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Voltammetric Studies on the Reduction of Polyoxometalate Anions in Ionic Liquids

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The electrochemical reduction of tetrabutylammonium salts of isostructural pairs of polyoxometalates $[\text{Bu}_4\text{N}]_2[\text{M}_6\text{O}_{19}]$, $[\text{Bu}_4\text{N}]_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$, and $[\text{Bu}_4\text{N}]_4[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]$ ($\text{M} = \text{Mo}$ or W) has been investigated at glassy carbon electrodes in dissolved and surface-confined states in ionic liquids and other media. In the ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate $[\text{BMIM}][\text{PF}_6]$, between two and six reversible one-electron-transfer processes were detected. Detailed studies on the process $[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]^{4-/5-}$ in a range of ionic liquids, water, and conventional organic solvents (containing 0.1 M electrolyte) suggest that the polarity of the medium plays a key role in the determination of the reversible potential. Reduction processes involving very highly charged $[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]^{8-/9-/10-}$ species are strongly influenced by the purity of the medium.

Introduction

The solvent dependence of reversible potentials has been of considerable interest since the pioneering work of Gutmann and co-workers,¹ who interpreted the influence of the medium in terms of donor–acceptor interaction between the redox active species and solvent molecules.

Polyoxometalate anion chemistry includes a wide range of interesting structural, electron-transfer, and catalytic properties.² Examination of their well-developed redox properties has included systematic studies of the role of the solvent (electrolyte).^{3,4} For example, Keita et al. found that

the formal potential E^0 for the reduction processes $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-/5-}$ and $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-/7-}$ depended strongly on the Lewis acidity of the solvent.^{4a} The more positive values observed in solvents with higher Lewis acidity were attributed to solvent stabilization of the more highly charged reduced forms which are stronger Lewis bases than the corresponding oxidized form.^{4c,5} Analogously, E^0 values of the six reversible one-electron-reduction processes of α and γ^* isomers of $[\text{Bu}_4\text{N}]_4[\text{S}_2\text{W}_{18}\text{O}_{62}]$ in aqueous media (obtained as a consequence of novel dissolution processes) were much more positive than those obtained in the acetonitrile (CH_3CN). This was attributed to the fact that water is a stronger Lewis acid than CH_3CN .⁶

Room-temperature ionic liquids, which frequently are nonvolatile, nontoxic, highly conductive, and highly stable, have been advocated as ideal replacements for volatile organic solvents presently used in organic synthesis, solar cell applications, and solvent extraction processes.^{7–9} Al-

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though electrochemical studies of polyoxometalates have been undertaken in a wide range of conventional solvents,^{6,10–12} studies of their reduction in ionic liquids have been reported only recently by Antonio and co-workers,¹³ who reported the influence of ionic liquids (neat or used as the supporting electrolyte in conventional organic solvents) on the voltammetry of some heteropolyoxotungstates with the Keggin structure.

In the Present Paper, we report the voltammetry of the tetrabutylammonium salts of the polyoxometalates [Bu₄N]₂[Mo₆O₁₉], [Bu₄N]₂[W₆O₁₉], [Bu₄N]₄[α-SiMo₁₂O₄₀], [Bu₄N]₄[α-SiW₁₂O₄₀], [Bu₄N]₄[α-S₂Mo₁₈O₆₂], and [Bu₄N]₄[α-S₂W₁₈O₆₂] in both dissolved and adhered solid-state forms.^{14,15} Initially, data are reported in the carefully dried ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] to establish the influence of the metal (Mo or W) and the structure of the anions on their reduction processes. These data are compared specifically with those obtained in CH₃CN (0.1 M Bu₄NPF₆). The latter system represents an example of a conventional solvent/electrolyte combination used widely in polyoxometalate electrochemistry. The weakest base [α-S₂W₁₈O₆₂]^{4–} exhibits an extensive series of one-electron-reduction processes and was chosen for further investigation of the medium dependence (ionic liquid, organic solvent, and water) of the reversible potential. Ionic liquids are more difficult to purify than volatile organic solvents. The influence of the purity of the ionic liquids on the voltammetric data was also assessed.

