



Nuclear magnetic resonance studies on vanadium(IV) electrolyte solutions for vanadium redox flow battery

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ABSTRACT

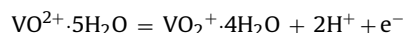
The vanadium(IV) electrolyte solutions with various vanadium concentrations are studied by variable temperature ¹H and ¹⁷O nuclear magnetic resonance (NMR) spectroscopy. The structure and kinetics of vanadium(IV) species in the electrolyte solutions are explored with respect to vanadium concentration and temperature. It was found that the vanadium(IV) species exist as hydrated vanadyl ion, i.e. [VO(H₂O)₅]²⁺ forming an octahedral coordination with vanadyl oxygen in the axial position and the remaining positions occupied by water molecules. This hydrated vanadyl ion structure is stable in vanadium concentrations up to 3 M and in the temperature range of 240–340 K. The sulfate anions in the electrolyte solutions are found to be weakly bound to this hydrated vanadyl ion and occupies its second-coordination sphere. The possible effects of these sulfate anions in proton and water exchange between vanadyl ion and solvent molecules are discussed based on ¹H and ¹⁷O NMR results.

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1. Introduction

The vanadium redox flow battery (VRB) is a promising candidate for large scale storage of electrical energy and can be useful when combined with non-continuous renewable power sources such as solar or wind power [1,2]. The VRB also offers economically viable backup system for large energy electrical grids with fluctuating loads [3,4]. The VRB operates on redox couples of V(II)/V(III) at negative electrode and V(IV)/V(V) at positive electrode reactions [5,6]. Hence the power, life cycle and performance of the VRB mainly depend on redox reactions between soluble ionic species in electrolytes. In particular, the much needed energy density is determined by the concentration of vanadium species in the electrolyte solutions. But, the solubility and stability of the vanadium species in the electrolyte solutions are limited, which leads to limited specific energy density of VRB [7]. Recently, several research papers have been published where the solubility and stability of the positive electrolyte systems vanadyl (i.e. V(IV)/V(V) solutions) have been investigated by spectroscopy and/or electrochemical studies [7–10]. Despite these studies the exact chemical identity of active

vanadium species and its electrochemical reactions are still unclear. In particular, the structure of both V(IV) and V(V) vanadium species at different concentrations of sulfate anions, metal cation and solvent molecules are not well-understood. Such an understanding could in turn help us to unravel the exact vanadium redox chemistry of different electrolyte solutions used in VRB. Recently, Gattrell et al. [11], proposed the mechanism of vanadium redox reactions of vanadyl (VO²⁺) and vanadic (VO₂⁺) species representing the positive half cell V(IV) and V(V) electrolyte solutions respectively. The proposed reaction is,



where the reaction toward the right side represents the charging cycle and the opposite direction represents the discharge cycle in the positive half cell of the VRB. From this model, we can infer that the water molecule plays the crucial role in this redox reaction. Such a metal ion bound with water molecules are prone to exchange with solvent molecule, which is a simple ligand substitution reaction, yet a necessary reaction in understanding the redox electrochemical behavior of ionic liquids [12]. Further, the proposed reaction does not taken into account the effect of counter anions (i.e. SO₄²⁻ or HSO₄²⁻), which is known to form complexes with the vanadium species in the electrolyte solutions [8,13]. Hence it is necessary to understand both the complex formation of vanadium ions and its water exchange mechanism in these electrolyte solutions.

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool to study the chemical identity and dynamics in ionic solutions.

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^1H and ^{17}O NMR spectroscopy are extensively used to study the water exchange reaction between metal ions and solvent [14]. For example, NMR has been successfully utilized to explore the water exchange kinetics in vanadium(IV) solutions containing both water and organic compounds as solvent [15–17]. However, to our knowledge there is no NMR study on vanadium(IV) electrolyte solutions (which is composed of a high concentration of vanadium with sulfuric acid as solvent) used in high energy density VRB. In this work, variable temperature ^1H and ^{17}O NMR studies on V(IV) electrolyte solutions with vanadium concentrations ranging from 0.1 M to 3 M that is typically used in VRB have been carried out. Our studies provide new insights into the mechanisms of the water exchange (or ligand substitution) kinetics and clarify the chemical identity of vanadium species in the solutions.

2. Experimental

Vanadium(IV) solutions of various vanadium concentrations (from 0.1 M to 3 M) were prepared by dissolving vanadyl sulfate (VOSO_4 , Aldrich) in 2 M sulfuric acid (H_2SO_4) aqueous solutions [9]. It should be noted that the increase in vanadium concentrations simultaneously increases the total sulfate concentrations in solution due to usage of vanadyl sulfate as vanadium source. The total sulfate concentration (S_m) in all solutions can simply be calculated as $S_m = V_m + 2M$. For ^{17}O isotopic enrichment, H_2^{17}O (>20% ^{17}O from Cambridge Isotopes Laboratories) solutions were used during synthesis. The ^1H and ^{17}O NMR measurements were performed using a Varian 500 Inova spectrometer ($B_0 = 11.1\text{ T}$) with ^1H and ^{17}O Larmor frequency of 500.19 MHz and 67.8 MHz respectively. All variable temperature measurements were done using tightly sealed 7.5 mm zirconia rotors. The quantitative NMR spectra were recorded using single pulse sequence with 1 s recycle delay at all temperatures. The ^1H chemical shifts were externally referenced to the solid adamantane as secondary reference ($\delta = +1.63$ ppm with respect to TMS $\delta = 0$ ppm) while, ^{17}O chemical shifts were externally referenced to a commercial H_2^{17}O solution ($\delta_{\text{iso}} = 0$ ppm). The estimated uncertainties in chemical shifts, determined through calibration using the same reference sample, were 0.1 ppm. Accurate chemical shifts and integral intensities of different contributions in each spectrum were obtained from fitting the line shapes of the resonance lines using the SpinWorks program [18]. The UV–visible absorption spectra are recorded with Beckman DU 640 spectrophotometer at room temperature with pure 2 M sulfuric acid as blank solution. Quantum chemistry calculations were carried out using the Amsterdam Density Functional (ADF) program [19,20]. Basis set used was QZ4P (quad Z, 4 polarization functions, all electron) with the Slater type functional implemented in the program for both geometry optimization and NMR calculation [21].

