



Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: [www.elsevier.com/locate/jelechem](http://www.elsevier.com/locate/jelechem)

# Electrolyte cation dependence of the electron transfer kinetics associated with the $[\text{SVW}_{11}\text{O}_{40}]^{3-/4-}$ ( $V^{V/IV}$ ) and $[\text{SVW}_{11}\text{O}_{40}]^{4-/5-}$ ( $W^{VI/V}$ ) processes in propylene carbonate

Jiezhen Li<sup>a</sup>, Cameron L. Bentley<sup>c</sup>, Tadaharu Ueda<sup>d</sup>, Alan M. Bond<sup>a,b,\*</sup>, Jie Zhang<sup>a,b,\*</sup><sup>a</sup> School of Chemistry, Monash University, Clayton, Vic 3800, Australia<sup>b</sup> ARC Centre of Excellence for Electromaterials Science, Monash University, Clayton, Vic 3800, Australia<sup>c</sup> Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK<sup>d</sup> Department of Marine Resource Science, Kochi University, 783-8502, Japan

## ARTICLE INFO

## Keywords:

Electron transfer kinetics  
 Polyoxometalates  
 Propylene carbonate  
 Cation dependence  
 Fourier transformed ac voltammetry

## ABSTRACT

Changing the supporting electrolyte cation from tetrabutylammonium to 1-butyl-3-methylimidazolium is known to significantly increase the apparent heterogeneous electron transfer rate constants ( $k^0$  value at the formal reversible potential,  $(E_F^0)$ ) associated with the  $[\text{SVW}_{11}\text{O}_{40}]^{3-/4-}$  ( $V^{V/IV}$ ) and  $[\text{SVW}_{11}\text{O}_{40}]^{4-/5-}$  ( $W^{VI/V}$ ) processes in aprotic organic media. In this study, supporting electrolytes containing 7 different cations, namely 1-ethyl-3-methylimidazolium ([EMIM]<sup>+</sup>), 1-butyl-3-methylimidazolium ([BMIM]<sup>+</sup>), 1-butyl-1-methylpyrrolidinium ([Py<sub>14</sub>]<sup>+</sup>), tetraethylammonium ([TEA]<sup>+</sup>), tetrapropylammonium ([TPA]<sup>+</sup>), tetrabutylammonium ([TBA]<sup>+</sup>) and tetrahexylammonium ([THA]<sup>+</sup>), have been investigated in order to provide a systematic account of the influence of the electrolyte cations on the rate of polyoxometalate (POM) electron transfer at a platinum disk electrode. Fourier transformed alternating current (FTAC) voltammetry has been used for the measurement of fast kinetics and DC cyclic voltammetry for slow processes. The new data reveal the formal reversible potentials and electron-transfer rate constants associated with the  $V^{V/IV}$  ( $k_V^0$ ) and  $W^{VI/V}$  ( $k_W^0$ ) processes correlate with the size of the supporting electrolyte cation.  $k_V^0$  and  $k_W^0$  values decrease in the order, [EMIM]<sup>+</sup> > [BMIM]<sup>+</sup> > [Py<sub>14</sub>]<sup>+</sup> ≈ [TEA]<sup>+</sup> > [TPA]<sup>+</sup> > [TBA]<sup>+</sup> > [THA]<sup>+</sup> for both processes. However, while  $k_V^0$  decreases gently with increasing cation size ( $k^0 = 0.1$  and  $0.002 \text{ cm s}^{-1}$  with [EMIM]<sup>+</sup> and [THA]<sup>+</sup> electrolyte cations, respectively), the decrease in  $k_W^0$  is much more drastic ( $k^0 = 0.1$  and  $2 \times 10^{-6} \text{ cm s}^{-1}$  for [EMIM]<sup>+</sup> and [THA]<sup>+</sup>, respectively). Possible explanations for the observed trends are discussed (e.g., ion-pairing, viscosity, adsorption and the double-layer effect), with inhibition of electron-transfer by a blocking “film” of electrolyte cations considered likely to be the dominant factor, supported by a linear plot of  $\ln(k^0)$  vs.  $\ln(d)$  (where  $d$  is the estimated thickness of the adsorbed layer on the electrode surface) for both the  $V^{V/IV}$  and  $W^{VI/V}$  processes.

## 1. Introduction

It is of fundamental importance in electrochemistry to understand the factors that govern the rate of heterogeneous electron transfer. For electrode reaction, this typically involves the transfer of charge (electrons) across an interface between a solid electrode and liquid electrolyte. It follows that the rate of electron transfer is governed by both the physicochemical properties of the electrode/electrolyte interface and the nature of the redox-active species. For an outer-sphere one electron transfer processes such as the reduction of  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  to  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  or the oxidation of ferrocene (Fc) to the ferrocenium cation ( $\text{Fc}^+$ ), very similar electrochemical behavior is observed at Pt,

Au, and carbon electrodes [1,2]. However, the kinetics of the  $\text{Fe}(\text{H}_2\text{O})_6^{2+/3+}$  process, also considered to be an outer-sphere reaction in some studies, is much slower and differs markedly at each of these electrode materials [3,4].

