COORDINATION STATE OF VANADIUM IN CHLORIDE MELTS:
AN ELECTRONIC ABSORPTION SPECTROSCOPY STUDY

B. D. Vasin,1 I. B. Polovoy,1 V. A. Volkovich,1 T. R. Griffiths,2 A. V. Berezin1

1 Department of Rare Metals, Ural State Technical University-UPI, Ekaterinburg, 620002, Russian Federation
2 School of Chemistry, University of Leeds, Leeds, LS2 9JT, United Kingdom

ABSTRACT

The coordination of the chloro complexes of vanadium in its lower oxidation states was studied spectroscopically in molten equimolar mixture of NaCl-KCl at 750 °C. V(III) is the most stable oxidation state that does not form oxygen-containing complexes. Addition of excess vanadium or a suitable reducing metal (silver) to V(III)-containing melts converts V(III) to V(II) and some V(II) chloro complex ions can then react with silica to form an oxygen-containing insoluble phase. Reaction of V(II)-containing melts with oxygen leads to precipitation of a vanadium oxo-species. When NaCl-KCl-VCl3 melts are exposed to an oxygen containing atmosphere the vanadium content remains constant but VCl63− is converted into VOCl42−. The reaction products of V metal with Cl2 in NaCl-KCl melt depend on the concentration of chlorine. V(II) and V(III) species are initially formed at low flow rates and V(IV) at high. Most of V(IV) in this case sublimes, or is swept from the melt with the chlorine, as volatile VCl4.

INTRODUCTION

Halide melts are attractive from a technological viewpoint due to their high electrical conductivity, comparatively low density and viscosity (and hence good transport properties), and relatively low vapour pressure at working temperatures. They can be used for electrodeposition and electrorefining of chemically active refractory metals, particularly vanadium. High purity vanadium is normally produced by electrorefining in molten chloride baths. Vanadium can be added into the melt by chlorinating the metal produced by aluminium, calcium or carbon thermal reduction of V2O5 (1-9), or by dissolving either anhydrous VCl3 or VCl2 (10-14). Chlorine and hydrogen chloride (or their mixture) are employed as chlorinating agents. If the vanadium in the melt is present in the trivalent state, the electrolyte is then held in contact with excess vanadium metal to reduce V(III) to V(II) (10,11). Electronic absorption spectroscopy is one of the techniques that can be used for a direct in situ study of the behaviour of vanadium and its coordination state in molten salts.

There are several works studies of spectroscopic investigations of the coordination state of vanadium in molten halides, particularly chlorides. The spectra of all the oxidation states of vanadium in chloride melts have been reported (15-20). Although the first uv-visible spectra of vanadium were reported over 40 years ago there is...
still a considerable controversy about the stable oxidation states of vanadium and the coordination geometry of its complex ions in the lower oxidation states in molten alkali chlorides. Gruen and McBeth (16) postulated for V(II) in molten LiCl-KCl eutectic an octahedral-tetrahedral equilibrium, $\text{VCl}_6^{4-} \leftrightarrow \text{VCl}_4^{2-}$, shifted to the right with increasing temperature. In its higher oxidation states, (IV) and (V), vanadium normally forms oxygen-containing ions, although vanadium(IV) can exist as the chloro-complex $\text{VCl}_4^{2-}$ (20).

In the present study we investigated the complexes of vanadium formed in a NaCl-KCl equimolar mixture at 750 °C.

EXPERIMENTAL

Spectroscopic measurements were performed using a custom-built set-up, schematically shown in Figure 1, based on an Ocean Optics SD2000 double-channel computer-controlled fibre optic spectrophotometer. Spectra were recorded between 200 and 1100 nm. CCD detectors allowed the use of relatively short time intervals, 150-200 ms, for registering the spectra and therefore the measurements could be performed in situ during the progress of various chemical reactions. The samples were heated in an optical furnace (Instron SFL model 1720), capable of achieving 1100 °C. When required, the experimental spectra were resolved into individual bands using the PeakFit software package.

Figure 1. Experimental set-up for measuring electronic absorption spectra of molten salts. 1, light source; 2 and 6, optical fibre cables; 3 and 5, collimating lenses; 4, furnace; 7, spectrometer; 8, ADC converter; and 9, PC.