Experimental Section

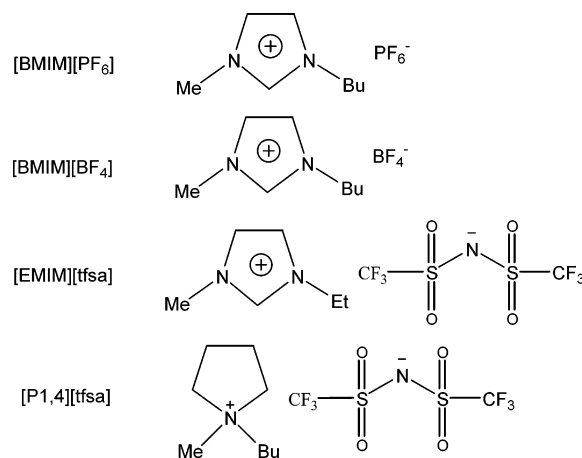
Chemicals. [Bu₄N]₂[Mo₆O₁₉], [Bu₄N]₂[W₆O₁₉], [Bu₄N]₄[α-SiMo₁₂O₄₀], [Bu₄N]₄[α-SiW₁₂O₄₀], [Bu₄N]₄[α-S₂Mo₁₈O₆₂], and [Bu₄N]₄[α-S₂W₁₈O₆₂] were synthesized, purified, and characterized according to literature procedures.^{2,11a} Their structures have been well documented.^{2,11a}

Ferrocene ([Fe(η⁵-C₅H₅)₂], Fc; BDH) and P₂O₅ (Chem Supply; 98%) were used as received. K₂CO₃ (APS Chemicals; 99.5%) was dried overnight under vacuum at ca. 130 °C. Dried¹⁶ acetone (Merck), purified and dried¹⁷ 1-chlorobutane (>99%; Merck), and

1-methylimidazole (Aldrich; redistilled, 99+%) were stored in a solvent tower under N₂. Ethyl acetate (Merck; 99.5%) was purified before use,¹⁷ and sodium hexafluorophosphate (Aldrich; 98%) was recrystallized from CH₃CN and was dried in a vacuum desiccator.¹⁷ Tetrabutylammonium hexafluorophosphate (GFS or Aldrich; 98%) was recrystallized twice from ethanol before use.¹⁸

In experiments undertaken in what is referred to as “dry” CH₃CN, a commercial solvent (Ajax Finechem; UV anhydrous, 99.9%) was purified according to a procedure adapted from the literature:¹⁶ K₂CO₃ (60 g) was dried overnight in a Schlenk flask under vacuum at 130 °C. After cooling, CH₃CN (1700 mL) was added to the flask and N₂ was bubbled through the mixture for 30 min before stirring overnight under N₂ at room temperature. A distillation apparatus was assembled with P₂O₅ in the distillation flask and with K₂CO₃ in the receiver flask. The apparatus was pumped under vacuum overnight at room temperature while the K₂CO₃ was dried at 130 °C. After cooling, the apparatus was subjected to four pump/N₂ fill cycles and the CH₃CN was transferred to the distillation flask via a cannula under N₂. The CH₃CN was then distilled off the P₂O₅ and was collected in the receiver flask containing the dry K₂CO₃. This distillate was redistilled over dry K₂CO₃ using the same technique and was collected in a solvent tower for storage under N₂ (boiling range 82–83 °C). Dichloromethane (DCM) (analytical grade; BDH) was dried over basic alumina. This solvent is considered to represent the purity level more typically employed in electrochemical studies.

Ionic Liquids. Unless otherwise stated, the ionic liquids (structure diagram 1) used in This Study, [BMIM][PF₆], 1-ethyl-



3-methylimidazolium bis(trifluoromethanesulfonyl) amide [EMIM]-[tfsa], and *N*-butyl-methylpyrrolidinium bis(trifluoromethanesulfonyl) amide [P1,4][tfsa], were synthesized and purified according to literature procedures.^{19–23} A survey of the physical properties

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of ionic liquids used in This Study (see structure diagram 1) is available in ref 24. [BMIM][BF₄] (>97%) was purchased from Fluka.

In view of the importance of the purity of [BMIM][PF₆] on electrochemical data, full details of its synthesis are provided below. [BMIM][PF₆] prepared this way is described below as “locally synthesized” [BMIM][PF₆].

[BMIM][Cl]. 1-Methylimidazole (40.0 mL, 0.501 mol) was added dropwise under nitrogen down a reflux condensor into a refluxing solution of 1-chlorobutane (57.6 mL, 0.552 mol) after which the solution was refluxed for 72 h under N₂. The excess solvent was removed (rotary evaporator), and the remaining liquid was transferred to a separating funnel containing distilled water (100 mL). The aqueous layer was washed with ethyl acetate (3 × 60 mL) and was collected, and the excess solvent was removed. Acetone (250 mL) was added with vigorous stirring to form a cloudy white solution. Ethyl acetate (100 mL) was added, and the solvent was removed until a white precipitate formed. This was collected on a Schlenk frit under a stream of N₂, washed with acetone, dried under vacuum overnight at room temperature, and stored under N₂.