3. Results and discussion

3.1. Structure of hydrated vanadyl ion

It is well known that V(IV) species exist as the hydrated form of the vanadyl ion $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ in aqueous solutions at moderately low pH [22,23]. Hence it is quite possible, to have this type of hydrated vanadyl ion in V(IV) electrolyte solutions used in the redox flow battery. The possible molecular and electronic structure of hydrated vanadyl ion has previously been reported in the literature using different techniques [23–26]. The hydrated vanadyl ion has octahedral coordination with four equivalent water molecules in the equatorial plane and a water molecule in the axial position opposite side to the vanadyl oxygen [23,27]. It is also possible that additional water molecules from the bulk solvent are weakly bound to this octahedron and forming a second-

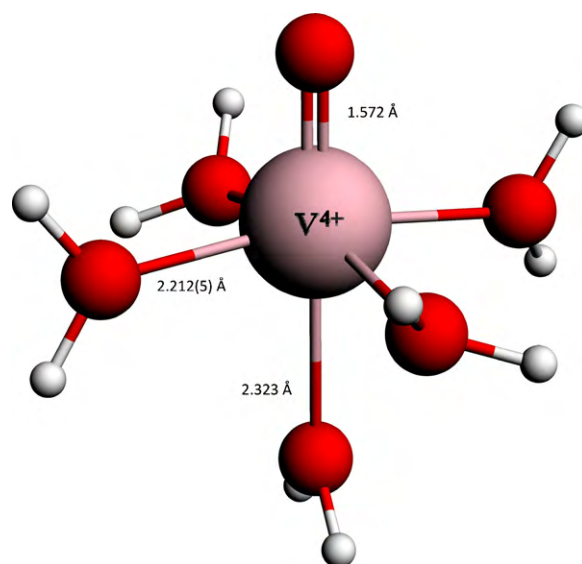


Fig. 1. The structure of hydrated form of vanadyl ion derived from geometry optimization method using ADF program (see text for details).

coordination sphere. To understand this structure better and get proper bond lengths of this molecule, we carried out a density functional theory (DFT) based geometry optimization study. Fig. 1a shows the hydrated form of vanadyl ion with respective bond lengths calculated from our DFT study. The calculated bond lengths of the optimized structure of $\text{VO}^{2+} \cdot 5\text{H}_2\text{O}$ ($\text{V}-\text{O}(\text{H}_2\text{O})$ axial = 2.323 Å, $\text{V}-\text{O}(\text{H}_2\text{O})$ equatorial = 2.123 Å, $\text{V}-\text{O}$ oxo = 1.572 Å) agree well with X-ray crystallography results of the analogous $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ ion [28].

3.2. Optical spectra

In order to confirm the presence of this hydrated form of vanadyl ion in our V(IV) electrolyte solutions, we carried out electronic spectra measurements on 0.5 M and 1 M vanadium(IV) solution. Fig. 2 shows the room temperature optical absorption spectrum of 0.5 and 1 M vanadium(IV) sulfate concentrations dissolved in 2 M H_2SO_4 solution. The electronic spectra show similar features as previously reported spectra for hydrated vanadyl ion found in

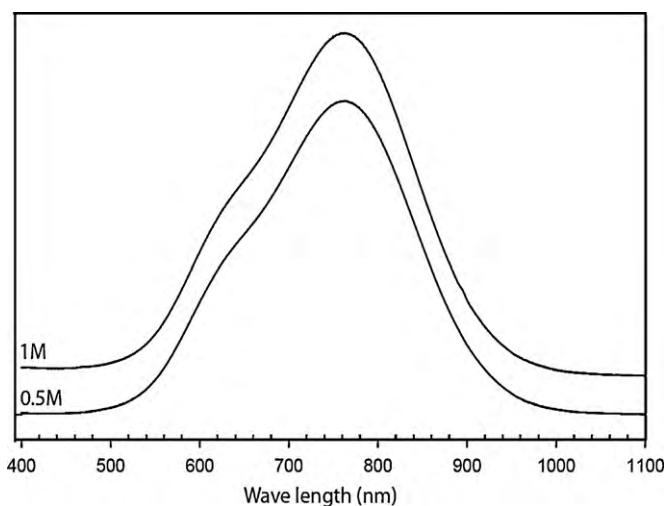


Fig. 2. The optical spectra of 0.5 M and 1 M vanadium(IV) electrolyte solutions measured at room temperature (the total sulphate/bisulphate concentrations of 2.5 M and 3 M respectively).

aqueous vanadium sulfate and chloride solutions [24,29]. The optical absorption spectrum exhibits two bands characteristic of VO^{2+} ions in tetragonal symmetry (not the octagonal symmetry because the distance between the V atom and the axial H_2O molecule is longer than that of the corresponding planar H_2O molecules). These two absorption bands are centered at $13,117\text{ cm}^{-1}$ (i.e. 762 nm) and $16,100\text{ cm}^{-1}$ (i.e. 621 nm) and assigned the transitions $\Delta_{\perp} = {}^2\text{B}_{2g} \rightarrow \text{E}_{2g}$ and $\Delta_{\parallel} = {}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$ respectively based on previous literature [24]. In general, the observed absorption bands are sensitive to new bonds with vanadium ion in the vanadyl molecular structure [29,30]. The V(IV) electrolyte solutions used in this study contain significant amount of sulfate anions and it is possible that these sulfate anions might complex with vanadyl ion in solutions. However, such a complex would change the charge of the vanadyl ion, such as $[\text{VO}(\text{H}_2\text{O})_4\text{HSO}_4]^{1+}$ or $[\text{VO}(\text{H}_2\text{O})_4\text{SO}_4]^{0}$ and greatly affect the absorption spectra. But the optical spectra of 0.5 and 1 M vanadium(IV) electrolyte solution shows similar feature as aqueous vanadyl ion solution, which strongly suggests the electronic structure of the vanadyl ion in the solution is not changed. Hence it is unlikely to have the sulfate ion chemically bonded with the vanadyl molecule in the concentration range of our study. Nevertheless, it is possible to have the sulfate anions weakly bound to vanadyl ion due to electrostatic interactions. At this point, the optical spectrum confirms the presence of hydrated vanadyl ion in our electrolyte solutions and hence further NMR results of our electrolyte will be discussed based on molecular structure of hydrated vanadyl ion derived from our DFT study.