V(III)-containing melts were prepared by dissolving anhydrous VCl₃ (99.5% purity, Uralredmet). These melts were contacted with excess of vanadium or silver metal and the reduction of vanadium(III) studied. A series of experiments was performed on the gradual oxidation of V(II)- and V(III)-containing melts by oxygen gas and also upon reacting vanadium metal with chlorine and hydrogen chloride.
The concentration of vanadium and its average oxidation state in rapidly quenched melt samples were determined by chemical analysis. Any insoluble precipitates formed during the experiments were separated from the bulk melt and analysed by X-ray powder diffraction (Philips PW 1710) and IR spectroscopy (Bruker Equinox-55 FTIR spectrometer).

RESULTS AND DISCUSSION

Direct dissolution of VCl$_3$ in molten NaCl-KCl mixture results in the formation in the melt of octahedral VC$_6^{3-}$ complexes, Figure 2. The average oxidation state of vanadium in the quenched melt sample was 2.94±0.10. The spectra obtained were resolved into individual bands and the maximum of the principal band was at 16990 cm$^{-1}$ (molar extinction coefficient of 45 l mol$^{-1}$ cm$^{-1}$). This band corresponds to the $^3$T$_{1g}$$\rightarrow$$^3$T$_{2g}$ electronic transition in the octahedral VC$_6^{3-}$ complex ion ($d^7$-configuration).

![Figure 2. Electronic spectra of octahedral V(II) and V(III) complex ions in NaCl-KCl melt at 750 °C.](image)

Holding a vanadium(III) containing melt in contact with vanadium metal results in conversion of dissolved vanadium species into V(II) ions. The spectra recorded during this reaction are shown in Figure 3. Chemical analysis of the final melt showed the presence of only vanadium(II). During the reaction the concentration of vanadium in the melt increased from 0.06 to 0.08 wt.%, a somewhat lower concentration of vanadium in the melt than that expected according to the reaction

$$2 \text{VCl}_6^{3-} + V + 6 \text{Cl}^- \rightarrow 3 \text{VCl}_6^{2-}. \quad [1]$$

This was due to the formation of an insoluble black vanadium-containing phase, here attributed to the reaction of V(II) with the silica of the optical cell.
An example of a spectrum of V(II)-containing melt is given in Figure 2. Interestingly, the position of the maximum in the spectrum of V(II) is very close to that of V(III) (Figure 2), being shifted to higher energy by only about 500 cm\(^{-1}\). The main band in the resolved spectra of vanadium(II)-containing melts was at 17550 cm\(^{-1}\) (molar extinction coefficient of 541 mol\(^{-1}\) cm\(^{-1}\)), corresponding to the \(4A_{2g} \rightarrow 4T_{2g}\) electronic transition in \(\text{VCl}_6^{2-}\) ion (d\(^3\)-configuration). An additional weak band around 13000-14000 cm\(^{-1}\) can be attributed to one of the spin-forbidden transitions (\(4A_{2g} \rightarrow 2E_g, \text{ or } 2T_{1g}, 2T_{2g}\)).

![Figure 3. Spectra of the reaction of a NaCl-KCl-VCl\(_3\) melt at 750 °C with V metal. Reaction time: 1, initial melt; 2, 10 min; 3, 20 min; 4, 23 min; 5, 33 min; and 6, 48 min.](image)

In order to keep the total concentration of vanadium in the melt constant during reduction another reducing agent was required. Reduction of V(III) to V(II) can be achieved by contacting the melt with various metals, including silver. In a simplified form the reaction can be represented by

\[
\text{VCl}_3 + \text{Ag} \rightarrow \text{VCl}_2 + \text{AgCl}
\]

An advantage of using silver is that the silver chloride formed does not absorb in the visible region and should thus not interfere with spectral measurements. Prolonged (190 min) contacting a V(III)-containing melt with metallic silver indeed resulted in reduction of V(III) to V(II) but the total concentration of vanadium in the melt decreased from 0.065 to 0.019 wt. % and a black insoluble phase was again formed.

XRD analysis of quenched samples containing this black phase showed that the diffraction pattern of this compound contains lines at \(2\Theta\) of 25.8, 30.0 and 53.0 degrees. These lines do not correspond to the XRD patterns of any of the vanadium oxides, chlorides, oxychlorides and silicides listed in (21). The IR spectra of the black compound contain a band around 1000 cm\(^{-1}\), corresponding to a vanadium-oxygen vibration but the exact nature of this compound remains unknown.

