Coordination State of Vanadium in Chloride Melts: an Electronic Absorption Spectroscopy Study

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Although first UV-viz spectra of vanadium in chloride melts were reported over 40 years ago (1,2) there is still a considerable controversy about stable oxidation states of vanadium and the coordination/geometry of its complex ions in these media. Vanadium is capable of forming ions containing the metal in oxidation states of (II), (III), (IV), and (V). In the higher oxidation states, (IV) and (V), vanadium normally forms oxygen-containing ions.

In the present work we investigated complexes of vanadium(II) and (III) in NaCl-KCl equimolar melt at 750 ^{o}C. V(III)-containing melts were prepared by dissolving anhydrous VCl_3. V(III) forms in the melt octahedral VCl_6^{3-} complexes with maximum in the resolved spectra at 16990 cm^{-1} corresponding to the $^3T_{1g} \rightarrow {}^3T_{2g}$ electronic transition.

Reduction of this melt with vanadium metal resulted in complete conversion of dissolved vanadium into V(II) ions. Interestingly, the position of the maximum in the spectrum of V(II) is very close to that of V(III) (Fig. 1) being shifted to the higher energy by only about 500 cm^{-1}. Reduction of V(III) to V(II) was also achieved by contacting the melt with metallic silver. The main band in the resolved spectra of vanadium(II) containing melts was found at 17550 cm^{-1} and attributed to $^4A_{2g} \rightarrow {}^4T_{2g}$ electronic transition in VCl_6^{4-} ion. An additional weak band around 13000-14000 cm^{-1} can be attributed to one of the spin-forbidden transitions ($^4A_{2g} \rightarrow {}^2E_g$, $^2T_{1g}$, $^2T_{2g}$).

Oxidation of V(II)-containing melts with oxygen results in gradual decrease of vanadium concentration and precipitation of an insoluble oxygen-containing phase. When vanadium(III)-containing melts are oxidized by oxygen the situation is different, the peak corresponding to VCl_6^{3-} gradually disappears and another band (around 700 nm) appears, Fig. 2. The latter is due to V(IV) complex formed according to the reaction:

$$2\ VCl_6^{3-} + O_2 \rightarrow 2\ VOCl_4^{2-} + Cl_2 + 2\ Cl^- \qquad [1]$$

In situ spectroscopy measurements were also applied to study the reaction of vanadium with chlorine in NaCl-KCl melt. The nature of the products formed depends on the flow rate of chlorine. When Cl_2 is introduced into the melt containing vanadium metal slowly and is completely absorbed by the melt the main product of the reaction is V(II). Gradual increase of Cl_2 flow rate leads to the oxidation of V(II) to V(III). When the melt is sparged with chlorine, vanadium is oxidized to the tetravalent state. Most of V(IV) is sublimed from the melt as volatile VCl_4. Remaining vanadium stays in the melt in the form of VCl_6^{2-} and the spectrum of the melt contains a relatively weak band at 14600 cm^{-1}, which is attributed to the $^2T_{2g} \rightarrow {}^2E_g$ electronic transition.

The reaction of vanadium with HCl in NaCl-KCl melt was also studied. Depending on the amount of vanadium metal in the system and the flow rate of hydrogen chloride, the reaction results in the formation of V(II) and V(III) complex ions.

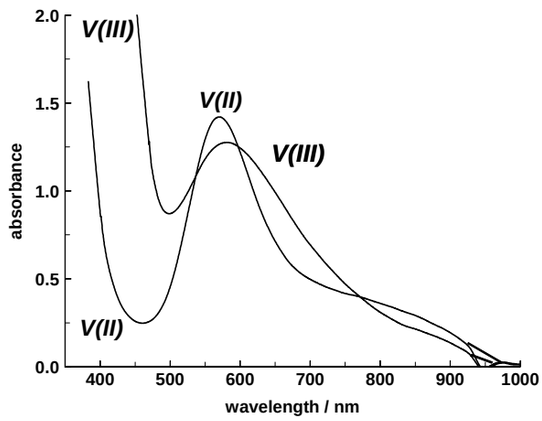

Fig. 1. Electronic spectra of octahedral V(II) and V(III) complex ions in NaCl-KCl melt at 750 ^{o}C.

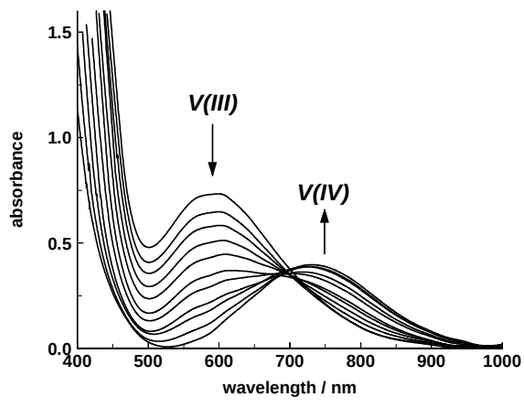

Fig. 2. Spectra recorded upon oxidation of VCl_6^{3-} by oxygen in NaCl-KCl melt at 750 ^{o}C.

REFERENCES

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