The effects of the nature of the solvent (donor/acceptor or acid/base properties), supporting electrolyte and electrode material on electrode kinetics have been studied extensively [5–12]. For example, it has been established that if the outer-shell contribution to the activation energy is the major factor governing the rate of electron transfer, the heterogeneous electron-transfer rate constant ( $k^0$ ) exhibits a strong dependence on the properties of the solvent (dielectric constant) [13,14]. In addition, the rates of electrode reactions can be profoundly affected by

\* Corresponding authors.

E-mail addresses: [alan.bond@monash.edu](mailto:alan.bond@monash.edu) (A.M. Bond), [jie.zhang@monash.edu](mailto:jie.zhang@monash.edu) (J. Zhang).<http://dx.doi.org/10.1016/j.jelechem.2017.10.028>Received 18 June 2017; Received in revised form 10 October 2017; Accepted 12 October 2017  
1572-6657/© 2017 Elsevier B.V. All rights reserved.

the identity of the ions present in the supporting electrolyte [15–19]. To this end, Peover and Davies [20] reported that the highly irreversible (kinetically sluggish) second step for the reduction of 9,10-anthraquinone in dimethylformamide (DMF) can be made reversible (kinetically facile) through the addition of alkali metal ions. This effect was attributed to interactions (ion-pairing) between the semiquinone anion and the alkali metal cations.

Polyoxometalates (POMs) are anionic oxoclusters containing early transition metals in high oxidation states. They display a wide variety of compositions and structures. Their broad range of properties has led to applications in diverse fields such as medicine, photochromic materials, solar energy, and so forth [21–23]. In particular, POMs can undergo fast, reversible and stepwise multielectron-transfer reactions without significant structural change, meaning they can be employed as catalysts for many redox based reactions [24–27]. Furthermore, the properties of POMs, such as solubility, redox potential, and acidity can be finely-tuned by varying the constituent elements [28].

The thermodynamic properties (formal reversible potentials,  $E_F^0$ ) of POMs have been studied extensively [28–30]. For example, the electrochemical behavior of  $[\text{Co}_2\text{W}_{12}\text{O}_{42}]^{8-}$  was found to be highly solvent dependent [31]. The reversible potentials associated with these W-based redox centers shift negatively in a 50% mixed solvent aqueous electrolyte of dimethylformamide/water, acetonitrile/water or acetone/water compared to a pure aqueous electrolyte solution, while in dioxane/water mixtures, the processes shift positively. The acidity of the media (proton availability) also influences the thermodynamic properties of POMs. Thus, while  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  undergoes successive one-electron transfer processes in acetonitrile, the addition of acid causes a substantial change in reversible potential, so that when a high concentration is present, overall two-electron processes are instead observed [32].

The kinetic properties (standard electron transfer rate constant,  $k^0$  at  $E_F^0$ , and charge transfer coefficient,  $\alpha$ ) of POMs remain much less explored than the thermodynamic ones. Recently, we have reported a series of studies on the electrode kinetics of POMs [33–36]. In aqueous media, the  $k^0$  values of the Keggin-type silicon tungstate POMs,  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  and  $[\text{SiW}_{12}\text{O}_{40}]^{5-}$ , were found to be electrode material dependent [33,34]. Much slower rate constants were found with boron-doped diamond (BDD) electrode compared to use of glassy carbon (GC) as the electrode material [33]. The effect of the electrolyte cation ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$ ) on the electrode kinetics of these processes has also been studied [34]. In organic media (dimethylformamide) containing supporting electrolyte, the electrode kinetics associated with the  $[\text{SVW}_{11}\text{O}_{40}]^{3-/4-/5-}$  processes are strongly dependent on the electrode material as well as the ionic strength [35]. In our most recent study, we showed that changing the electrolyte cation from tetrabutylammonium to 1-butyl-3-methylimidazolium can significantly increase the electron-transfer kinetics of the  $[\text{SVW}_{11}\text{O}_{40}]^{3-/4-/5-}$  processes at Pt, Au and BDD electrodes. We attributed this and other trends to double layer effects and the nature of the electron-transfer processes (outer-sphere for the  $\text{V}^{\text{V}/\text{IV}}$  reaction vs. inner-sphere for the  $\text{W}^{\text{VI}/\text{V}}$  one) [36].

In the present study, our previous work is expanded systematically to provide a general account of the influence of electrolyte cations on the rate of POM electron transfer, using the  $[\text{SVW}_{11}\text{O}_{40}]^{3-/4-/5-}$  redox reactions as exemplar processes. The structure of  $[\text{SVW}_{11}\text{O}_{40}]^{3-}$  [37] shown in Fig. 1 shows the location of the V and W metal constituents.  $[\text{SVW}_{11}\text{O}_{40}]^{3-}$  exhibits three well-defined one-electron reduction processes in aprotic solvent (electrolyte) media [37]. The two initial processes, which are the focus for the current study, correspond to the reduction of  $\text{V}^{\text{V}}$  to  $\text{V}^{\text{IV}}$  (Eq. (1)) and  $\text{W}^{\text{VI}}$  to  $\text{W}^{\text{V}}$  (Eq. (2)).