In addition to the melts spectra, the spectra of quenched samples were also

264 Electrochemical Society Proceedings Volume 2004-24
measured by diffuse reflectance. For both V(III) and V(II) systems the spectra of molten and solid samples differed considerably, (Figure 4). Vanadium(II) or (III) were present in the melt as octahedral ions $\text{VC}_6^{n-}$ ($n = 4$ or 3, respectively). In the solid state, vanadium forms $\text{M}_2\text{VCl}_4$ for V(II) and $\text{M}_3\text{VCl}_6$, for V(III), and the species and site symmetry of vanadium is no longer octahedral. Lowering the symmetry causes changes in the spectra.

![Figure 4. Comparison of the spectra of vanadium(III) and (II) complexes in NaCl-KCl-based melts at 750 °C (dashed lines) and in quenched melts at room temperature (solid lines).](image)

Oxidation of V(II)-containing melts with oxygen (by slowly admitting $\text{O}_2$ into the atmosphere above the melt) resulted in a gradual decrease of vanadium concentration and the precipitation of a black insoluble oxygen-containing phase. The oxidation state of vanadium in the melt increased from 2.02 to 2.78.

When vanadium(III)-containing melts were also oxidized by oxygen (as above) the intensity of the peak at 590 nm, corresponding to $\text{VC}_6^{3+}$, gradually decreased and eventually disappeared, and another band (around 700 nm) appeared, Figure 5. The latter is due to an oxygen-containing V(IV) complex, formed according to:

$$2 \text{VC}_6^{3+} + \text{O}_2 \rightarrow 2 \text{VOCl}_4^{2-} + \text{Cl}_2 + 2 \text{Cl}^- \quad [3]$$

The total concentration of vanadium in the melt (0.05 wt.%) remained unchanged, as also illustrated by the presence of an isosbestic point in the spectra, and the oxidation state of vanadium in the melt increased from 3.0 to 3.9, indicating that nearly all the vanadium(III) was oxidized to vanadium(IV). The profile of the final spectrum corresponds to that of the vanadyl chloride complex (16,18-20).

In situ spectroscopy measurements were also applied to a study of the reaction of vanadium with chlorine in a NaCl-KCl melt. The nature of the products formed appeared to depend on the flow rate of chlorine. When $\text{Cl}_2$ is introduced slowly into the melt...
containing vanadium metal (flow rate around 3.5 ml Cl₂ min⁻¹) it is completely absorbed by the melt, the main product of the reaction being V(II). Gradual increase of the Cl₂ flow rate led to partial oxidation of V(II) to V(III), and vanadium concentration in the melt increases as shown in Figure 6. It was not possible to determine a linear relationship and hence rate constants. The reason is because the initial reaction step is to oxidize the elemental vanadium to the V(II) octahedral chloro complex and it was not possible to admit a stoichiometric amount of chlorine into the melt to oxidize all of the metal to this complex. Consequently, the continuous flow of chlorine meant that some of this complex was oxidized further to VCl₆³⁻ while some of the metal still remained. By controlling the chlorine it was possible to convert essentially all the vanadium into the +3 state. This oxidation state is readily further oxidized and thus addition of even more chlorine into the melt oxidized this complex to, initially, VCl₆²⁻, most of which then lost two chloride ligands and the volatile VCl₄ was then essentially distilled from the melt (and possibly also carried out of the melt in the now effectively sparging chlorine gas).

**Figure 5.** Spectra of the oxidation of VCl₆³⁻ by oxygen in NaCl-KCl melt at 750 °C. Total time of reaction 145 min.

**Figure 6.** Increase of vanadium concentration in NaCl-KCl melt during chlorination of V metal with Cl₂ at 750 °C, chlorine flow rate of 5 ml min⁻¹.
Thus an increase in the Cl₂ flow rate to ca. 5 ml min⁻¹ resulted in the formation of essentially only vanadium(III) ions in the melt. Further increase in the flow rate (to 7 ml min⁻¹ and above) oxidized the vanadium to the tetravalent state. Most of V(IV) was then sublimed from the melt, as volatile VCl₄, which condensed as a liquid in the cooler parts of the cell and in the outlet tube. The vanadium remaining in the melt was VCl₂⁺ since the melt spectrum contained a relatively weak band at 14600 cm⁻¹, which corresponds to the ²T₂g → ²Eg transition in the VCl₂⁺ complex ion (22,23). Additional experiments on large-scale chlorination of vanadium metal in NaCl-KCl melt at various temperatures confirmed the above observations, see Table 1.

