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LETTERS TO THE EDITOR

Investigation of Extraction of Vanadium(V) with Di-2-ethylhexylphosphoric Acid

L. D. Kurbatova

Institute of Solids State Chemistry, Ural Branch, Russian Academy of Sciences,
ul. Pervomaiskaya 91, Yekaterinburg, 620990 Russia
e-mail: kurbatova@ihim.uran.ru

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Di-2-ethylhexylphosphoric acid is known as the cation-exchanging extractant. It is widely used for the extraction of vanadium(IV) [1-5]. The extraction of vanadium(V) in a form of dioxocation with this substance proceeds with the very low distribution coefficient, and due to that it is not utilized [6]. We have worked up the conditions under which the change in the extraction mechanism from the cation-exchanging to the solvate one takes place in the course of extraction what permits to extract vanadium(V) with di-2-ethylhexylphosphoric acid with high distribution coefficient. In this work we present the results of study of extraction of vanadium(V) with di-2-ethylhexylphosphoric acid.

The investigation of extraction of vanadium(V) with di-2-ethylhexylphosphoric acid was carried out by means of IR and electronic spectroscopy. For the evaluation of the composition of extracted complex IR spectra of pure di-2-ethylhexylphosphoric acid and the vanadium(V) extract were recorded. In the IR spectra of the extract together with the absorption bands of di-2-ethylhexylphosphoric acid the bands at 1650, 1750, 2140, and 3390 cm^{-1} are present which are characteristic of dioxonium ion [7]. The bands at 1170, 1370, and 2900 cm^{-1} which are also characteristic of $H_5O_2^+$ ion are partially overlapped with more intense bands of di-2-ethylhexylphosphoric acid. The absorption band of P=O bond ($\nu^{as}_{P=O}$) in the vanadium(V) extract has the frequency 1210 cm^{-1}. In the IR spectrum of pure di-2-ethylhexylphosphoric acid the band of P=O bond ($\nu^{as}_{P=O}$) has a maximum at 1225 cm^{-1}. As it was shown above, in the vanadium(V) extracts the dioxonium ion is presented. Due to that the shift of the band of P=O bond to the side of low frequencies may be attributed to the formation of hydrogen bond between the dioxonium ion and the phosphoryl group P=O. It indicates that di-2-ethylhexylphosphoric acid extracts vanadium(V) with the formation of ionic associates. For the evaluation of the number of extractant molecules solvating the dioxonium ion the method of molar ratios was used. It follows from the extraction isotherm that one molecule of di-2-ethylhexylphosphoric acid corresponds to 10 vanadium ions. Considering our previous data on the ionic state of vanadium(V) in the range under study this means that one molecule of extractant corresponds to one decavanadate anion [8]. Hence, the method of saturation of organic phase permits not only to establish the number of solvating molecules of extractant in the composition of complex, but also to make the preliminary conclusion that vanadium(V) enters the composition of extracted complex as decavanadate anion. It is confirmed by the results of studies of the IR spectra of extracts of vanadium(V) with di-2-ethylhexylphosphoric acid. At high concentrations of vanadium(V) a broadening of absorption band at 1030 cm^{-1} is observed at the side of low frequencies and two shoulders at ~970 cm^{-1} and ~920 cm^{-1} appear. The comparative analysis of IR spectra of the extract of vanadium(V) with di-2-ethylhexylphosphoric acid and the reported data on the IR spectra of vanadium(V) dioxocation and decavanadate anions [8] permits to attribute the low intensity bands at ~960 cm^{-1} and ~920 cm^{-1} to two types of binding of vanadium with terminal oxygen atoms of *f*- and *g*-type of decavanadate anion.

Hence, the method of saturation and the results of IR studies of the extracts of vanadium(V) with di-2-

ethylhexylphosphoric acid showed that vanadium enters the composition of extracted complexes as decavanadate anion. Considering that dioxonium ion has the coordination number equal to four [7], the composition of extracted complexes may be represented as follows.

$$[H_5O_2{}^{+}\cdot n(\text{di-2-ethylhexylphosphoric acid})\cdot(4-n)H_2O]$$
$$[H_2V_{10}O_2{}^{4}{}_{8}{}^{-}],\ \text{where } n \le 1.$$

But these data are insufficient for the choice of re-extraction regime. Besides the range of existence and the composition of extracted complexes it is necessary to know the stability of extracted compounds. In connection with that we have studied the stability of extracted complex of vanadium(V) with di-2-ethylhexylphosphoric acid, and its stability constant was evaluated.

