A variable temperature study of the transport properties of aqueous solutions of VOSO$_4$ and NH$_4$VO$_3$ in 2 M H$_2$SO$_4$

Sophia Suarez[*], Meriam Sahin, Yara Adam, Lucy Moussignac, David Cuffari, Domenec Paterno

Physics Department, Brooklyn College, The City University of New York, 2900 Bedford Ave, Brooklyn, NY 11210, USA

HIGHLIGHTS

- Ion and proton transport processes mediated strongly by viscosity.
- Activation energies calculated from ionic conductivity and solution viscosity.
- Greater metal ion concentration ion association more prevalent for vanadyl ion.

ARTICLE INFO

ABSTRACT

Variable temperature ionic conductivity, viscosity and ^{1}H NMR spin-lattice relaxation times, linewidths and chemical shifts measurements were determined for various concentrations of aqueous ammonium metavanadate (NH$_4$VO$_3$) and vanadyl sulfate (VOSO$_4$) over the temperature range of 20–100 °C. Concentration ranges of 0.05–2 M and 0.05–0.2 M were investigated for VOSO$_4$ and NH$_4$VO$_3$ respectively in 2 M H$_2$SO$_4$. Results show ion and proton transport processes that are mediated strongly by increasing solution viscosity, especially in the case of VOSO$_4$. Activation energies calculated from ionic conductivity and solution viscosity show greater energy being needed for translational ion dynamics with increasing concentration for both solutions. Additionally, data suggest that with greater metal ion concentration ion association is more prevalent for the vanadyl ion. The differences between the transport capabilities of the two solution are discussed in terms of the ^{1}H NMR, ionic conductivity and viscosity data.

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1. Introduction

The vanadium redox flow battery (VRB) is a candidate for large-scale electrical energy storage [1–5]. The VRB operates on redox couples of V(II)/V(III) and V(IV)/V(V) at the negative and positive electrodes respectively, with each cell consisting of an anode, a cathode, and an ion exchange membrane (IEM). Energy is stored in the concentrated vanadium electrolyte solutions, which are separated by an IEM that allows diffusion of protons but prevent the two electrolytes from mixing. As an electrical energy storage (EES) device the VRB offers long cycle life, flexibilities in design and installation location, reduction in cost and fast response time. It also offers the separation of power and energy densities in that the power density depends on the size of the cells whereas the energy

density depends on the concentration of the electrolytes. Despite these attributes, the VRB suffers from loss of energy capacity resulting from the crossover of vanadium ions through the IEM. In order to improve the efficiency of the device, the transport of vanadium ions across the IEM must be significantly reduced or eliminated. This however requires a better understanding of the ions interactions in the electrolyte solutions.

In an effort to determine the differences in transport of V(IV) and V(V) ions in aqueous solutions we performed ^{1}H NMR, Impedance Spectroscopy and Falling Ball viscosity measurements on varying concentrations of aqueous vanadyl sulfate (VOSO$_4$) and ammonium metavanadate (NH$_4$VO$_3$) in 2 M H$_2$SO$_4$, over the temperature range of 20–100 °C. V(V) is a diamagnetic d^0 metal while V(IV) is a paramagnetic d^1 metal. The compounds VOSO$_4$ and NH$_4$VO$_3$ in 2 M H$_2$SO$_4$ dissociate to provide the V(IV) and V(V) oxidation states respectively. Depending on the solvent pH and vanadium concentration, there are various vanadium species for both oxidation states in an aqueous acidic solution. For the V(V)

state it has been accepted that it exist mostly as the mononuclear aquadioxo cation $VO_2(H_2O)_4^+$ or VO_2^+ for short at low pH (<~3) [6]. This specie exists in hydrated form with a six-coordinated octahedral structure in which two oxygen atoms are coordinated in *cis*-configuration along with four complexed water molecules [7]. However, studies on V(V) in concentrated sulfuric acid media have shown the existence of various species coordinated with sulfate ions in solution, resulting in species such as $VO_2SO_4^{4-}$, $VO_2(SO_4)_2^{3-}$ and VO_2HSO_4 and so forth, the amount of which depends on the actual V(V) and total sulfate concentrations and their ratio [6]. In low pH environments, the V(IV) specie exist as the hydrated vanadyl ion — $VO(H_2O)_5^{2+}$ in octahedral coordination with four equivalent water molecules in the equatorial plane and one water molecule in the axial position on the opposite side of the vanadyl oxygen [8,9]. Additional forms include $[VO(OH)(H_2O)_4]^+$ and the dimmer $[(VOOH)_2(H_2O)_n]^{2+}$ [6]. The objective of the present work is not to determine the various vanadium species present in solution, but to determine fundamentally the effect of the vanadium ions and their possible speciation on the proton transport capability in aqueous H_2SO_4. NMR offers a direct and non-destructive probe of the nuclei local environment, providing information on physical characteristics over a wide time ($1–10^{-10}$ s) scale, depending on the particular experiment being performed [10–12]. Parameters such as NMR spin-lattice (T_1) relaxation time measurements and spectra can provide information on ion and molecular mobility and interactions. This is the first in a series of fundamental studies aimed at understanding the effect of vanadium oxidation states on the proton transport of IEMs for possible application in RFBs.