3.3. ${}^1\text{H}$ NMR

Solution ${}^1\text{H}$ NMR of various vanadium(IV) concentrations in 2 M H_2SO_4 solution was recorded at 300 K using 11.1 T magnetic field is shown in Fig. 3a. For all vanadyl ion concentrations ${}^1\text{H}$ NMR spectra show only a single peak at 300 K. This is intriguing considering the presence of different proton sites such as water molecules from bulk solvent solution, water molecules bounded with vanadyl ions and sulfate anions (HSO_4^{2-}). However, if there is fast proton exchange between different hydrogen bonds (will be discussed later) the ${}^1\text{H}$ NMR spectra will show chemically averaged single resonance. Hence, the observed ${}^1\text{H}$ NMR might represent a chemically averaged signal due to fast proton exchange between free solvent water molecule, sulfate anion (HSO_4^{2-}) and metal ion bound water molecules [31]. The effect of vanadium(IV) concentration on observed ${}^1\text{H}$ chemical shift and line width are shown in Fig. 3b. The increase in vanadium(IV) concentration induces a positive chemical shift (i.e. towards higher frequency) of proton spectra. The observed proton chemical shift of solution containing paramagnetic ions is given by [25]:

$$\delta^{\text{obs}} = \delta^{\text{con}} \chi P_M \quad (1)$$

δ^{con} is the chemical shift of the protons of the solvent molecules which are complexed to the vanadyl ion (VO^{2+}) and P_M is the fraction of the total solvent molecules complexed to VO^{2+} ions. The vanadyl ion has five water molecules, hence the value of P_M can be defined as, $(5V_m/55.5 - S_m)$, where V_m is the molar concentration of vanadyl ion, i.e. vanadium concentration of the solution. The presence of paramagnetic ions in solution can cause two types of contact shifts (δ^{con}) to NMR peaks, namely pseudo contact shift and Fermi contact shifts [32]. The small electron magnetic moment anisotropy resulting in small 'g' factor for VO^{2+} compounds rules out any major contribution from the pseudo contact shift [25]. This suggests that any observed chemical shift is arising from Fermi contact shift, which occurs when some unpaired spin density is transferred from the ligand (solvent molecule) to the metal or vice versa. The vanadium metal ions contain unpaired electrons in both the π -type t_{2g} and the σ type e_g of the d orbitals. Thus two types of bonding,

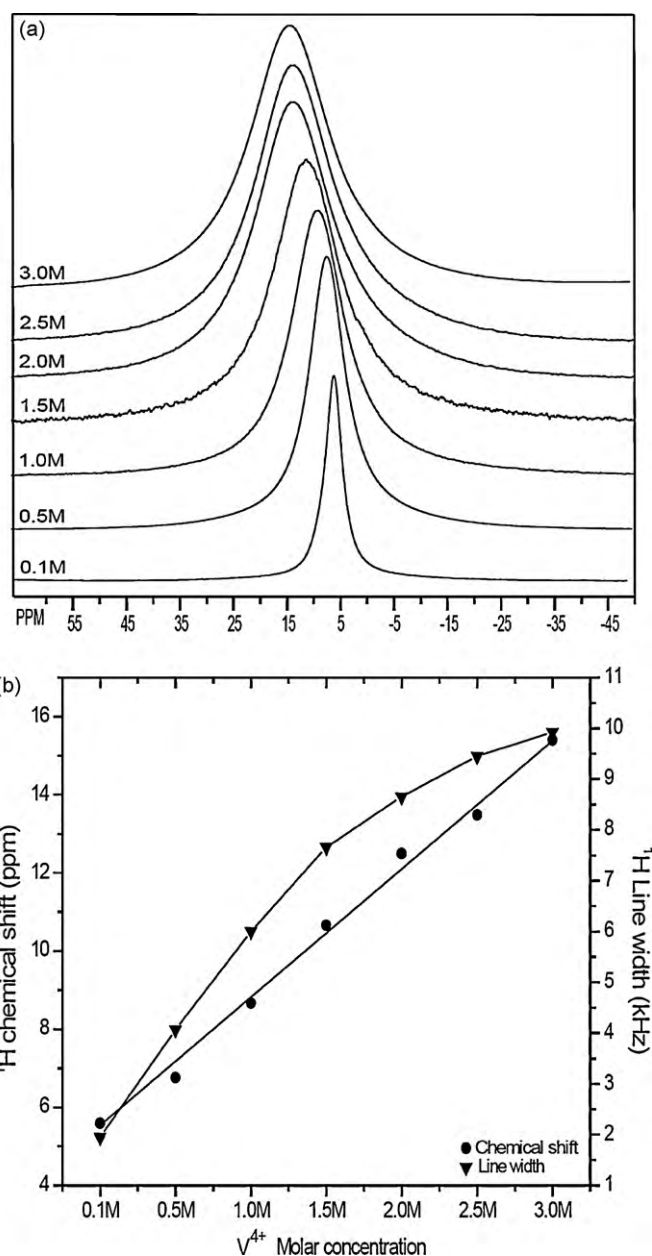


Fig. 3. ${}^1\text{H}$ NMR spectra of vanadium(IV) electrolyte solutions measured at 300 K using 11.1 T magnetic field for different vanadium(IV) concentrations. (a) ${}^1\text{H}$ NMR resonances; (b) isotropic chemical shift and line width of ${}^1\text{H}$ resonances.

i.e. σ or π bonds are possible during complex formation between vanadyl ions and water molecules. It is well known that the π bonds produce positive shift towards high frequency for proton nuclei [33,34]. The positive shift observed in our ${}^1\text{H}$ experiments for all vanadium concentrations (see Fig. 3b) clearly indicates that the presence of π bonding between vanadium and oxygen in water molecule. This result is similar to the aqueous VOSO_4 solutions reported previously [25] and confirms the presence of hydrated vanadyl ion in our V(IV) solutions.

In paramagnetic solutions the measurement of line width ($\Delta\nu$) represents a simple and straightforward way of measuring transverse relaxation time [35]:

$$(T_{2p})^{-1} = \pi(\Delta\nu_{\text{obs}} - \Delta\nu_{\text{sol}}) \quad (2)$$

where $\Delta\nu_{\text{obs}}$ is the observed line width of electrolyte solution and $\Delta\nu_{\text{sol}}$ is the line width of the solvent (i.e. 2 M sulfuric acid) with-

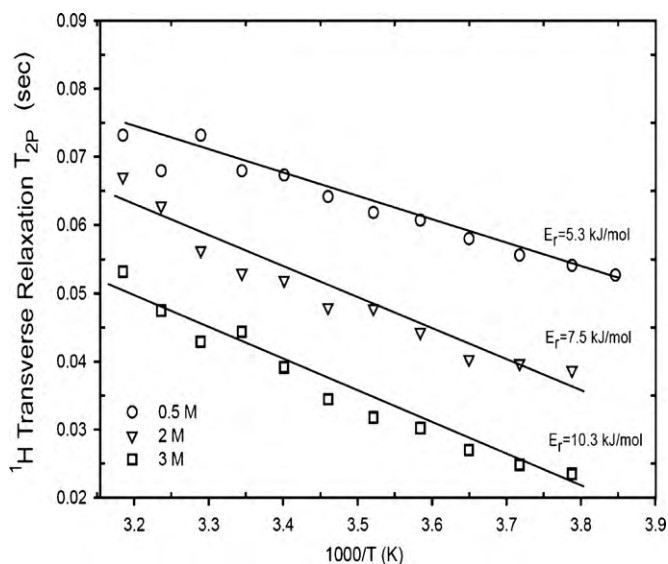


Fig. 4. The temperature dependent ^1H transverse relaxation time (T_{2p}) of vanadium(IV) electrolyte solutions measured using 11.1 T magnetic field.

