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Raman spectroscopy studies of concentrated vanadium redox battery positive electrolytes

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Abstract

Spectroscopic changes in highly concentrated vanadium(V)-sulfate solutions to be used in the 'vanadium redox battery' are consistent with the presence of more than one V(V)-sulfate species. The results of Raman spectroscopy indicate that the major species in highly acidic conditions are $VO_2SO_4^-$, $VO_2(SO_4)_2^{3-}$, $VO_2(HSO_4)_2^-$, VO_3^-, V(V) dimers with $V_2O_3^{4+}$ and $V_2O_4^{2+}$ central units. The nature and amount of these species depends upon the V(V) and total sulfate concentrations as well as on S to V and H^+ to V ratios in the positive half-cell electrolyte. V(V) forms $V_2O_3^{4+}$, $VO_2(SO_4)_2^{3-}$ and their copolymer species at higher total sulfate concentrations, which tends to stabilize the vanadium (V) positive electrolyte in the vanadium redox battery. The V(V) and V(IV) species show the least interaction with each other. Ageing of concentrated V(V) solutions at elevated temperature (50 °C) produces decomposition of species causing formation of V_2O_5 precipitates with a decrease in the amount of vanadium polymer.

1. Introduction

The chemistry of vanadium has recently attracted considerable research interest as a result of its increasingly recognized biochemical and industrial importance. With the introduction of the redox flow battery concept for energy storage the V(II)/V(III) and V(IV)/V(V) redox couples were successfully employed as the negative and positive half-cell electrolytes in a 'vanadium redox flow battery' [1–3]. Despite extensive studies of the electrochemistry and stability of vanadium ions in strongly acidic solutions (pH < 0) under cell working conditions, there is still limited information available on understanding the relationship between chemical speciation of the solutions and the thermal precipitation of V(V) at elevated temperatures (>40 °C) [4, 5]. Furthermore, the lack of accurate information on vanadium speciation, particularly in the V(IV)/V(V) positive half cell electrolyte of the vanadium redox battery (VRB), makes it impossible to calculate the ionic strength of the two half-cell electrolytes so as to predict osmotic pressure and water transfer effects across different types of membranes in the cell. In addition, the unexpected stabilization of 4 M V(V) in concentrated H_2SO_4 solutions [3] has provided more evidence of ionic interactions occurring between the vanadium, sulfate and bisulfate species in these highly concentrated electrolytes which require further elucidation.

Numerous vanadium (V) species have been identified, which mainly depend upon the pH and concentration of the solution [6]. It is generally acknowledged that in weakly acidic solutions (pH 1.0–0.8) vanadium exists as the mononuclear aquadioxo cation $VO_2(H_2O)_4^+$ [7]. Studies on aquadioxovanadium(V) in concentrated sulfuric acid media have indicated the existence of different V(V) monomeric as well dimeric species coordinated with sulfate ions in solution [6, 8–10]. Discrepancies in the interpretation of results are associated with the use of different analytical techniques for varying vanadium concentration ranges. In the present study, we report the probable vanadium(V) species in highly concentrated solutions of vanadium(V) and H_2SO_4 by using Raman spectroscopy.

2. Experimental details

2.1. *Vanadium(V) solution preparation*

Vanadium(IV) stock solution of various compositions were prepared by the electrolytic oxidation of the correspondingly $VOSO_4$ solution in sulfuric acid. During the electrolysis, the following reaction occurs at the anode:

$$VO^{2+} + H_2O \longrightarrow VO_2^+ + 2\,H^+ + e^- \qquad (1)$$

The cell employed a cation selective membrane (Nafion® 112) and two lead electrodes were immersed in each compartment of the cell for connection with the electric supply. A current density of 18–20 mA cm^{-2} was used for electrolysis. Nitrogen was bubbled during electrolysis to enhance mass transport in the cell and allow high current efficiencies to be obtained.