[BMIM][PF₆]. [BMIM][Cl] (17.70 g, 0.101 mol) was dried overnight in a two-necked Schlenk flask under vacuum at 80 °C. NaPF₆ (17.87 g, 0.106 mol) was dried under vacuum at room temperature overnight in a vacuum desiccator. Acetone (100 mL) was added to the [BMIM][Cl] under N₂ via a cannula followed by solid NaPF₆ under a flow of nitrogen. The milky solution was stirred overnight at room temperature. The contents of the flask were filtered through Celite under N₂ (using a cannula to transfer the mixture from the reaction flask to the filtration apparatus), and the filter pad was washed with acetone. The excess solvent was removed (rotary evaporator), and the residue was transferred to a separating funnel using ethyl acetate (30 mL) to aid in the transfer. The organic layer was washed with distilled water (6 × 20 mL), collected, dried (Na₂SO₄), filtered, and collected in a Schlenk flask. The excess solvent was removed leaving a clear viscous liquid with a light yellow tinge, which was dried overnight under vacuum at 50 °C. The ionic liquid was stored in a plastic vial (20.3 g, 70%). ¹H and ¹³C NMR data obtained after dissolution in d₆-acetone and IR spectrometry data were consistent with those reported previously.^{7,25} The presence of the PF₆[−] anion was confirmed via ¹⁹F and ³¹P NMR: ¹⁹F (d₆-acetone) [δ (ppm)]: 71.26 (d) and ³¹P (d₆-acetone) [δ (ppm)]: −137.52 (m).

In certain experiments, [BMIM][PF₆] (99.3%, Sigma-Aldrich) was used. These ionic liquids, except [BMIM][BF₄] and “locally synthesized” [BMIM][PF₆], were dried over basic alumina for at least 24 h before use.

Instrumentation and Procedures. Cyclic voltammetric data were obtained with BAS 100B (Bioanalytical Systems, Indiana) or AD Instruments Mac/2e or Autolab (PGSTAT100) (Eco Chemie, Utrecht, The Netherlands) electrochemical workstations. The rotating disk electrode (RDE) experiments utilized a Metrohm 628-10 rotating disk unit with these workstations. A conventional three-electrode cell was employed, with either a 1- or 3-mm diameter glassy carbon (GC) or Au disk electrodes as the working electrode and Pt wire as the counter electrode. Effective working electrode areas were determined by measurement of the peak current value obtained for the reversible one-electron oxidation of a 1 mM solution of Fc in CH₃CN (0.1 M Bu₄NPF₆) by cyclic voltammetry

and the use of the Randles-Sevcik equation²⁶ with a known diffusion coefficient of $2.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.²⁷ A Ag wire dipped in a tube containing ionic liquid, which was separated from the test solution by a glass frit, was used as a quasi-reference electrode for measurements in ionic liquids. In contrast, a conventional Ag⁺/Ag (CH₃CN, 10 mM AgNO₃) double junction reference electrode was used in studies in CH₃CN media. However, in both media, the potential scale was then calibrated against the value of the reversible potential obtained for the Fc⁺/Fc process using either 1 mM Fc as an internal reference²⁸ or an Fc microparticle modified electrode in the case of ionic liquids.²⁹

The procedure for mechanical attachment of microcrystalline solids onto the electrode surfaces has been described in detail in previous studies.³⁰ To achieve this, either the relevant polyoxometalate was ground in a mortar and pestle and mechanically attached to the electrode surface by transfer from solid attached to a cotton bud or a few milligrams of solid was placed onto weighing paper and the electrode was pressed onto this substrate and then was rubbed over the solid material so that some of the microcrystalline material was transferred to the electrode surface. The working electrode was polished before the attachment of solid compounds.

The rate of dissolution of polyoxometalates in ionic liquids was very slow. To prepare solutions containing known concentrations of polyoxometalates, the ionic liquid containing the appropriate amount of solid polyoxometalate salt was either sonicated for several hours in an ultrasonic bath (Unisonics Pty Ltd. Australia) or warmed to a temperature of 80–100 °C to enhance the rate of the dissolution process.

For experiments in dry CH₃CN, the Bu₄NPF₆ electrolyte was dried overnight at 100 °C in a Schlenk tube and the relevant solid polyoxometalate salt was dried overnight in another Schlenk tube at room temperature. Both tubes were then subjected to four pump/N₂ fill cycles, before dry CH₃CN was transferred from a solvent tower to the Schlenk tube containing the Bu₄NPF₆, via a gastight syringe. After the Bu₄NPF₆ was dissolved, this solution was transferred, via a gastight syringe, to the tube containing the polyoxometalate salt. This solution was transferred similarly to a flame-dried electrochemical cell (which had been cooled in a stream of N₂) and was bubbled with dry N₂ for 15 min before voltammetry.

