ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 6, pp. 1169–1170. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © L.D. Kurbatova, P.A. Slepukhin, D.I. Kurbatov, E.V. Zabolotskaya, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 6, pp. 1035–1036.

LETTERS TO THE EDITOR

Spectroscopic Study of Vanadium(IV) Extraction with Di-2-ethylhexylphosphoric Acid

L. D. Kurbatova[a], P. A. Slepukhin[b], D. I. Kurbatov[a], and E. V. Zabolotskaya[a]

[a] *Institute of Solid State Chemistry, Ural Branch, Russian Academy of Sciences,*
ul. Pervomayskaya 91, Yekaterinburg, 620990 Russia
e-mail: kurbatova@ihim.uran.ru
[b] *Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia*

Received December 20, 2011

DOI: 10.1134/S1070363212060229

Di-2-ethylhexylphosphoric acid is a bifunctional extractant having two functional groups, the hydroxy and the phosphoryl. Depending on the conditions like the concentration of chemical element and the acidity of the medium the extraction proceeds according to the cation exchange or the solvate mechanism. Di-2-ethylhexylphosphoric acid extracts vanadium(IV) according to the cation exchange mechanism. This process is sufficiently thoroughly studied [1, 2], but all the investigations were carried out in pure sulfuric and perchloric acid solutions. The effect of salts of alkali and alkaline earth metals on the extraction of vanadium (IV) was not evaluated. In this work the extraction of vanadium(IV) in the presence of sodium sulfate was studied.

The investigation of extraction of vanadium(IV) with di-2-ethylhexylphosphoric acid in the presence of sodium sulfate was carried out using ESR and electronic spectroscopy. For identification of complexes of vanadium(IV) which were extracted with 2-ethylhexylphosphoric acid the investigation of extracts of vanadium(IV) with this extractant depending on the concentration of vanadium(IV) in water solution the ESR spectroscopy was used.

At low concentrations of vanadium(IV) [$c_{\mathrm{V(IV)}}$ 0.01 M] an axial anisotropic ESR spectrum of extract of vanadium(IV) with 2-ethylhexylphosphoric acid is observed. It has a well resolved superfine structure appearing due to the interaction of unpaired electron with the magnetic nucleus of vanadium. Values of coupling constants $A_{\|}$ 190 Gs and $A_{\perp}$ 90 Gs sufficiently well agree with the previously reported data for complex compounds of vanadium(IV) [4].

The increase in the concentration of vanadium(IV) in starting water solution leads to changes in ESR spectrum and to the appearance of blue crystals in the organic phase. At the concentrations of vanadium(IV) 0.30 M on the background of spectrum with the resolved superfine structure obtained by us before a broad unresolved signal appears. Note that peak locations and values of superfine coupling constants remain the same. The appearance of the broad signal may be due to the formation of crystals of vanadium(IV) compound in the extract. Due to the strong magnetic dipole-dipole interactions a significant broadening of components of the superfine coupling with the ^{51}V nuclei takes place in the solid phase. It leads to the overlapping and the appearance of a broad singlet in ESR spectrum [5].

X-ray study at 150(2) K of the crystals obtained showed that at high concentrations of vanadium(IV) the crystals of the sulfate complex of vanadium (IV) oxocation trihydrate $VOSO_4 \cdot 3H_2O$ are formed in the organic phase. It was established that the vanadium(IV) oxocation sulfate trihydrate crystallized in a centrosymmetric space group as a dimers with bridging sulfate groups. The crystal system of crystals is monoclinic, space group $P2_1/n$, $a = 7.3561(4)$ Å, $b = 7.3837(4)$ Å, $c = 12.0066(5)$ Å, $\beta = 106.404(4)°$, $V = 625.60(5)$Å^3 for the substance with the empirical formula H_6O_8SV $M = 217.05$ g mol^{-1}, $F(000)$ 436, $Z = 4$, $d_{\mathrm{calc}} = 2.304$ g cm^{-3}, $\mu = 1.915$ mm^{-1}. The structural study of this aquacomplex was recently carried out at room temperature [6, 7]. The results agree well with our data. Hence, X-ray study showed that in the organic phase the sulfate complex of vanadium(IV) oxocation is formed. As known [4], the sulfate complex of vanadium(IV) oxocation in water solutions has an ESR spectrum with the coupling constant of 106–108 Gs. Therefore it may be assumed that the ESR spectrum with coupling constants $A_{\|}$ 190 Gs and $A\perp$ 90 Gs belongs to the complex of vanadium(IV) oxocation with di-2-ethylhexylphosphoric acid.