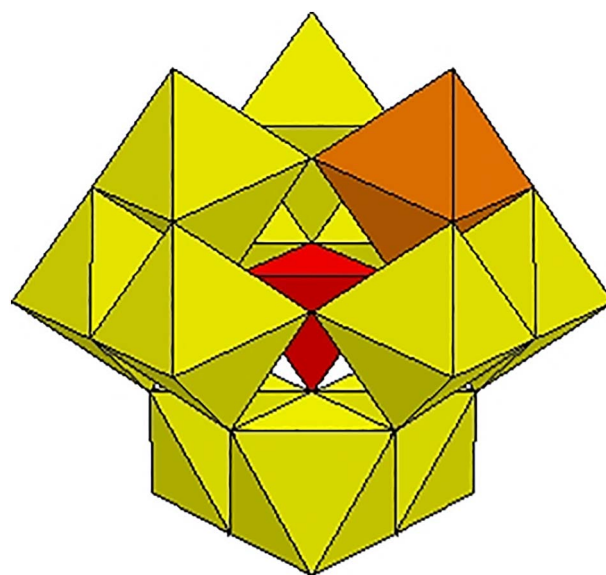
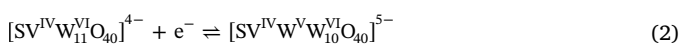
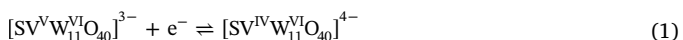


Fig. 1. The structure of  $[\text{SVW}_{11}\text{O}_{40}]^{3-}$ . Color code: S (red), V (orange), W (yellow) [37]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Seven different electrolyte cations were used in this study, including imidazolium and tetraalkylammonium based cations (structures shown in Scheme 1). Salts containing large singly-charged cations such as tetraalkylammonium ions are commonly used for investigations in dipolar aprotic solvents due to their relatively high solubility and weak tendency to form ion associates with anions. However, a number of studies have been reported which demonstrate that the electrode kinetics can depend on the nature (size or structural symmetry) of the tetraalkylammonium cations [38–41]. For example, the  $k^0$  values of a series of organic molecules have been shown to decrease with an increase in the size of the alkyl group [38]. The solvent chosen in this study is propylene carbonate (PC), which has a high dielectric constant (64.9 at 25 °C [42]), reducing the influence of ion pairing effects. Supporting electrolytes were added at a concentration of 0.5 M to provide a well-defined double layer and a low level of uncompensated resistance ( $R_u$ ). As is the case in our previous study, fast electrode kinetics were measured using large-amplitude Fourier-transformed alternating current (FTAC) voltammetry, which exhibits superior kinetic sensitivity in comparison with conventional dc voltammetry [43] and slow processes were quantified by DC cyclic voltammetry.

## 2. Experimental section

### 2.1. Chemicals

Propylene carbonate (PC, 99.7%, Sigma-Aldrich), acetonitrile ( $\text{CH}_3\text{CN}$ , 97%, Sigma-Aldrich), ethanol (96%, Merck), 1-ethyl-3-methylimidazolium tetrafluoroborate ( $[\text{EMIM}][\text{BF}_4]$ , 98%, Sigma-Aldrich), 1-butyl-3-methylimidazolium tetrafluoroborate ( $[\text{BMIM}][\text{BF}_4]$ , 99%, IoLiTec), 1-butyl-3-methylimidazolium hexafluorophosphate ( $[\text{BMIM}][\text{PF}_6]$ , 99%, IoLiTec), 1-butyl-1-methylpyrrolidinium tetrafluoroborate ( $[\text{Py}_{14}][\text{BF}_4]$ , 99%, IoLiTec), tetraethylammonium tetrafluoroborate ( $[\text{TEA}][\text{BF}_4]$ , 99%, Sigma-Aldrich), tetrabutylammonium hexafluorophosphate ( $[\text{TBA}][\text{PF}_6]$ , 99%, Sigma-Aldrich) and tetrahexylammonium perchlorate ( $[\text{THA}][\text{ClO}_4]$ , 99%, Sigma-Aldrich) were used as received from the manufacturer. Ferrocene (Fc, Sigma-Aldrich,  $\geq 98\%$ ) was recrystallized from *n*-pentane (Merck) prior to use. Tetrapropylammonium tetrafluoroborate ( $[\text{TPA}][\text{BF}_4]$ ) was prepared by a metathesis reaction between sodium tetrafluoroborate ( $\text{Na}[\text{BF}_4]$ , Sigma-Aldrich) and tetrapropylammonium bromide ( $[\text{TPA}]\text{Br}$ , Sigma-Aldrich) in  $\text{CH}_3\text{CN}$  and recrystallized at least

Download English Version:

<https://daneshyari.com/en/article/6661740>

Download Persian Version:

<https://daneshyari.com/article/6661740>

[Daneshyari.com](https://daneshyari.com)