The oxidation state of the final vanadium solutions was determined by potentiometric titration with $KMnO_4$, using a saturated calomel electrode (SCE) and a platinum wire electrode as the reference and indicator electrodes, respectively. Final vanadium and sulfur concentrations were analysed from ICP (inductivity coupled plasma analysis) results.

2.2. *Raman spectra*

Raman spectroscopy experiments on V(V) and V(IV) species in solutions of various total sulfates (i.e., $HSO_4^- + SO_4^{2-}$) were conducted under different sets of conditions as shown below:

(a) varying V(V) concentration (0.1–3.0 M) in 5 M total sulfates
(b) varying total sulfates concentration (4–9 M) at fixed V(V) concentration
(c) varying V(IV) content at fixed V(V)-total sulfates concentration to examine the effect of state-of-charge of the positive half-cell electrolyte on the vanadium speciation
(d) ageing of V(V) solutions at 50 °C.

The samples were placed on an ordinary glass microscope slide, being both inert and weak Raman scatter, causing little or no interference to the Raman spectrum. One drop of sample can give reasonable Raman bands of the desired intensity. However, due to thermal sensitivity of the samples, care was taken by using only 1 min total spectrum time for each sample. These vanadium samples were excited by using He–Ne Raman Renishaw image microscope (632.8 nm, 12,798 cm^{-1}, red) laser which provides a strong monochromatic beam. Slit widths were in the range of 0.5–2 cm^{-1}. Spectral measurements were made by rotating the plane of polarization of the exciting laser light by 90°. A polarization scrambler was used in the light path just before entry into the monochromator. Experiments were repeated many times to get reproducibility in the results. Spectra were run using the 'Wire Raman Software 1.2' on a Renishaw Raman imaging microscope which was interfaced with a 'Grams-32C Software' programme for manipulating data information.

Raman spectral graphs were rectified by using smooth.AB, Baseline.AB and Curvefit.AB applications. After applying the Deconvulation operation for resolving overlapped peaks, few new peaks were observed and their presence was confirmed at the same frequency from various sets of V(V)–total sulphate concentration solutions.

3. Results

As mentioned previously, the V(V) solutions prepared by electrolytic oxidation of V(IV) sulfates in sulfuric acid are expected to consist of VO_2^+, H^+, HSO_4^- and SO_4^{2-} ions, the amount of each depending upon the actual concentration of V(V) and total sulfates as well as on H^+ to V(V) and S to V(V) ratios [11, 12]. Higher H_2SO_4 concentration can prevent precipitation of VO_2^+ ions to V_2O_5 by forming sulfate complexes with VO_2^+ or the increase in stability could be achieved due to dimerization of VO_2^+ ions to $V_2O_4^{2+}$ and $V_2O_3^{4+}$ species [4, 8, 10].

The Raman spectra in the range of 350–1200 cm^{-1} for 4–7 M sulfuric acid are given in Figure 1. All the Raman bands in the spectra except for the bands at 985 cm^{-1} SO_4^{2-} are due to HSO_4^- ion. The band frequencies and the relative intensity trend of the bands at 985 cm^{-1} due to sulfate ion and 1046 cm^{-1} due to bisulfate ion are consistent with the previous results of sulfuric acid Raman spectral studies [13–16].

According to the reported Raman spectra of vanadium oxides [17–19], frequencies of V–O vibrations can be divided into V–O terminal stretching (800–1000 cm^{-1}), V–O bridging mode (400–800 cm^{-1}), V–O bending and lattice modes (below 400 cm^{-1}). Among these vibrations, critical structural information, pertaining to geometry and bond distance can usually be obtained from the analysis of the feature of V–O stretching.

Raman spectra of highly concentrated V(V)–sulfate solutions are shown in Figure 2, while the band frequencies corresponding to various vibrational modes of different species and their respective assignments have been summarized in Table 1.