The investigation of the stability of the extracted complex of vanadium(V) with di-2-ethylhexylphosphoric acid was performed by recording electron absorption spectra of freshly prepared extract of vanadium(V) with di-2-ethylhexylphosphoric acid after appropriate intervals of time. In the spectrum of freshly prepared extract intense band at 24000 cm^{-1} is observed. The other bands, in particular the band at 13500 cm^{-1}, are absent. That shows the absence of vanadium(IV) in the freshly prepared extract of vanadium(V) with di-2-ethylhexylphosphoric acid. The spectrum of this extract remains unchanged in the course of 4.5 h. After that slight increase in the optical density in the range of 13000–14000 cm^{-1} takes place. It is connected evidently with the partial reduction of vanadium(V). Two days after preparing the extract a clearly expressed band at 13500 cm^{-1} caused by *d–d* transfer in vanadium(IV) is observed. Studies of the IR spectra of vanadium(V) with di-2-ethylhexylphosphoric acid confirm our conclusion on the reduction of vanadium(V) in extract in the course of time. The band at 980 cm^{-1} which according to [9] can be attributed to the vibrations of ν_1 type of oxovanadium(IV) cation was observed in freshly prepared extract of vanadium(V) with di-2-ethylhexylphosphoric acid as a shoulder. In the course of time it becomes more intense. IR studies permit to obtain additional data about the changes taking place in the extract under study. In the IR spectrum of freshly prepared extract together with the bands of di-2-ethylhexylphosphoric acid the absorption bands at 1659, 1750. 2140, and 3390 cm^{-1} characteristic of dioxonium ion [7] are present. The bands at 1170, 1370, and 2900 cm^{-1} which are also characteristic of $H_5O_2^+$ ion are partially overlapped with more intense bands of di-2-ethylhexylphosphoric acid. In the IR spectrum of the extract after two months storage the band at 1750 cm^{-1} caused by bending vibrations of OH_2 group of the $H_5O_2^+$ ion disappears. The intensity of bands at 3390 and 1650 cm^{-1} belonging to the stretching and bending vibrations of molecules of water bound with $H_5O_2^+$ ions also decreases. It indicates the dehydration of extract of vanadium(V) with di-2-ethylhexylphosphoric acid [7].

The evaluation of stability constant of associate of vanadium(V) with di-2-ethylhexylphosphoric acid was carried out at 25±0.5°C. For this purpose a series of solutions was prepared. The concentration of vanadium(V) in them varied from 5×10^{-3} to 2×10^{-1} M. The extraction was carried out with undiluted di-2-ethylhexylphosphoric acid (V = 3 ml). The obtained values of extraction parameters are as follows: The equilibrium constant of extraction of vanadium(V) with di-2-ethylhexylphosphoric acid $K_{\text{ex}} = (1.59\pm0.03)\times10^3$, the stability constant of vanadium(V) associate with di-2-ethylhexylphosphoric acid $\beta = 11.48\pm0.02$.

Hence, the performed studies showed that di-2-ethylhexylphosphoric acid extracts vanadium(V) according to the hydrate-solvate mechanism with the formation of ionic associates. Their cation is the hydrated and solvated dioxonium ion, and decavanadate ion plays the role of anion. The obtained data permit to recommend di-2-ethylhexylphosphoric acid as the effective extractant for vanadium(V).

The extraction was carried out by non-diluted di-2-ethylhexylphosphoric acid at V_0:V_{B} ratio 1:1 and 25±0.5°C. Di-2-ethylhexylphosphoric acid was preliminary purified from mono-2-ethylhexylphosphoric acid according to [10]. The concentration of vanadium in water solutions was measured titrimetrically or by means of the bound plasma method. The vanadium content in the organic phase was evaluated by the difference of concentrations in water solution before and after the extraction. Solutions under study were prepared from chemically pure sodium metavanadate, sulfuric acid, and sodium sulfate. The concentration of sodium sulfate was maintained constant equal to 0.5 M. IR spectra of extracts were recorded on a Specord 75 IR spectrophotometer in the range 400–4000 cm^{-1}. Electron absorption spectra of extracts were registered on a Specord UV VIS spectrophotometer in the range 30000–13000 cm^{-1}. The concentration of hydrogen ions was evaluated with the Anion 4100 pH-meter with a glass electrode.

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