out metal ions. Fig. 4 shows the temperature dependent proton T_2 relaxation time of various vanadyl ion concentrations. The relaxation shows Arrhenius type behavior in the temperature range of our study (240–340 K). In order to identify the exact nature of the proton dynamics and understand the activation energy derived, we need to analyze the possible mechanism of relaxation. The temperature dependent T_{2p} can be analyzed by means of the modified Swift–Connick equation [36]:

$$(T_{2p})^{-1} = P_M \tau_m^{-1} \frac{T_{2m}^{-2} + (T_{2m} \tau_m)^{-1} + \Delta\omega_m^2}{(T_{2m}^{-1} + \tau_m^{-1})^2 + \Delta\omega_m^2} \quad (3)$$

where τ_m is the correlation time for chemical exchange between the metal ion molecule and the solvent molecule, T_{2m} is relaxation time due to electron interaction (unpaired electron in metal center) and is the chemical shift difference between bound and free solvent $\Delta\omega_m$ in absence of ligand exchange. For vanadium(IV) solutions, $\Delta\omega_m$ has negligible effect [37] and hence based on Eq. (3), we can consider the transverse relaxation (T_{2p}) might mainly depend on the correlation time for chemical exchange between metal ion molecule and solvent molecule (τ_m) and the electron-nuclear relaxation mechanism (T_{2m}). Hence, the transverse relaxation time (T_{2p}) can be defined as [35],

$$(T_{2p})^{-1} = P_M T_{2m}^{-1} \left(\frac{\tau_m^{-1}}{T_{2m}^{-1} + \tau_m^{-1}} \right) = P_M (T_{2m} + \tau_m)^{-1} \quad (4)$$

Based on Eq. (4), we can infer the line width (or relaxation time T_{2p}) depends on not only the metal ion concentration (P_M) but also the chemical exchange correlation time (τ_m) and electron-nuclear relaxation time (T_{2m}). Such a complex relationship of line width is the reason for slightly non-linear increase of proton line width with increase in metal ion concentration (see Fig. 3b). In order to separate and identify the main contribution for the line width of proton resonance, we carried out variable temperature ^1H NMR study.

If the chemical exchange is rapid compared with electron-nuclear relaxation (i.e. $1/\tau_m \gg 1/T_{2m}$, or $t_m \ll T_{2m}$), then the observed line width (or T_{2p}) is controlled by the T_{2m} relaxation process [36]. The increase of relaxation time (or decrease of line width) with increase in temperature clearly indicates that proton relaxation is in very fast chemical exchange limit [33,38]. In this temperature region, the proton transverse relaxation time (or

line width) is mainly controlled by T_{2m} relaxation time. The T_{2m} relaxation mechanism due to unpaired electron-nuclear coupling is described by [35,39]:

$$\frac{1}{T_{2M}} = \frac{7}{15} S(S+1) \frac{\gamma^2 g^2 \beta^2}{r^6} \tau_c + \frac{1}{3} S(S+1) \left(\frac{A}{\hbar} \right)^2 \tau_s \quad (5)$$

where τ_c and τ_e are the correlation times, g is the electron g factor, β is Bohr magneton and r is the distance between the observed nucleus and the free electrons of metal ion. The first term in Eq. (5) represents the contribution of the dipolar interaction and the second term is due to electron-nuclear hyperfine interaction. For proton, the hyperfine coupling constant (A/\hbar) is much smaller than the dipolar interaction [27] and hence the T_{2M} relaxation time (or line width) is mainly dominated by the correlation time (τ_c) through dipolar interaction (first term in Eq. (5)). The correlation time (τ_c) in dipolar contribution normally arise from rotational motion of the spherical molecules described by [35]:

$$\tau_r = \frac{4\pi\eta a^3}{3kT} \quad (6)$$

where η is the viscosity of the solution ($\text{kg s}^{-1} \text{m}^{-1}$), a is the radius of the rotating molecule. The rotational correlation time represents either re-orientation or rotational motion of hydrated vanadyl ion in electrolyte solutions. Such a temperature dependent correlation time can also be described by simple Arrhenius equation:

$$\tau_r = \tau_0 \exp\left(\frac{E_r}{RT}\right) \quad (7)$$

Hence, the temperature dependence of ^1H transverse relaxation time (T_{2p}) can be fitted with Eq. (7) and the respective activation energies (E_r) for rotational motion are tabulated in Table 1. It is interesting to note that the energy required for rotational motion in 3 M solution is nearly two times larger than the 0.5 M and 1 M solutions. Based on Eq. (6), the rotational correlation time greatly depends on the radius of rotating molecule (a^3), so the observed increase in activation energy might indicate an increase in the radius of the vanadyl ion. It is equally possible that the increase in activation energy might be due to increase in viscosity (η) of the solution. More insights in to the possibility of increase in effective radius of vanadyl ion will be discussed later, based on ^{17}O NMR results. At this point, we can clearly say that with an increase in vanadium concentration the vanadyl ion becomes less mobile. Unfortunately, our variable temperature proton relaxation measurement shows only the T_{2M} controlled region and not the chemical exchange (i.e. $1/\tau_m < 1/T_{2M}$) controlled region, which restricts the direct observation of proton exchange between vanadyl ion and solvent molecules. So we need other probe such as ^{17}O NMR to look in to the exchange mechanism of vanadyl ions.