For experiments in locally synthesized [BMIM][PF₆], the polyoxometalate salt was weighed into a Schlenk flask and [BMIM][PF₆] was added. This mixture was dried under vacuum at 60 °C for 72 h, after which the flask was subjected to four pump/N₂ fill cycles. The solution was transferred under a stream of nitrogen to the flame-dried electrochemical cell and was bubbled with dry N₂ overnight before any voltammetric experiment. The analogous procedure was used with experiments in locally purified [BMIM][BF₄].

For experiments in dry CH₃CN, locally purified [BMIM][BF₄], or locally synthesized [BMIM][PF₆], the counter electrode was flame-dried before use. The working electrodes (GC or Au) were polished with Al₂O₃ (Buehler, 0.3 μm) slurry, rinsed with water, sonicated, repolished, washed with water, ethanol, dried with a tissue, and then dried with a hair-dryer before being inserted into the electrochemical cell. The reference electrode was rinsed with

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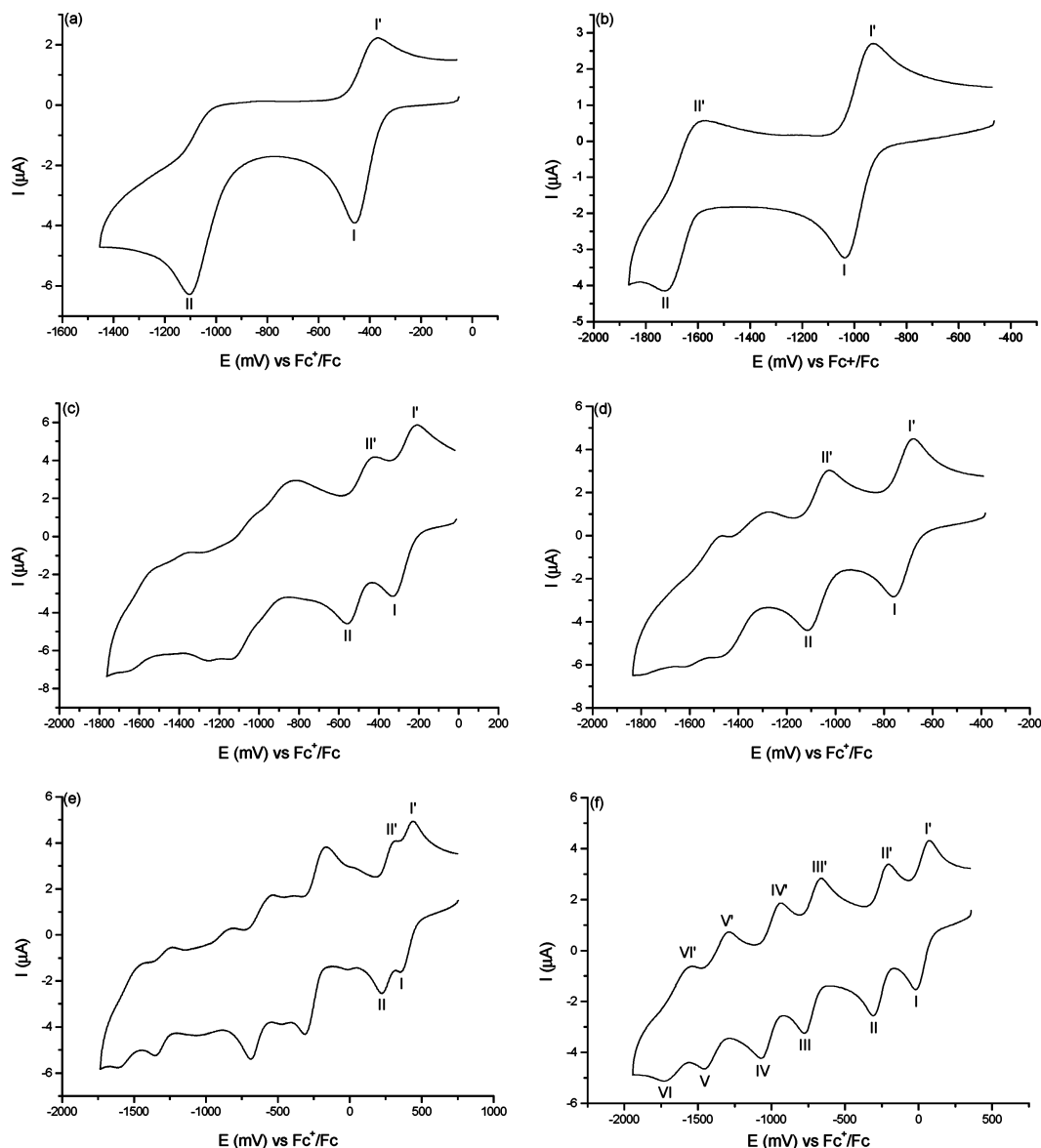