Table 1. Chlorination of vanadium metal in NaCl-KCl equimolar melt

| T / °C | Cl₂ flow rate / ml min⁻¹ | Time / min | (mᵥI/mᵥ₂) / %* | nᵥ** |
|-------|------------------------|-----------|----------------|------|
| 681   | 30                     | 180       | 0.9            | 3.98 |
| 680   | 15                     | 180       | 32.6           | 3.78 |
| 684   | 9.3                    | 180       | 55.2           | 3.22 |
| 680   | 7                      | 180       | 75.6           | 2.99 |
| 681   | 8.2                    | 220***    | 86.1           | 3.00 |
| 701   | 8.2                    | 120***    | 90.7           | 3.01 |
| 800   | 8.2                    | 50***     | 70.6           | 3.04 |
| 897   | 8.2                    | 45***     | 83.5           | 3.01 |

* mᵥI, mass of vanadium in the final melt; mᵥ₂, mass of initially added vanadium.
** Vanadium oxidation state at end of experiment.
*** Time when process was stopped because VCl₄ started to sublime from the melt.

The reaction of vanadium with HCl in a 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 resulted in the formation of the chloro complex ions V(II) and V(III).

ACKNOWLEDGMENTS

IBP thanks INTAS (Grant No. 03-55-1453) for financial support.

REFERENCES

1. D. H. Baker and J. D. Ramsdell, *J. Electrochem. Soc.*, 107, 985 (1960).
2. F. R. Cattoir and D. H. Baker, Jr., *U. S. Department of the Interior. Bureau of Mines. Investigation report No. 5630* (1960).
3. T. A. Sullivan, *J. Metals*, 17, 45 (1965).
4. D. H. Baker and T. A. Sullivan, U. S. Department of the Interior. Bureau of Mines. Investigation report No. 6631 (1965).
5. K. P. V. Lei, F. R. Cattoir and T. A. Sullivan, U. S. Department of the Interior. Bureau of Mines. Investigation report No. 6972 (1967).
6. K. P. V. Lei and T. A. Sullivan, U. S. Department of the Interior. Bureau of Mines. Investigation report No. 7036 (1967).
7. K. P. V. Lei and T. A. Sullivan, J. Less-Common Metals, 14, 145 (1968).
8. K. P. V. Lei and T. A. Sullivan, U. S. Department of the Interior. Bureau of Mines. Investigation report No. 7484 (1967).
9. K. P. V. Lei and T. A. Sullivan, Met. Trans., 2, 2312 (1971).
10. Yu. U. Samson, V. E. Baru and N. S. Datлина, Nauch. Tr. GIREDMET, 42, 124 (1972).
11. Yu. U. Samson, F. V. Kovalyov, V. E. Baru, N. S. Datлина and V. E. Kartsev, Nauch. Tr. GIREDMET, 42, 5 (1972).
12. P. V. S. Pillai, K. U. Nair, T. K. Mukherjee and C. K. Gupta, Trans. Indian Inst. Metals, 26, 24 (1973).
13. K. Elayaperumal, J. Electrochem. Soc. India, 25, 67 (1976).
14. P. K. Tripathy, J. L. Sehra, D. K. Base and R. P. Singh, J. Appl. Electrochem., 26, 887 (1996).
15. G. Hurrington and B. R. Sundheim, Ann. N. Y. Acad. Sci., 79, 950 (1960).
16. D. M. Gruen and R. L. McBeth, J. Phys. Chem., 66, 57 (1962).
17. B. D. Vasin, S. V. Maslov and I. B. Polovov, Rasplavy, No. 2, 51 (1999).
18. D. M. Gruen and R. L. McBeth, Pure Appl. Chem., 6, 23 (1963).
19. R. Molina, Bull. Soc. Chim. Fr., 301 (1961).
20. I. B. Polovov, V. A. Volkovich, S. A. Shipulin, S. V. Maslov, A. A. Khokhryakov, B. D. Vasin, T. R. Griffiths and R. C. Thied, J. Mol. Liquids, 105, 105 (2003).
21. Powder Diffraction File, Search Manual, Inorganic Compounds, L.G. Berry, Editor, Joint Committee on Powder Diffraction Standards, Swarthmore (1976).
22. R. D. Bereman and C. H. Brubaker, Jr., Inorg. Chem., 8, 2480 (1969).
23. P. A. Kitty and D. Nichols, J. Chem. Soc., 4195 (1965).