3.4. ^{17}O NMR

Fig. 5a shows the ^{17}O NMR of 2 M sulfuric acid (bottom spectra) and our electrolyte solutions with various vanadyl ion concentrations recorded at 300 K using 11.1 T magnetic field. The 2 M sulfuric acid shows two sharp peaks at 2.4 ppm and 162 ppm representing two different oxygen environments arising from hydronium ions (H_3O^+) and protonated sulfate ion (SO_4^{2-} or HSO_4^{2-}) in sulfuric acid. Based on previously reported ^{17}O NMR parameter for hydronium ions [40,41] the peak 2.5 ppm could represent the hydronium ions (H_3O^+) and the other small intensity peak at 162 ppm obviously represents remaining anions, i.e. sulfate ions (SO_4^{2-} or HSO_4^{1-}). The small integral intensity of peak representing sulfate ions does not represent the total concentration of sulfate and bisulfate ions in sulfuric acid, but simply indicates the limitation of oxygen exchange between bisulfate ion and ^{17}O isotope enriched water. The electrolyte solutions with different vanadyl

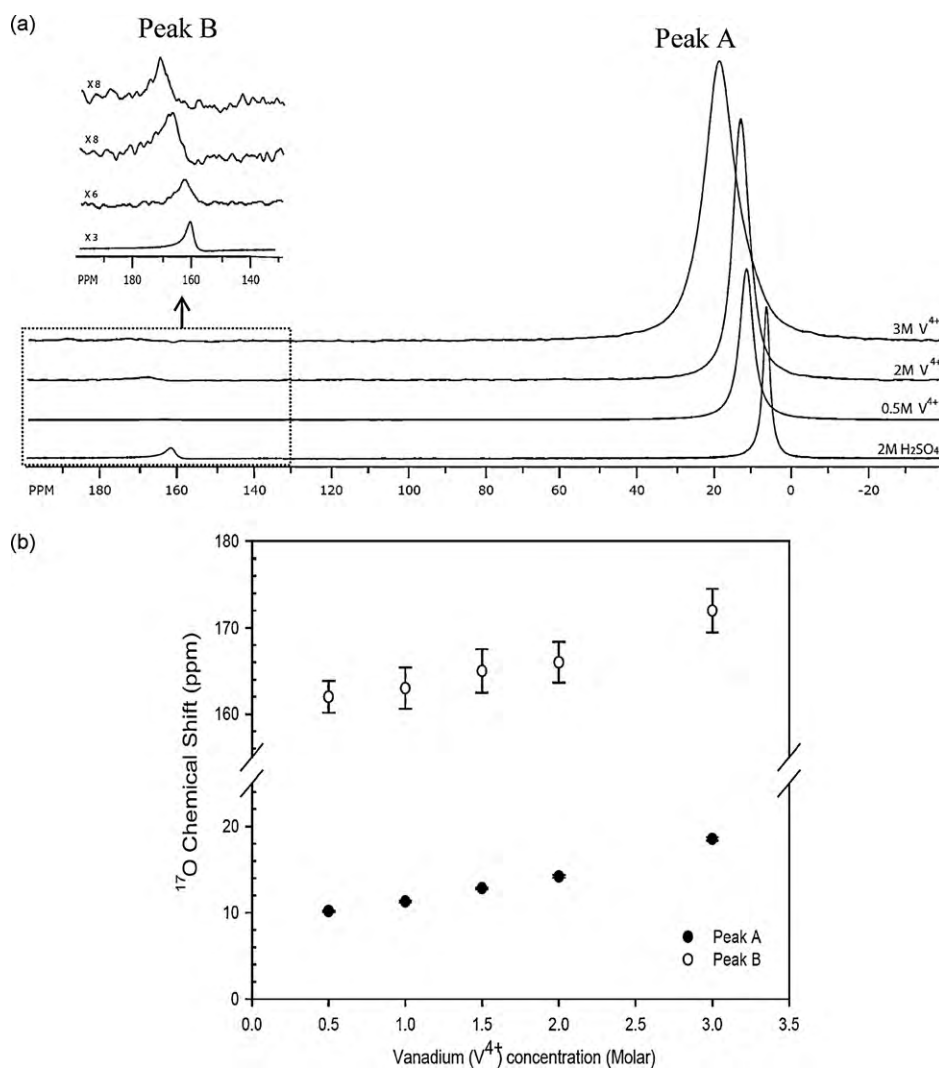
Table 1The kinetics of hydrated vanadyl ion in vanadium(IV) electrolyte solutions calculated from variable temperature ^1H and ^{17}O NMR measurements.

V^{4+} molar concentration (V_M) ^a	^{17}O NMR				^1H NMR, E_r (kJ mol^{-1})
	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger (J mol^{-1})	k_{ex}^{298} ($\times 10^3 \text{ s}^{-1}$)	E_a (kJ mol^{-1})	
0.5 (2.5M)	22.9 ± 0.5	-11.4	2.1	14.0 ± 0.8	5.3 ± 0.6
2.0 (4M)	22.5 ± 0.7	-14.5	2.9	12.9 ± 0.5	7.5 ± 0.5
3.0 (5M)	29.5 ± 0.7	-11.2	3.2	17.9 ± 0.9	10.6 ± 0.9

^a The total sulfate concentration ($=V_M + 2$) is given in the parenthesis.

ion solutions show a high intensity peak around 8 ppm labeled as peak A and low intensity (intensity less than 2% for all solutions) peak around 170 ppm labeled as peak B. This low intensity peak matches the solvent peak, hence can be labeled to the SO_4^{2-} or HSO_4^- ions in electrolyte solutions. Similarly, the high intensity ^{17}O NMR resonance (peak A) represents the oxygen related to solvent and vanadyl ion molecular cluster. This single ^{17}O NMR resonance representing vanadyl ion is intriguing, since based on the vanadyl ion molecular structure discussed earlier (see Fig. 1) there are three possible oxygen positions involved in the hydrated vanadyl ion namely, vanadyl oxygen (i.e. axial $\text{V}=\text{O}$), equatorial water molecules and an axial water molecule. Our geometry optimized vanadyl structure (see Fig. 1) shows the double bonded vanadyl oxygen has short bond length (1.572 Å) which means it

is strongly bonded to the vanadium ion. Such a strongly bonded oxygen needs high potential to actively participate in exchange process, so its exchange with oxygen in solvent water molecule would be extremely small [42,43]. Hence, it is unlikely to have any signal from the axial vanadyl oxygen. In contrast, the water molecule bound to vanadyl ion (both axial and equatorial water molecules) are well known to be exchanging with the free water molecules in bulk solvent [33,44]. Such a fast chemical exchange between different chemical sites of water molecule could lead to coalescence of NMR resonances and lead to a single resonance. At this condition, the chemical shift of the coalesced resonance will be the weight average of chemical shift of bound water molecule and bulk solvent water molecule [35]. In our study, for all concentrations of vanadyl ion solutions, the molar concentration of bulk

**Fig. 5.** ^{17}O NMR spectra of vanadium(IV) electrolyte solutions measured at 300K using 11.1T magnetic field for different vanadium(IV) concentrations. (a) ^{17}O NMR resonances; (b) isotropic chemical shift of ^{17}O resonances.

solvent molecule is much higher than the bound water molecule hence any such coalesced signal will be close to isotropic shift of bulk solvent water molecule (i.e. 2 M sulfuric acid solution). The isotropic shift of the high intensity peak A is closer to the expected solvent water molecule peak and contains most of the signal; hence it clearly represents average peak position of bulk solvent water molecule which is exchanging fast with bound water molecule (i.e. both axial and equatorial water molecules) of the vanadyl ion.