Figure 1. Cyclic voltammograms (ν , 0.1 V s^{-1}) obtained for solutions (5 mM) in locally synthesized [BMIM][PF₆] at 20 °C using a GC electrode (d, 3 mm) (a) [Bu₄N]₂[Mo₆O₁₉], (b) [Bu₄N]₂[W₆O₁₉], (c) [Bu₄N]₄[α -SiMo₁₂O₄₀], (d) [Bu₄N]₄[α -SiW₁₂O₄₀], (e) [Bu₄N]₄[α -S₂Mo₁₈O₆₂], and (f) [Bu₄N]₄[α -S₂W₁₈O₆₂].

acetone and then ethanol, dried with a tissue, and dried with a hair-dryer before being inserted into the electrochemical cell. At all times, the electrochemical cell was kept under a positive pressure of nitrogen, and if the working electrode was removed, it was done so under a flow of nitrogen.

Voltammetric experiments were conducted at temperatures of 20, 35, 50, and 65 °C with a variation of ± 1 °C. For the higher temperatures, the electrochemical cell was thermostated in a water bath (Julabo F20).

NMR spectra were obtained with a Varian Unity 400 MHz instrument in *d*₆-acetone, where 20% CFCl₃ (in *d*₆-acetone) and 85% H₃PO₄ (in D₂O) were used as the external references for ¹⁹F and ³¹P NMR, respectively (set to 0 ppm). IR spectra were obtained with a Bio-Rad FTS 165 FT-IR spectrometer.

Safety Consideration. It is well-known that the [BMIM][PF₆] hydrolyzes to toxic compounds such as HF.³¹ It is recommended that care be taken when handling this substance. Its storage in a plastic vessel is recommended as it degrades glassware over time.

Results and Discussion

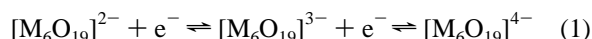
Voltammetry of Polyoxometalate Salts Dissolved in Locally Synthesized [BMIM][PF₆]. Cyclic Voltammetry.

The electrochemical reduction of solutions (5 mM) of [Bu₄N]⁺ salts of [Mo₆O₁₉]²⁻, [W₆O₁₉]²⁻, [α -SiMo₁₂O₄₀]⁴⁻, [α -SiW₁₂O₄₀]⁴⁻, [α -S₂Mo₁₈O₆₂]⁴⁻, and [α -S₂W₁₈O₆₂]⁴⁻ was studied as a function of temperature at GC and Au macrodisc electrodes. Cyclic voltammograms obtained at 20 °C at a GC electrode (d, 3 mm) using a scan rate of 0.1 V s^{-1} are displayed in Figure 1. The potential range available under optimal conditions in the negative region was -2.3 V versus Fc⁺/Fc. However, the need to use elevated temperature to dissolve the polyoxometalate in [BMIM][PF₆] may have led to some adventitious impurities which lowered the negative potential limit.

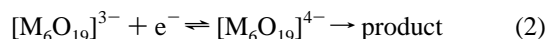
On the basis of data obtained in aprotic media containing 0.1 M electrolyte,^{2a,14} a series of chemically reversible one-electron-reduction processes would be expected for studies

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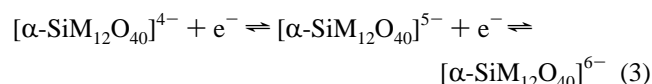
in [BMIM][PF₆]. The high viscosity of [BMIM][PF₆] ionic liquid²⁹ implies that diffusion coefficients and hence faradaic currents per unit concentration are much lower in this ionic liquid than those found in organic solvents. Consequently, faradaic-to-background current ratios are relatively poor even though 5 mM concentrations were employed. In general, the W compounds give simpler voltammetry than their Mo analogues. For example, for [Mo₆O₁₉]²⁻, the initial process is reversible (forward and reverse peaks of equal magnitude), but the second is chemically irreversible (no reverse peak over scan rate range examined). In the case of [W₆O₁₉]²⁻, the second process exhibits a considerable degree of chemical reversibility (reverse peak smaller than forward peak), even at a scan rate of 0.1 V s⁻¹. The two relevant reduction processes are labeled I and II in Figure 1a and b. These systems are therefore characterized by eqs 1 and 2