There may be an overlapping of the SO_4^{2-} symmetrical stretch band with another band of a V(V)–sulfates complex possibly due to V=O terminal stretch. The peak in the range of 760–790 cm^{-1} is associated with V–O–V stretch [7, 10, 14] possibly due to V(V) dimer species. The band between 660–680 cm^{-1} becomes more prominent at high total sulfate concentrations which reflects the coordination of sulfates ions within the V(V) complex formation at higher total sulfate concentration. Similarly, the intensity behaviour of the 485 and

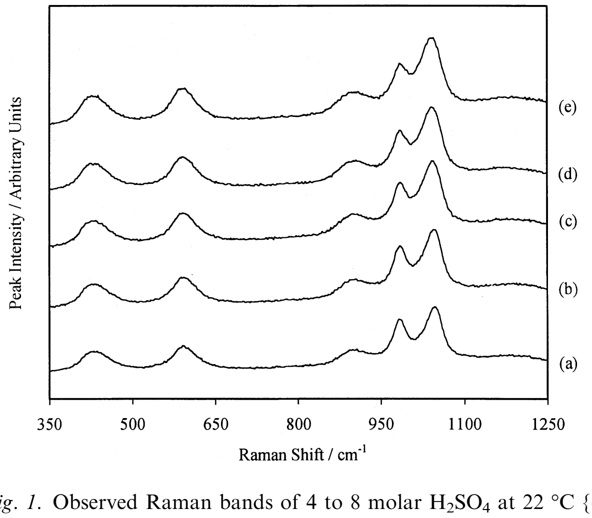


Fig. 1. Observed Raman bands of 4 to 8 molar H_2SO_4 at 22 °C {(a), (b), (c), (d) and (e) represents 4, 5, 6, 7 and 8 M H_2SO_4 concentration, respectively}. Excitation = 632.8 nm or 12 798 cm^{-1}.

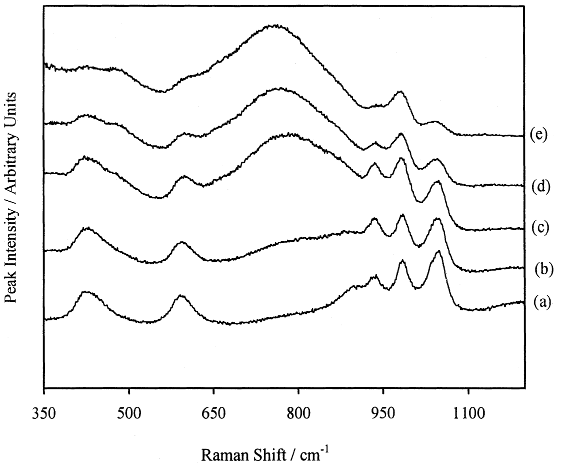


Fig. 2. Raman spectrum of 0.5–3.0 M V(V) in 5 M total sulphates {(a), (b), (c), (d) and (e) are the 0.5, 1.0, 1.5, 2.0 and 3.0 M V(V) in 5 M total sulphates. Excitation = 632.8 nm or 12 798 cm^{-1}.

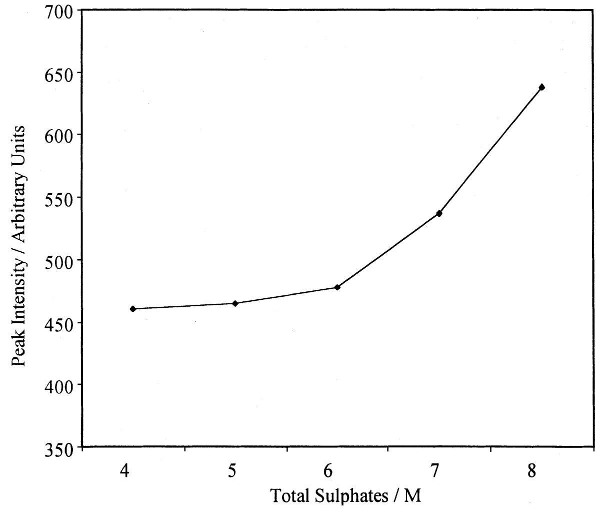


Fig. 3. Correlation between free bisulphate ions and Raman peak intensity with variation of total sulphates concentration. V(V) concentration = 2 M.

