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LETTERS TO THE EDITOR

Anion Exchange Extraction of Vanadium(V) with Trioctylamine

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Extraction is among promising methods of separation and purification of vanadium compounds. It is generally advantageous over sorption, precipitation, and other methods due to high efficiency, easy automation, and possibility of application in continuous processes. Vanadium is usually extracted from acidic solutions. For example, neutral extracting agents (tributyl phosphate or alcohols) are applied for vanadium(V) extraction from solutions in concentrated hydrochloric acid; however, the process is not that efficient due to side processes decreasing vanadium recovery: co-extraction of HCl and reduction of V(V) into V(IV). Vanadium(IV) can be extracted with cation exchanging agents, for instance, di(2-ethylhexyl)-phosphonic acid [1–3]. Process liquors usually contain vanadium(V), and it should be reduced to V(IV) prior to extraction with di(2-ethylhexyl)phosphonic acid. Furthermore, the process should be carried out under inert or reducing atmosphere to prevent vanadium(IV) oxidation with air oxygen. Partition coefficient in this process is not high (6–8), and at least six extraction steps are required to recover vanadium(IV) from the solution.

In order to develop a simple extraction process showing higher partition coefficient of vanadium, we have studied its extraction from weakly acidic solution with anion exchanging agent, trioctylamine. In particular, herein we report on effects of pH, the extracting agent concentration, temperature, and solvent on vanadium(V) extraction.

Amines are known to react with acids to form ammonium salts. Hence, partition coefficients of vanadium(V) upon extraction with amine can be a function of pH. Indeed, we demonstrated that at each vanadium concentration its recovery with trioctylamine was the highest at certain optimal pH. Increasing of initial concentration of vanadium in the giving water phase shifted the optimal pH towards more acidic medium. At V(V) concentrations typical of process liquors, its extraction with trioctylamine was the most efficient at pH of 2.0–3.5.

Previously we investigated the state of V(V) in the solution as function of its total concentration and the solution pH [4]. Taking into account those results, we concluded that under optimal acidity conditions of vanadium(V) extraction from its concentrated solution ($c > 0.01$ mol/L) it was extracted with trioctylamine in the form of doubly protonated decavanadate anion $H_2V_{10}O_{28}^{4-}$.

In order to determine the extracted complex composition, we studied the recovery efficiency as function of the extracting agent concentration, other conditions (pH and vanadium concentration) being the same. As the partition coefficient was proportional to forth power of trioctylamine concentration, the extraction could be expressed by the following equation.

$$2[(C_8H_{17})_3NH]_2SO_4 + H_2V_{10}O_{28}^{4-} \rightarrow [(C_8H_{17})_3NH]_4H_2V_{10}O_{28} + 2SO_4^{2-}.$$

We further investigated temperature effect on vanadium(V) extraction with trioctylamine solution in toluene containing isodecyl alcohol at pH of 2.0–3.0. Increasing temperature from 25 to 60°C enhanced vanadium(V) recovery; hence, the extraction process was endothermic. Further heating of the solution resulted in decreasing of vanadium(V) recovery, likely, due to partial V(V) reduction. Hence, 60°C was the optimal temperature in view of efficiency of vanadium(V) extraction with trioctylamine.

In the above-described experiment, isodecyl alcohol was used as polar additive to solubilize trioctylamine and to enhance its solubility in nonpolar toluene. Other alcohols could be used as well, and we studied the effect of alcohol alkyl length on the extraction efficiency; in particular, we used propanol, butanol, and isodecyl alcohol. The experiments revealed that less of the higher alcohol was required to attain the extracting solution homogeneity. Hence, isodecyl alcohol appeared the best solubilizing additive.

To conclude, in this work we elaborated the optimal conditions of vanadium extraction with trioctylamine to attain high partition coefficients allowing for perfect vanadium(V) recovery: weakly acidic aqueous giving solution (pH of 2.0 to 3.0), elevated temperature (60°C) and addition of high alcohol (isodecyl alcohol) as solubilizer. Under the optimal conditions, vanadium(V) partition coefficient reached**.**

Extraction experiments were carried out using solution of 0.1 mol/L of trioctylamine in toluene; volumes of the aqueous and the organic phases were equal. Concentration of vanadium in the aqueous phase was determined by titration of using the coupled plasma method. Concentration of vanadium in the organic phase was calculated as difference between the total vanadium content and its amount in the aqueous phase. The solutions were prepared using sodium metavanadate and sulfuric acid of "chemical pure" grade. pH was measured with the Anion-4100 instrument equipped with glass electrode.

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