2. Experimental

2.1. Samples preparation

The compounds $VOSO_4$ (97%), and NH_4VO_3 (98%), and the acid H_2SO_4 (99.99%) were purchased from Sigma Aldrich. 250 ml of 2 M H_2SO_4 was first prepared by combining the required volume of the acid with distilled water according to the $M_1V_1 = M_2V_2$ relationship. Solutions of $VOSO_4$ and NH_4VO_3 were prepared by dissolving the required mass of the compounds in 10 ml of 2 M H_2SO_4. The mass of $VOSO_4$ was calculated assuming it was anhydrous because the correct hydration number (up to 4) was unavailable. Concentrations were 0.05, 0.1, 0.2, 0.5, 1.0, and 2 M for $VOSO_4$; and 0.05, 0.1, 0.2 M for NH_4VO_3.

2.2. NMR measurements

The solutions were pipetted into 5 mm OD NMR tubes and capped. ^1H NMR measurements were performed on a Varian Unity Plus spectrometer with a 7.1 T superconducting magnet and a Varian four-frequency 5 mm probe. NMR spectra were obtained from the Fourier Transform of single $\pi/2$ pulses. Spin-lattice relaxation times (T_1) were determined by the Inversion Recovery ($\pi-\tau-\pi/2$-acquire) pulse sequence using 15τ values. Water was used as the reference and set to 0 ppm. The temperature range studied was 20–100 °C with wait times of 15–20 min for equilibration. Errors of less than 5% were obtained for chemical shifts, T_1s, and linewidths. The spectra were fitted using the MestRenova version 7.1 program. The files were opened as FIDs, phase corrected using the program's manual Phase correction, and normalized to maximum height of 100. The linewidths were determined using the cross hair tool by sandwiching the width at the height of 50. The program calculated the difference between these points hence giving us the full width at half max.

2.3. Ionic conductivity measurements

The solutions (>1 ml) were pipetted into sample cells consisting of 5 cm of Tygon tubing capped at both ends by silver electrodes of 3.175 mm diameter. Extreme care was taken when filling the tubing with the solution to reduce the presence of air bubbles, which can negatively affect the measurements. Each cell was allowed to equilibrate for 15–20 min before the electrodes were fully inserted to further eliminate the formation of air bubbles. Additionally, excess solution was used for each cell so as to allow run-off during final insertion of the electrodes. The variable temperature measurements were accomplished by the use of a bath consisting of silicon oil (Alfa Aesar) and the temperature verified by two digital and two mercury thermometers. Equilibration times of 45–60 min were used for all measurements. The measurements were performed successively to reduce the formation of bubbles that can occur in solutions containing water. The temperature range studied was 20–80 °C.

The reference was a 1 M KCL solution which accompanied every sample run to ensure accuracy of the instrument and reproducibility of the measurements. Errors of less than 3% were obtained for each measurement. Five measurements were determined for each sample and the conductivity values presented are the averages of these measurements. AC and DC potentials of 10 mV and 0 V were used respectively in all measurements. Nyquist plots were obtained and the intercept of the arc which corresponds to the ohmic resistance were obtained. ZView and ZPlot programs were used to collect and analyze the data.

2.4. Viscosity measurements

About 8 ml of the solution was placed into the viscometer flask, sealed, and allowed to equilibrate in the water bath for about 30 min. Variable temperature (20–80 °C) was accomplished by the use of a hot plate and the temperature was verified by the use of three different thermometers. For each sample, at least three sets of measurements were done to ensure reproducibility and integrity in the results.

Viscosity measurements were performed on the solutions using the Gilmont falling ball method. Viscosity values were obtained by the following equation:

$$\eta = k\left(\rho_f - \rho\right)t$$

where η is the viscosity of liquid, k is the constant for the viscometer and stainless steel ball combination which was determined experimentally using reference solvents of known viscosity, ρ_f is the density of the steel ball, ρ the density of the liquid, and t is the time it takes for the ball to fall in the viscometer. To calculate the viscosity, solution density was required. This was determined using the simple mass and volume relationship and solution densities were determined at each temperature. Errors of about 3–5% were obtained for each measurement.

3. Results

3.1. Spectra

^1H spectra for $VOSO_4$ (V(IV), left) and NH_4VO_3 (V(V), right) in 2 M H_2SO_4 solutions are shown in Fig. 1 and consisted of a single peak over the entire concentration and temperature ranges studied. In general, the environment of a cation in an aqueous solution consists of several regions: (1) the primary solvation shell of the cation which often contains the water molecules directly