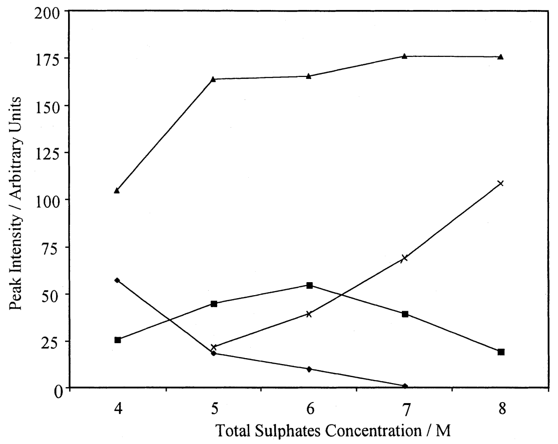


Fig. 4. Variation of different V(V) species as a function of Raman peak intensity at different total sulphates. V(V) concentration = 2 M. (♦) VO_2^+; (■) VO_3^- and $VOSO_4^-$; (×) $[VO_2(SO_4)_2]^{3-}$; (▲) $V_2O_3^{4+}$.

Table 1. Band frequencies and assignments of V(V)-sulfate species

	Wavenumber/cm^{-1}	Assignment
(i)	430	HSO_4^- band, (δ_{as}, SO_3)
(ii)	477	V–O bridging involving sulfate oxygen (V–O–S) [20]
(iii)	599	HSO_4^- band, (δ_s, SO_3 deformation)
(iv)	660–680	V–O–S bridging stretch (as) [20]
(v)	770	V–O–V stretch in V(V) dimer [7, 10, 14, 21]
(vi)	860–880	V=O stretch in $VO_2SO_4^-$ [21, 22], VO_3^- stretch
(vii)	935	VO_2^+, symmetrical stretch [10]
(viii)	984	SO_4^{2-}, symmetrical stretch, polarized
(ix)	995	V=O (ss)
(x)	1045	HSO_4^- asymmetrical stretch
(xi)	1200	H_3O^+, deformation

660 cm^{-1} bands, in the case of increasing sulfates at constant V(V) concentration, suggests that SO_4^{2-}/HSO_4^- ions definitely take part in forming a complex with the V(V) species.

The effect of solution V(V), total sulfates concentration and V(IV)/V(V) ratio variation on speciation were assessed for a series of solutions and the results are presented in Figures 3–8. The intensity of the HSO_4^- bands at 1045, 595 cm^{-1} and SO_4^{2-} band at 984 cm^{-1} increase linearly with the increase in total sulfate concentration from 4–8 M (Figure 3), however, the intensity trend due to the SO_4^{2-} ion concentration is difficult to assess, because of its overlap with the V(V)–sulfates complex band at 988 cm^{-1}.

It appears that the activity of VO_2^+ ion is drastically reduced by increasing the total sulfates concentration (Figure 4). The band at 860 cm^{-1} due to V–O stretch in $VO_2SO_4^-$ and VO_3^- shows a parabolic behaviour with its maximum intensity at 6 M total sulfates. On the other hand, the proposed 660 cm^{-1} band due to V–O–S stretch in $VO_2(SO_4)_2^{3-}$ shows a linearly increasing trend with the increase in total sulfates. However, no significant change in 770 cm^{-1} band due to V–O–V stretch is observed with increase in total sulfates above 5 M. Few other broader weak bands possibly due to H_3O^+ at 1195 cm^{-1} and H_2O at 1600 cm^{-1} were also observed which are not shown in present graph.