The effect of vanadium(IV) concentration on chemical shift of the high intensity peak A and low intensity peak B is shown Fig. 5b. The peak A chemical shift shows a positive chemical shift (i.e. towards higher frequency) with increase in vanadium(IV) concentration. Such a linear chemical shift represents the metal ion concentration effect as described in Eq. (1). This also confirms the vanadyl ion structure remains stable in all vanadium/sulfate concentrations, because any change in structure with concentration would cause significant changes in respective chemical shifts. This result is in good agreement with the optical spectra results discussed earlier. Interestingly, the concentration dependent ^{17}O NMR studies show that the peak B representing the sulfate anions also shifts towards higher frequency (positive shift) with increase in vanadium concentrations. This clearly indicates interaction between vanadyl ion and the sulfate ion in the solution (SO_4^{2-} or HSO_4^-). Due to the low intensity of peak B it is difficult to quantify the shift with respect to the vanadium/sulfate concentrations in the solution. However, chemical shift towards higher frequency is evident. Now considering the structure of the vanadyl ion is not changing with vanadium concentration, it is only possible that the sulfate anions might exhibit only a weak interaction with vanadyl ions in the solution. Such a weak interaction will not change the electronic structure of vanadyl ion but merely represents the sulfate anions that exist as pair with vanadyl ion due to electrostatic forces as discussed earlier with optical spectra. Combining these results we can safely predict that the sulfate anions (SO_4^{2-} or HSO_4^-) are weakly bound to vanadyl ion and contribute to the second-coordination sphere around the vanadyl ions. The presence of such a second-coordination sphere in vanadyl ion has previously been reported and generally consists of solvent molecules [39,45]. Now considering the octahedral coordination of vanadyl ion it can be inferred that the sulfate anions in second-coordination sphere is most likely to be near to the pyramidal faces of octahedral vanadyl ion molecule (see Fig. 7). Recently Oriji et al. [46] reported the increase of Stokes radius of V(IV) species in electrolyte solutions with increase in sulfate concentrations. This result can be explained based on our NMR results, as with increase in vanadium concentration the total sulfate concentration is also increasing, hence has higher probability of having (SO_4^{2-} or HSO_4^-) ions in the second-coordination sphere of vanadyl ion. Such an increase in sulfate ion in second-coordination sphere could increase the effective radius or Stokes radius of the vanadyl ion as observed by Oriji et al. [46]. This type of second-coordination sphere with anions could affect both the proton/water exchange mechanism and re-orientational mechanism of vanadyl ion due to obvious electrostatic interactions. As discussed earlier, the variable temperature proton NMR revealed the increase of activation energy for re-orientation motion of vanadyl ion (E_r) with increase in vanadium concentration (see Table 1). This increase could be due to presence of sulfate anions in second-coordination sphere of the vanadyl ion.

Now, it is imperative to understand the temperature effect on the sulfate anion in second-coordination sphere and the core vanadyl ion structure. It is possible that the sulfate anions could complex with vanadyl ion above or below room temperature and change the structure of vanadyl ion. The variable temperature ^{17}O isotropic chemical shift is a direct and efficient probe for any temperature dependent structural changes within the observed molecule. Fig. 6a shows the temperature dependence of ^{17}O chem-

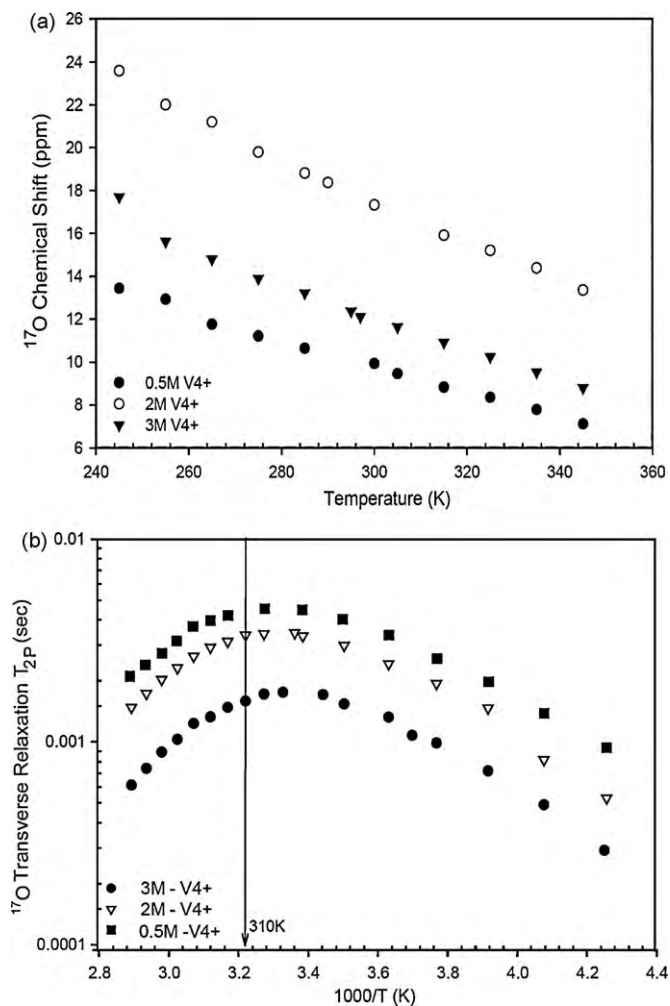


Fig. 6. The temperature dependent (a) ^{17}O isotropic chemical shift; (b) ^{17}O transverse relaxation time (T_{2p}) of vanadium(IV) electrolyte solutions measured using 11.1 T magnetic field.

ical shift for all vanadium concentrations. The chemical shift shows a monotonous decrease towards the solvent peak (towards lower frequency) with increasing temperature. Such a shift generally represents the water exchange kinetics of vanadyl ion with the solvent molecules. There is no significant change in the peak positions observed with temperature for all vanadium concentrations, which indicates the structure of vanadyl ion remains unaffected by temperature. This means, the sulfate anions are not directly bonded to the vanadyl ion in the observed temperature range (240–340 K) and possibly the sulfate anions only remain in the second-coordination sphere of vanadyl ion. However, such presence of sulfate anions in the second coordination could affect the water exchange kinetics of the vanadyl ion.