To confirm the results obtained and to identify the vanadium(IV) complexes formed in the organic phase electronic spectra of extract of vanadium(IV) with di-2-ethylhehylphosphoric acid and water solution of vanadium(IV) oxocation sulfate were registered. The electronic spectrum of water solution of the vanadium(IV) oxocation sulfate contains two absorption bands at 16000 and 13000 cm^{-1}, and in the electronic spectrum of extract of vanadium(IV) with di-2-ethylhexylphosphoric acid three bands at 16000, 15000, and 13000 cm^{-1} are observed. The registered bands correspond to the transitions from the occupied states of valence zone to the conductivity zone. Basing on the values of ionization potentials [8] it can be suggested that the upper part of valence zone is formed by 3*p*-states of sulfur (I_{3p} = –10.78 eV). Lower 3*p* states of phosphorus (I_{3p} = –10.84 eV) and 2*p* states of oxygen (I_{2p} = –15.85 eV) contribute to the bottom part of the valence zone. Therefore the absorption band at 13000 cm^{-1} (1.61 eV) can be regarded as the transition with a charge transfer from the occupied 2*p* states of oxygen to unoccupied 3*d* states of vanadium. The band at 15000 cm^{-1} (1.86 eV) may be attributed to the transitions from 3*d* state of phosphorus, and the band at 16000 cm^{-1} (1.98 eV), to the transitions from 3*d* states of sulfur. Such interpretation of electronic spectrum confirms the formation of two complex compounds of vanadium(IV) oxo-cation with the anions of sulfuric and di-2-ethylhexylphosphoric acid in organic medium.

Hence, the extraction of vanadium(IV) with di-2-ethylhexylphosphoric acid in the presence of sodium sulfate proceeds according to the cation exchange mechanism. Under these conditions two complex compounds of vanadium(IV) oxocation with the anions of sulfuric and di-2-ethylhexylphosphoric acids are formed evidently by the following reactions.

$$VO^{2+} + 2HR_2^- \rightleftarrows VO(HR_2)_{2(o)}, \quad (1)$$

$$VOHSO_4^+ + HR_2^- \rightleftarrows VOHSO_4(HR_2)_{(o)}, \quad (2)$$

$$VOHSO_4(HR_2)_{(o)} + HR_2^- \rightleftarrows VO(HR_2)_{2(o)} + HSO_4^-, \quad (3)$$

$$HSO_4^- \rightleftarrows H^+ + SO_4^{2-}, \quad (4)$$

$$VO(HR_2)_{2(o)} + SO_4^{2-} \rightleftarrows VOSO_4 + 2HR_2^-. \quad (5)$$

Here HR_2^- is the anion of 2-ethylhexylphosphoric acid.

ESR spectra were registered on a CMS 8400 apparatus in the X-range at room temperature. X-ray study was carried out according to the standard procedure on a Xcalibur 3 diffractometer equipped with CCD detector [λMoK_α = 0.71073 Å, graphite monochromator, ω-scanning, scanning step 1°, time of freim measuring 20 s, T = 150(2) K]. The correction for extinction was introduced by the multiscanning method [9]. The structure was solved by the direct method according to SHELXS97 program and refined by SHELXL97 program [10] using the root-mean-square method in the anisotropic full-matrix approximation for nonhydrogen atoms. Electron absorption spectra of vanadium(IV) extract with di-2-ethylhexylphosphoric acid and water solution of vanadium(IV) oxocation sulfate were registered on the Specord UV-VIS spectrophotometer in the range 30000–13000 cm^{-1}. The concentration of sodium sulfate in the solution was constant and equal to 0.4 M.

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