In the case of the spectral analysis of 0.1–3.0 M V(V) in 5 M total sulfates (Figures 2, 5 and 6), the broader overlapped bands between 600–900 cm^{-1} are nearly negligible until the V(V) concentration was increased above the 0.5 M mark in 5 M total sulfates. The corresponding decreasing peak intensity trend for unbound HSO_4^- ions band (1045 cm^{-1}) with increasing V(V) concentration (Figure 5) indicates the increasing interaction between HSO_4^- and the vanadium species in the electrolyte. A similar trend was also observed for the H_3O^+ ion band at 1195 cm^{-1} and predicts the increased coordination of HSO_4^- with the central vanadium species.

The V–O band due to $VO_2SO_4^-$ and VO_3^- decreases in intensity when V(V) concentration in 5 M total sulfates exceeds 1.5 M. However, with an increase in V(V)

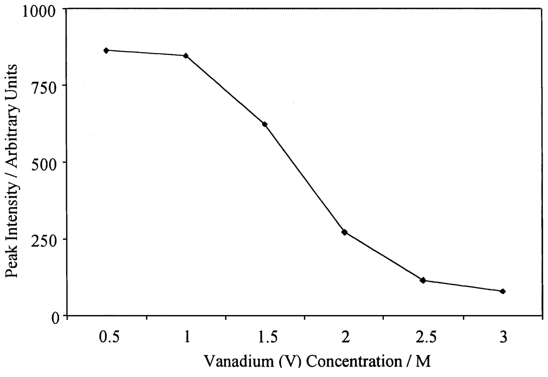


Fig. 5. Correlation between free bisulphates and Raman peak intensity with variation of V(V) concentration. Total sulphates concentration = 5 M.

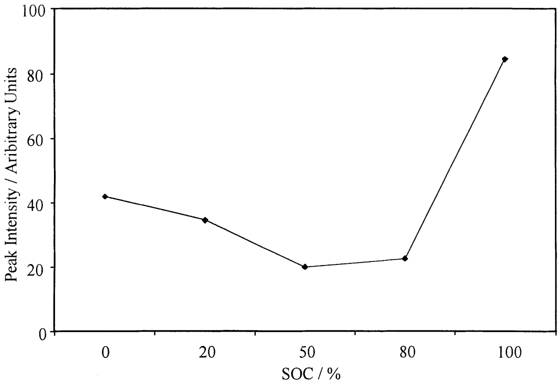


Fig. 7. Correlation between free bisulphates and Raman peak intensity with variation of State of charge in 2 M V(V) in 5 M total sulphates.

concentration above 1.0 M in 5 M total sulfates, a sharp increase in peak intensity due to V–O–V stretching band (770 cm^{-1}) is observed indicating the dimerization V(V) species in solution (Figure 6). The linear increase in 660 cm^{-1} band due to V–O–S stretch indicates the closer interaction between V(V) and sulfates species with increase in V(V) concentration. In the case of the mixed V(V)/V(IV) solutions, corresponding to different states of charge (SOC) of the positive half-cell electrolyte in the vanadium redox battery, we observed the existence of another band in the middle range of 20–80% SOC at 365 cm^{-1}. The presence of this band suggests some close interaction between V(V) and V(IV) species.