The water exchange kinetics between vanadyl ion and solvent molecule can be explored by temperature dependence of the line width of the ^{17}O NMR spectra [14]. Due to the very small intensity of the sulfate anions signal (peak B), hereafter we will only focus on the high intensity resonance (peak A) which can provide more accurate insight into the water exchange reaction. According to our DFT study of the vanadyl ion, the axial water molecule has slightly longer bond length compared with equatorial water molecules (see Fig. 1). This relatively longer bond length indicates less overlap between the vanadium and axial oxygen bonding orbital of the water molecule. This means that the axial water molecule is weakly bound with vanadium ion and can easily exchange with

bulk solvent water molecules. This result is in good agreement with previous studies on vanadyl ion in different solutions [37,39]. This means that the water molecules co-ordinated at four equatorial positions (see Fig. 1) are the dominant factors affecting the broadening of ^{17}O line width, while the extremely fast ($\sim 10^{11}$ s) water exchange between water molecule in solvent and axial position can, in principle, only affect the isotropic shift but not the line width [44] [see supporting information]. Hence, the temperature dependent line width and its evaluated parameters discussed hereafter mainly represent the exchange kinetics of water molecules involving four equatorial positions. Fig. 6b shows the temperature dependence of the ^{17}O transverse relaxation (T_{2p}) of peak A of various concentrations of vanadyl ion solutions measured at 11.1 T magnetic field. Unlike the proton relaxation, the ^{17}O transverse relaxation shows two different regions, where relaxation (T_{2p}) is controlled by different mechanisms as defined in Eq. (4). The bend over at high temperature (>315 K) is reversible and observed both during heating and cooling cycle and hence represents a possible water exchange reaction. The increase of transverse relaxation with increasing temperature in the low temperature region (<300 K) clearly shows the chemical exchange is rapid (i.e. $1/\tau_m > 1/T_{2M}$) and hence the relaxation is dominated by the electron-nucleus relaxation (T_{2M}) similar to proton relaxation discussed earlier. The low temperature region is then fitted with simple type Arrhenius equation (see Eq. (7)) and the activation energies have been calculated (see Table 1). Even though, the low temperature region of ^{17}O transverse relaxation is dependent on T_{2M} similar to the protons, it shows nearly two times larger activation energy (E_a) than the protons (see Table 1). As discussed earlier, the electron-nucleus relaxation (T_{2M}) has two contributions namely dipolar and scalar represented as first term and second term in Eq. (5). Unlike the proton relaxation, the low temperature region of ^{17}O relaxation would be dominated by scalar contribution (second term in Eq. (5)). This is due to the fact that the dipolar relaxation is proportional to the square of magnetic moment of the nucleus (γ) as seen in Eq. (5). Since ^{17}O nuclei possess much lower magnetic moment than the proton, their dipolar interaction with unpaired electrons will be weaker. Further, the oxygen atoms are directly co-ordinated to the vanadium metal centers, leading to increase in the electron spin density around ^{17}O nuclei. This in turn gives rise to higher hyperfine coupling constant (A/h) values for ^{17}O nuclei [43] compared to the protons [27]. Hence, for ^{17}O nuclei it is very likely that the scalar coupling (second term in Eq. (5)) is dominant relaxation process and hence shows different activation energy than the protons. This means, while the activation energy (E_r) calculated from proton relaxation represents energy requirement for tumbling motion of vanadyl ion in the solution, where as the activation energy (E_a) derived from low temperature ^{17}O relaxation time represents the electron-oxygen nuclei relaxation behavior. Owing to the completely different mechanisms involved in the line broadening the derived activation energies are different for these two different probes (i.e. ^1H and ^{17}O NMR).

On the other hand, at high temperature (>315 K) relaxation is inversely proportional temperature indicating electron-nucleus relaxation is rapid (i.e. $1/\tau_m < 1/T_{2M}$) and hence it is dominated by chemical exchange correlation time (τ_m). This region allows direct observation of water exchange kinetics involving equatorial position of vanadyl ion. The temperature dependence of τ_m can be related to pseudo-first-order reaction rate constant (k) for solvent exchange using Eyring equation [14]:

$$\frac{1}{\tau_m} = k_{\text{ex}} = \frac{k_B T}{h} \exp \left\{ \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \right\} \quad (9)$$

$$\frac{1}{\tau_m} = \frac{k_{\text{ex}}^{298} T}{298.15} \exp \left\{ \frac{\Delta H^\ddagger}{R} \left(\frac{1}{298.15} - \frac{1}{T} \right) \right\} \quad (10)$$

where ΔS^\ddagger and ΔH^\ddagger are the entropy and enthalpy of activation for the water exchange, and k_{ex}^{298} is the exchange rate at 298 K. Using the above equations, the water exchange parameters (such as, ΔH^\ddagger , ΔS^\ddagger and k_{ex}^{298}) are calculated from the high temperature region of ^{17}O relaxation time for different vanadium concentrations and are tabulated in Table 1. The water exchange rate involving equatorial sites (k_{ex}^{298}) does not show significant changes with vanadium/sulfate concentrations, i.e. between 2.1 and 3.2 kHz. So does the values of ΔS^\ddagger and ΔH^\ddagger . However, it will be discussed below that the sign of ΔS^\ddagger and ΔH^\ddagger involved in water exchange reaction are the crucial indicators for understanding the mechanism of exchange reactions.

The water exchange in metal ion containing solutions can be explained by two major mechanisms namely, associative (A) where an intermediate of increased coordination number is inferred and dissociative (D) where an intermediate of reduced coordination number is inferred [12]. In addition to these two mechanisms, a more common interchange (I) mechanism is also possible, when there is no kinetically detectable intermediate present in the exchange reaction. This interchange (I) mechanism can have an associative activation mode (I_a) or a dissociative activation mode (I_d). The variation of enthalpy and entropy of activation (i.e. ΔS^\ddagger and ΔH^\ddagger) obtained from temperature dependent ^{17}O NMR resonances (see Table 1) can give hints to the mechanism responsible for water exchange in vanadyl ion solutions. Normally, the dissociative (D) mechanisms tend to have greater ΔH^\ddagger value than associative (A) mechanism based reactions. Similarly, the entropy (ΔS^\ddagger) tend to be positive for D- and negative for A-based reactions [47]. But, it should be noted here that the assignment of water exchange mechanism based on ΔH^\ddagger and ΔS^\ddagger value is not quantitative and only give a general assumption due to the second-coordination shell interactions on the calculated parameters. However, comparing the ΔH^\ddagger value (~ 57 kJ mol $^{-1}$) of aqueous vanadyl ion with water as solvent [47] to the ΔH^\ddagger value (ca. 25 kJ mol $^{-1}$) of our electrolyte solutions provides insights into the water exchange mechanism in vanadium(IV) electrolyte solution. The significant decrease of enthalpy (more than 25 kJ mol $^{-1}$) and negative entropy (see Table 1) indicates that the water exchange mechanism in vanadium(IV) electrolyte solution is probably an intermediate associative activated (I_a) exchange reaction. Such a intermediate associative activated (I_a) mechanism has also been reported for vanadyl ions in organic solvent such as CH_3OH , CH_3CN , DMF, DMA and DMSO [48].