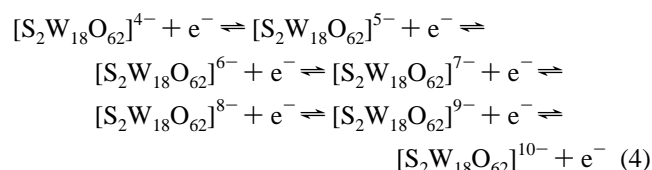
at fast scan rates (short time scales), while at slow scan rates, the second process can be represented by the reaction scheme



For reduction of [α-SiM₁₂O₄₀]⁴⁻ (M = Mo or W), two well-defined one-electron processes (labeled I and II in Figure 1c and d) are detected and are consistent with the reaction scheme



Processes associated with more extensive reduction are much more complicated. Since the relative isomeric stabilities may change upon reduction,³² at least some of the complexity may be associated with formation of other isomeric forms of this polyoxometalate anion as reported by Chiang et al. in their studies of the reduction of [α-PW₁₂O₄₀]³⁻ in ionic liquids.¹³ Alternatively, coupled proton-transfer processes arising from the presence of adventitious water protons or other cation impurities may introduce complexity.¹⁴ An increased complexity in voltammetric responses also was observed after the second electron-transfer step in the case of reduction of [S₂Mo₁₈O₆₂]⁴⁻ (see Figure 1e). In contrast, reduction of the [α-S₂W₁₈O₆₂]⁴⁻ anion gives rise to an extensive series of stable-reduced polyoxometalate anions on the voltammetric time scale. Thus, six well-defined reversible one-electron-transfer processes (I–VII) are detected at all scan rates examined (0.02–1 V s⁻¹). These data are in accordance with the reaction scheme



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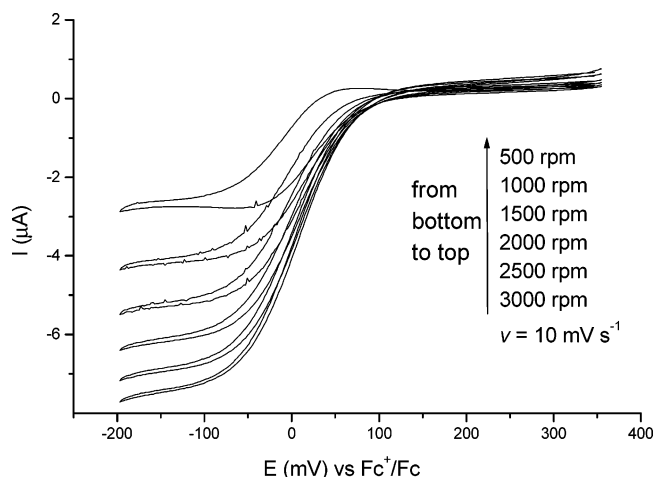


Figure 2. Rotating disk voltammograms obtained for the first reduction process of [Bu₄N]₄[α-S₂W₁₈O₆₂] (5 mM) in locally synthesized [BMIM][PF₆] at 65 °C using a 3-mm diameter GC electrode. Note the presence of a small non-steady-state transient component at a rotation rate of 500 rpm.

Although differences exist with respect to the stability of highly reduced forms of the polyoxometalate anions, the first one-electron-reduction processes of the six anions examined here exhibit the characteristics predicted for an electrochemically reversible one-electron-reduction process. Since the peak-to-peak separation value (ΔE_p) of 78(5) mV is obtained with a GC electrode (d, 3 mm) at a scan rate of 0.10 V s⁻¹ for 5 mM solutions and its scan rate dependence is almost the same as that obtained for the known reversible Fc⁺/Fc one-electron-oxidation process under identical conditions, small departures from ideality are attributed to uncompensated resistance rather than to quasi reversibility. Moreover, in all cases, the magnitude of the peak current for the reduction process (I_p^{red}) depended linearly on the square root of the scan rate ($\nu = 0.02\text{--}1\text{ V s}^{-1}$), and the magnitude of the ratio $I_p^{\text{red}}/I_p^{\text{ox}}$ was unity, within experimental error. Consequently, process I for all polyoxometalates was assigned as being a diffusion-controlled one-electron-reduction process.