This may be interpreted in terms of charge neutralization which becomes effective due to competition of VO^{2+} and VO^{2+} for coordination with HSO_4^-/SO_4^{2-} [10]. The explanation could also be seen by looking at the intensity of the HSO_4^- bands which decreases in the middle SOC range (Figure 7). The peak intensity of the V(V) dimer band at 760 cm^{-1} decreases uniformly at lower SOC and the band is also shifted toward high frequency. The band at 982 cm^{-1} becomes sharper and less broad and is shifted towards higher frequencies by 10 cm^{-1} at lower SOC. This may be explained by the higher concentration of V(IV) species which give a strong band at 990 cm^{-1} due to the V=O stretch (Figure 8). Spectra were also obtained of 2 M V(V) in 5 M total sulfate after aging at 50 °C for six days. There seems to be no change in the number of bands after the solution aging period, However, a decline in peak intensity of the band at 765 cm^{-1} due to V(V)-sulfates complex is observed and is due to the increase in the amount of V(V) precipitates formed with time. The peak was also shifted towards high frequency (cm^{-1}). In contrast the peak intensity of the HSO_4^- bands increased showing the liberation of HSO_4^- previously bound to the complex. Also evidenced is the peak intensity increase in the VO_2^+ band at 935 cm^{-1} as well as a small change in the H_3O^+ band at 1200 cm^{-1} which gradually increased with precipitation.

4. Discussion

The structure and symmetry of the complex molecule, the strength of its coordinate bonds, as well as its interaction with the environment (solvent, ions bound in the outer sphere, other molecules) all affect the vibration spectrum of the complex. From (Figure 2), it appears that at least five more V(V) species other than VO_2^+ exist

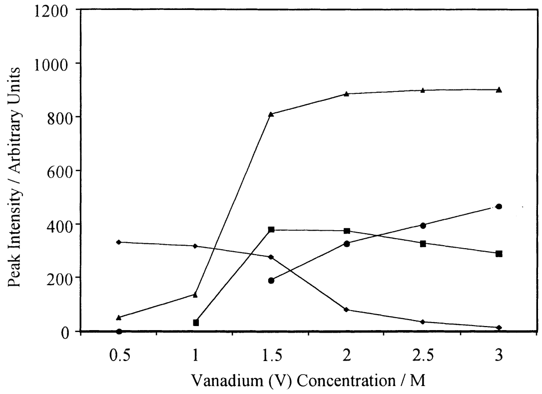


Fig. 6. Variation of different V(V) species as a function of Raman peak intensity at different V(V) concentration. Total sulphates concentration = 5 M. (♦) VO_2^+; (■) VO_3^- and $VOSO_4^-$; (●) $[VO_2(SO_4)_2]^{3-}$; (▲) $V_2O_3^{4+}$.

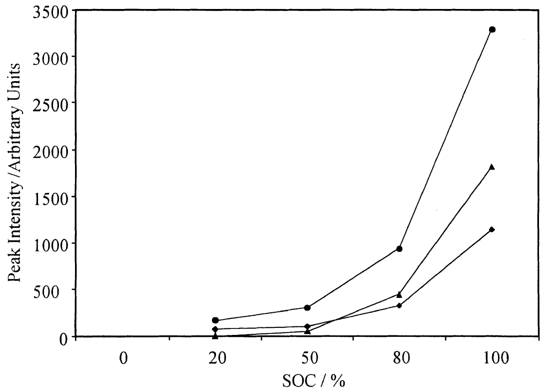
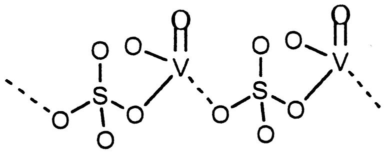


Fig. 8. Variation of different V(V) species as a function of Raman peak intensity at different State of charge in 2 M V(V) in 5 M total sulphates. (♦) VO_3^- and $VOSO_4^-$; (▲) $[VO_2(SO_4)_2]^{3-}$; (●) $V_2O_3^{4+}$.