3.5. Kinetics of vanadyl ion

Combining both ^1H and ^{17}O NMR results of various vanadium/sulfate concentration electrolyte solutions, we can explain the kinetics of vanadyl ion in electrolyte solutions. The chemically averaged single resonance observed in proton spectra (see Fig. 1a) indicates, fast proton exchange between vanadyl ion and solvent molecules. The ^{17}O NMR results suggests that the vanadyl ion is surrounded by weakly bonded sulfate anions (SO_4^{2-} or HSO_4^{2-}) and hence constituting second-coordination sphere where it probably occupies the pyramidal faces of octahedral vanadyl ion. Such a sulfate anions are close to equatorial position of vanadyl ion and might have active proton exchange between equatorial water molecules. Nagypal et al. [49] proposed that possible protonation site for vanadyl ion is either equatorial or axial water molecules, and not through the axial vanadyl oxygen. Integrating this previously reported result, we can propose that the protonation can significantly proceed through proton exchange between sulfate anions and equatorial water molecules and possibly to an extent through axial molecule. Such a proton exchange could lead to redox reactions as proposed by Gattrell et al. [11] and shown in Section 1. Fig. 7 shows a schematic view of possible pro-

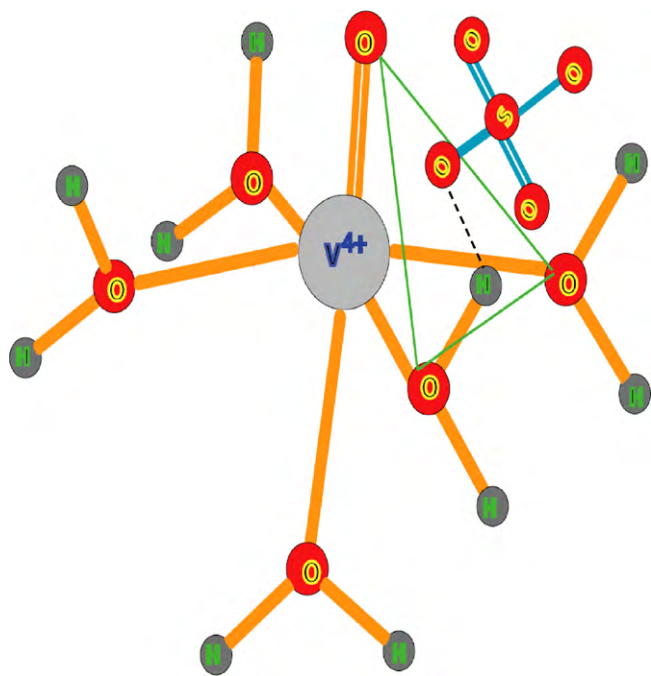


Fig. 7. Schematic view of vanadyl ion with sulfate anions occupying second-coordination sphere of the hydrated vanadyl ion. The dashed line represents formation of new hydrogen bonds leading to proton exchange between sulfate anion and equatorial water molecule.

ton exchange between hydrated vanadyl ion and sulfate anions which occupy the second-coordination sphere. Now considering the water exchange reaction, the energy requirements (i.e. enthalpy ΔH^\ddagger) derived from ^{17}O relaxation study predicts the water exchange in our electrolyte solutions proceeds through interchange mechanism with associative activation mode (I_a). Based on Kim et al. [48] the I_a exchange mechanism for vanadyl ion can proceed through two process. The first process is the interchange between water molecule in the second-coordination sphere above the pyramidal faces and water molecule in the equatorial site. The second process involves intra-molecular rearrangement where the solvent molecule enters the vanadyl ion through axial water molecule and then exchanges with the equatorial sites. While, both processes shows equally possible scenario for water exchange, the process involving intra-molecular rearrangement might need more energy. This is due to relatively large distance involved intra-molecular rearrangement compared with exchange between equatorial and second-coordination sphere. We observe a slight increase in enthalpy of water exchange (see Table 1) with increase in vanadium (or sulfate) concentration, such an increase might represent increased probability of water exchange through intra-molecular rearrangement process in higher concentration solutions. In fact, increase in vanadium (or sulfate) concentration means more sulfate anions in the second-coordination sphere and hence decrease in probability for water exchange between second-coordination sphere and water molecule in the equatorial site. This could lead to higher probability for water exchange through intra-molecular rearrangement process in vanadyl ions. At this point, we can confidently suggest that the sulfate anions in second-coordination sphere of vanadyl ion plays a significant role in the proton and water exchange kinetics of vanadyl ions. This means, the sulfate anions could have effect on redox reactions of vanadium(IV) electrolyte solutions. However, we need further NMR and computational molecular dynamic studies in wide range of metal ion concentration, sulphate ion concentrations and temperatures to fully understand the redox reaction mechanisms.

4. Conclusion

The hydrated structure and water exchange kinetics of vanadyl ion in various metal concentrations of V(IV) electrolyte solution are studied using ^1H and ^{17}O NMR technique. The hydrated vanadyl structure is found stable in the vanadium concentrations from 0.1 M to 3 M and in the temperature range of 240–340 K. The ^{17}O NMR results suggests the vanadyl ion is surrounded by weakly bonded sulfate anions (SO_4^{2-} or HSO_4^{2-}) where it probably occupies the pyramidal faces of octahedral vanadyl ion. These sulfate anions along with water molecules constitutes the second-coordination sphere of the hydrated vanadyl ions. The single proton resonance observed for all vanadium concentrations reveals very fast proton exchange between hydrated vanadyl ion and counter ions (i.e. sulfate anions and hydronium ions). The increase in re-orientation activation energy for vanadyl ion indicates it become less mobile with increase in vanadium (or sulfate) concentration. This is due to the increase of sulfate anion in second-coordination sphere of vanadyl ion, which is confirmed by our ^{17}O chemical shift measurements. The increase in sulfate concentration also seems to increase the probability of water exchange through intra-molecular rearrangement process as observed by higher enthalpy values. In summary, the sulfate anions in second coordination of vanadyl ions play a crucial role in both the proton and water exchange mechanism in the vanadyl ion. So it is very likely that counter anions in the second-coordination sphere could play a role in the redox reaction in the positive half cell of vanadium redox flow battery.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2010.05.008.

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