Rotating Disk Electrode Voltammetry. The simplicity of process I for each of the polyoxometalate anions implies that the RDE technique applied to this process can be used to determine diffusion coefficients via measurement of the steady-state limiting current and application of the Levich equation.²⁶ As predicted, RDE voltammograms at GC and Au RDE electrodes are well-defined. However, at 20 °C, rather than the usual sigmoidal-shaped steady-state response, voltammograms exhibited distinct peaks even when the rotation rate was as high as 3000 rpm. In contrast, RDE voltammograms obtained in locally synthesized [BMIM][PF₆] at 65 °C exhibit steady-state mass transport limited currents for rotation rates ≥ 1000 rpm (Figure 2). Detection of transient behavior under conditions where steady-state behavior is found classically has also been reported in voltammetric studies in viscous ionic liquids utilizing RDE³³ or microelectrode techniques.³⁰ The viscosity of [BMIM][PF₆] at 65 °C is significantly less than that at 20 °C which

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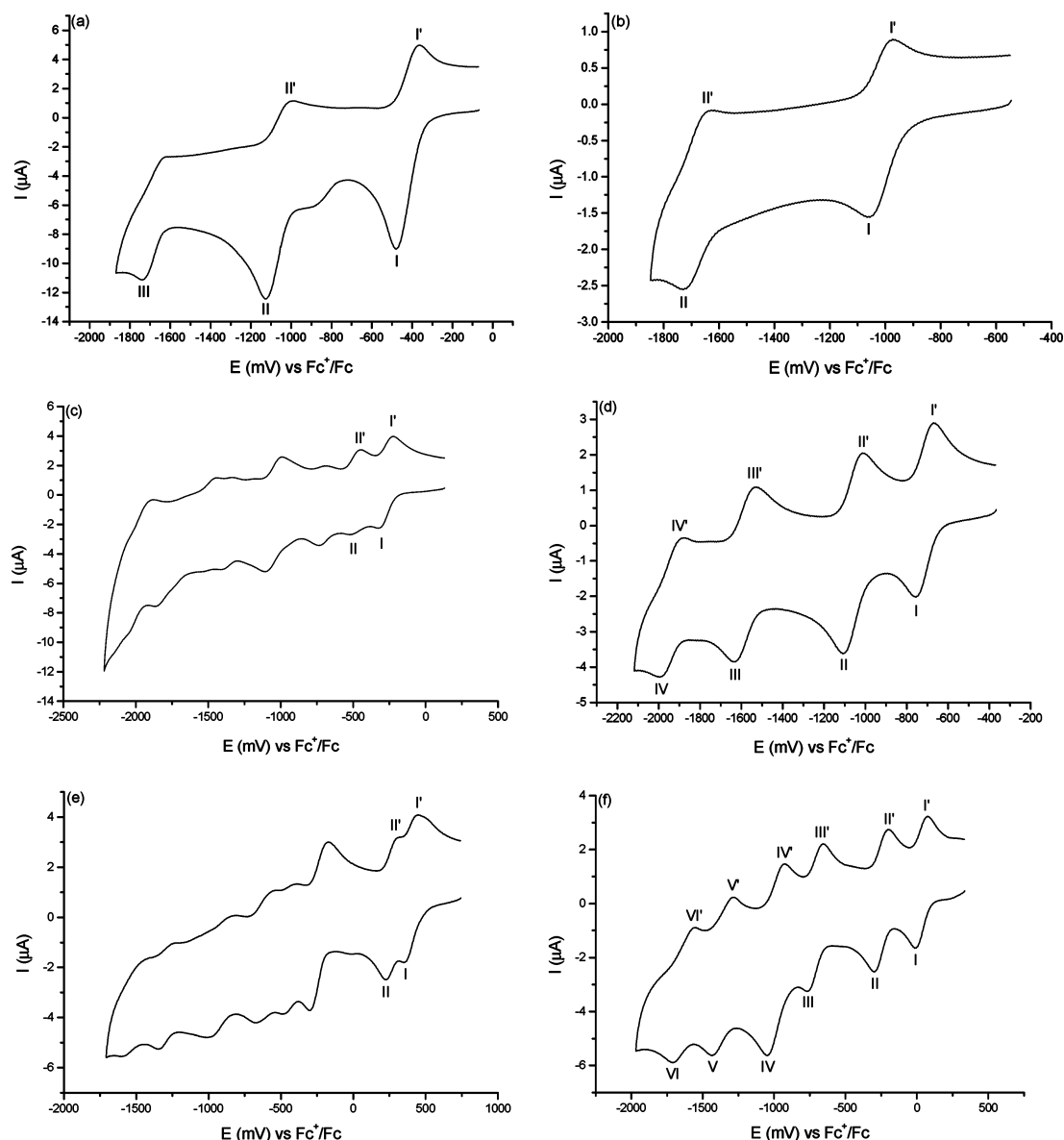