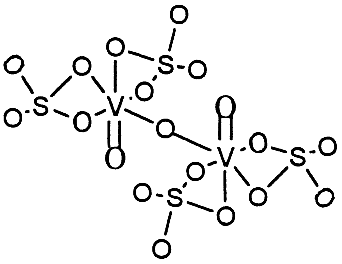
in the concentrated V(V)-sulfates system. In the case of lower concentration of V(V) in up to 4 M total sulfates concentration, VO_2^+ reacts with sulfate ions leading to the formation of $VO_2SO_4^-$ due to the following reaction:

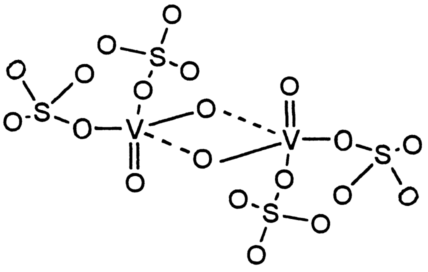
$$VO_2^+ + SO_4^{2-} \longleftrightarrow VO_2SO_4^- \qquad (2)$$

The possible structure of $VO_2SO_4^-$ is



Increasing the V(V) concentration at constant total sulfates not only increases the intensity of the 795 cm^{-1} band but also a significant red shift of about 35 cm^{-1} occurs. Apparently there seems to be a corresponding change in intensity for the bands due to V–O–S bridging (477, 680 cm^{-1}) involving sulfate oxygen in response to the decrease in HSO_4^- band at 1045 cm^{-1} which indicates a direct linkage of V(V) with bidentate bridging sulfate groups. Many related configurations of bridging S–O–V and V–O–V bands appear as a broadened band which causes lowering in the symmetry of species. The V(V) complex in this case is a V(V) polymeric species linked bidentately with SO_4^{2-}/HSO_4^- groups in a six coordinate vanadium environment under distorted symmetry [23]. The possible reaction would lead to the formation of $V_2O_3^{4+}$ and $V_2O_4^{2+}$ dimer species with possible structure as follows:





The interaction of SO_4^{2-} and HSO_4^- with central V(V) units as well as with outer-sphere ions (i.e., H_3O^+, HSO_4^-, H_2O) also deforms the molecular structure of V(V) complex. The resultant effect would be a mixed copolymer species which will cause the observed sudden increase in viscosity of solutions with small increase in V(V) [4].

The presence of a linear V–O–V structure can permit effective interactions between the d_{xy} orbital of the participating vanadium nuclei via the pπ orbital of the bridging oxygen atom. However, in the present case, as well as in others, substantial departures of the V–O–V bridge angles from linearity generate a valance-trapped situation due to poor overlap of symmetry-constrained d_{xy} orbital. This creates a relatively high energy difference between the highest occupied molecular orbital and lowest occupied molecular orbital resulting in a high-energy charge transfer transition. So the interaction of two VO_2^+ ions to give a $V_2O_4^{2+}$ does not seem to prove a stable product at higher concentrations. The $V_2O_3^{4+}$ dimer may predominate at higher sulfates concentrations.

The involvement of either the SO_4^{2-} or HSO_4^- ligand in the V(V)-sulfates complex is equally possible, although the HSO_4^- is the most likely ligand because of the concentration range used. The concentration of HSO_4^- would be much higher than that of the concentration of SO_4^{2-} in the 4–8 M H_2SO_4 solutions used in the present study [15].

The increase in V(V) and/or total sulfates concentration provides an increase in intensity of V–O bridging bands (477, 680 cm^{-1}) involving sulfate oxygen which reflects the closer interaction between V(V) and sulfates species. However, the V–O–V band (771 cm^{-1}) and V–O–S band (660 cm^{-1}) shows little blue shift (Figure 2). Thus addition of sulfates or bisulfates results in formation of V(V) complex which contains coordinated sulfate groups exhibiting smaller distortion to their symmetry. These ligands are attached with the V(V) bidentately by covalent bonds as well as with van der Waal forces. There is a possibility of cleavage of the V–O–V bridge at higher total sulfates, favors the formation of $VO_2(HSO_4)_2^-$ or $VO_2(SO_4)_2^{3-}$ species, which are more stable species and having higher molecular symmetry.

