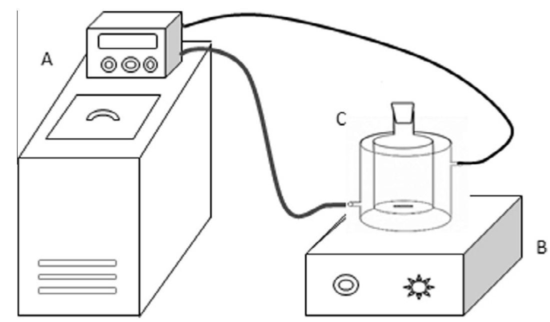

FIGURE 2. Schematic diagram of experimental setup: A—thermostat, B—magnetic stirrer, C—vessel.

2.3. Determination of extraction conditions

Figure 3 illustrates the extraction yield (E), as a function of initial pH_0 for (0.009815 and 0.01963) $mol \cdot L^{-1}$ initial element vanadium. As shown in figure 3, the initial pH_0 has a significant effect on the extraction yield, and the 100% extraction yield was achieved at about initial pH_0 value of 2.7. It is noted that at the beginning, when the initial pH_0 is below 4.0, the extraction yield decreases sharply as the increase of pH_0, and then it decreases gently within the continuous pH range for the studied system. It can be explained that low pH_0 produces more vanadium acid, such as H_3VO_4, $H_3V_3O_9$ and $H_6V_{10}O_{28}$, which are needed to react with RNH_2 into the organic phase.

Figure 4 shows the effect of time on the vanadium extraction yield, as a function of initial pH_0 of 3.13 and the vanadium concentration of 0.01963 $mol \cdot L^{-1}$ at $T = 298.15$ K. It can be seen in figure 4 that the extraction yield increased with increasing extracting time, and levelled off up to 15 min and longer time. For the reliability of experimental results, the extraction time was fixed in 30 min for the purpose of reaching equilibrium.

In order to determine the pH_e at different conditions, the effect of pH_e on the initial concentration of N1923 $(m_{RNH_2})_0$ was studied, and the results are depicted in figure 5. The tendency of pH_e in figure 5 represents the pH_e values increase rapidly with increase of N1923 concentration up to a certain concentration, and then level off in higher concentration of N1923. In other words, the extraction yield reaches the maximum, and the extractant can no longer extract vanadium. Therefore, the experimental values used in the slope method should be confined to the N1923 concentration before the level appeared for the validity of the slope.

2.4. Determination of extraction reactions with the slope method

In the $NaVO_3$ solution, there exist several vanadium species and the corresponding dissociation reactions. The main species, such as $H_2VO_4^-$, HVO_4^{2-}, VO_2^+, $H_3VO_{4(aq)}$, $V_3O_9^{3-}$, $V_4O_{12}^{4-}$, $V_{10}O_{28}^{6-}$, $V_{10}O_{27}OH^{5-}$, $V_{10}O_{26}(OH)_2^{4-}$, some of the standard Gibbs free energies, corresponding dissociation reactions and their equilibrium constants related to this system are listed in table 3. Meanwhile, the phase