Increasing the V(V) concentration at constant total sulfates shows an increase in peak intensity of 880 cm^{-1} band up to 1.5 M V(V), further increasing in V(V) concentration produces insignificant change in peak intensity of 880 cm^{-1} band. On the other hand the peak intensity of 880 cm^{-1} band was drastically decreased, when total sulfate concentration was increased above 6 M. The difference in behavior of 880 cm^{-1} band due to VO_3^- species may be explained under the following equilibrium reaction:

$$VO_3^- + 2H^+ \longleftrightarrow VO_2^+ + H_2O \qquad (3)$$

which reflects the higher involvement of H^+ ions to improve the vanadium(V)-total sulfates electrolyte stability by increasing the sulfuric acid concentration in V(V) solutions. Whereas the higher V(V) concentration seems to destabilize electrolyte due to the presence of VO_3^-.

The presence of VO_3^- was further evidenced from the Raman spectra of V(V) precipitates which gave the bands at 500 and 890 cm^{-1} under different drying conditions. However, the precipitates obtained on heating at 470 °C gave spectra consistent with the spectra of V_2O_5 which can be explained as follows:

$$2\,HVO_3 \xrightarrow{heat} V_2O_5 + H_2O \tag{4}$$

From this discussion we may predict that complexes present in concentrated V(V)-sulfate solutions coexist in equilibrium with each other, the nature and amount of these depending primarily on the actual V(V) and total sulfate concentration in solution. The presence of Raman vibrational bands in the narrow frequency range together with a continuous ligand exchange transfer occurring at a faster rate will cause band broadening of these species.

The sudden increase in viscosity of vanadium redox battery positive electrolyte at higher solution concentrations (above 2 M V(V) in 5 M total sulfates) is due to formation of many copolymeric vanadium species involving extensive V–O–V, V–O–S, bonding and closer interaction. The conductivity decrease with increasing V(V) and total sulfates could be due to consumption H^+, HSO_4^- and SO_4^{2-} ions and forming different complexes with vanadium species as

$$VO_3^- + 2H^+ \longleftrightarrow VO_2^+ + 2H_2O \tag{5}$$

$$VO_2^+ + SO_4^{2-} \longleftrightarrow VO_2SO_4^- \tag{6}$$

$$VO_2^+ + HSO_4^- \longleftrightarrow VO_2HSO_4^- \tag{7}$$

and their polymer complex.

The stability of V(V) electrolyte could be increased at elevated temperature (above 50 °C) by maintaining the higher levels of H^+, HSO_4^- ions together with an appropriate amount of V(V) concentration to enable Reaction 3 to proceed in the forward direction. Otherwise, the presence of closer interaction of VO_3^- will cause the unwanted V(V) precipitation.

The vanadium also forms an oxo-bridged dimer with a stable $V_2O_3^{3+}$ central ion in most of the dinuclear vanadium (IV/V) compounds [24–26] which were further characterized by X-ray crystallography [27]. Therefore, under certain circumstances (1:1 interaction of V(V) and V(IV) species at 50% SOC), the formation of $V_2O_3^{3+}$ may be suggested. However, the above product will be quite unstable due to the weak interaction between the V(V)/V(IV) couple.

5. Conclusion

The colour change behaviour of V(V) in solutions of different total sulfates concentration may be explained by the presence of a range of different species. The species identified from the present study are VO_2^+, $VO_2SO_4^-$, $VO_2(SO_4)_2^{3-}$, VO_3^-, VO_2HSO_4, $VO_2(HSO_4)_2^-$, $V_2O_3^+$, and $V_2O_4^{2+}$ and their polymers. The amount of each species depends upon the actual V(V) and total sulfate concentrations and their ratio. It was concluded that the presence of higher V(V) concentration in the absence of higher H^+ ion in the positive half-cell electrolyte in the VRB will tend to cause precipitation at elevated temperature (>30 °C), so that higher H^+ and sulfate concentrations are required for the stabilization of the concentrated V(V) solutions for application in the vanadium redox battery.

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