Figure 3. Cyclic voltammograms obtained when (a) $[\text{Bu}_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$, (b) $[\text{Bu}_4\text{N}]_2[\text{W}_6\text{O}_{19}]$, (c) $[\text{Bu}_4\text{N}]_4[\alpha\text{-SiMo}_{12}\text{O}_{40}]$, (d) $[\text{Bu}_4\text{N}]_4[\alpha\text{-SiW}_{12}\text{O}_{40}]$, (e) $[\text{Bu}_4\text{N}]_4[\alpha\text{-S}_2\text{Mo}_{18}\text{O}_{62}]$, and (f) $[\text{Bu}_4\text{N}]_4[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]$ microparticles are adhered to a GC electrode (d, 3 mm) in contact with locally synthesized $[\text{BMIM}][\text{PF}_6]$. $T = 20\text{ }^\circ\text{C}$. $\nu = 0.1\text{ V s}^{-1}$.

Table 1. Temperature Dependence of E^0 and D Values Obtained from Voltammetric Measurements for the First Reduction Process When 5 mM Polyoxometalate Anions Are Dissolved in Locally Synthesized $[\text{BMIM}][\text{PF}_6]^a$

polyoxometalate	$E^0/\text{mV vs Fc}^+/\text{Fc}$		$D^b/10^{-8}\text{ cm}^2\text{ s}^{-1}$			
	(20 °C)	(65 °C)	(20 °C)	(35 °C)	(50 °C)	(65 °C)
$[\text{Mo}_6\text{O}_{19}]^{2-}$	-419	-442	1.4			9.3
$[\text{W}_6\text{O}_{19}]^{2-}$	-989	-1013	1.3			9.2
$[\alpha\text{-SiMo}_{12}\text{O}_{40}]^{4-}$	-274	-290	0.7	1.8	3.7	7.6
$[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$	-720	-728	0.8	2.0	3.9	7.9
$[\alpha\text{-S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$	390	383	0.6			5.7
$[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]^{4-}$	20	9	0.6			5.5

^a Values obtained at 3 mm GC and Au electrodes are identical within experimental error of $\pm 3\text{ mV}$ for E^0 and $\pm 5\%$ for D . ^b Values obtained from RDE (Levich equation) and cyclic voltammetry (Randles–Sevcik equation) are identical within experimental error.

enables higher mass transport rates to prevail, and therefore a higher ratio of the steady state to transient component exists in RDE voltammograms at elevated temperatures.

Diffusion Coefficient and Reversible Potential Data.

Diffusion coefficients D obtained from cyclic voltammetry at stationary electrodes (calculated from peak currents using the Randles–Sevcik equation)²⁶ and RDE voltammetry (calculated from steady-state limiting currents using the Levich equation)²⁶ are summarized in Table 1. Also listed are reversible potentials E^0 versus Fc^+/Fc obtained from cyclic voltammetry by averaging the reduction (E_p^{red}) and oxidation (E_p^{ox}) peak potentials $[(E_p^{\text{red}} + E_p^{\text{ox}})/2]$. In general, E^0 values versus Fc^+/Fc (temperature dependence of reference unknown) obtained at 20 °C are slightly more positive than those obtained at 65 °C, and Mo polyoxometalate anions are much more easily reduced than their isostructural W analogues. D values obtained in $[\text{BMIM}][\text{PF}_6]$ are at least 2 orders of magnitude smaller than those found in the conventional organic solvent (electrolyte) media. This is expected on the basis of the much higher viscosity of

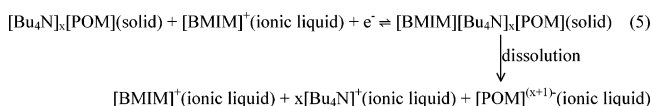
Table 2. E^0 (vs Fc^+/Fc) Data for One-Electron-Reduction Processes Obtained When $[\text{Bu}_4\text{N}]^+$ Salts Are Dissolved in Locally Synthesized $[\text{BMIM}][\text{PF}_6]$ or Are Mechanically Adhered to the Electrode Surface in Contact with Locally Synthesized $[\text{BMIM}][\text{PF}_6]^a$

polyoxometalate	state	E^0/mV vs Fc^+/Fc					
		I	II	III	IV	V	VI
$[\text{Mo}_6\text{O}_{19}]^{2-}$	dissolved	-419	-1104 ^b				
	solid	-422	-1059	-1739 ^b			
$[\text{W}_6\text{O}_{19}]^{2-}$	dissolved	-989	-1649				
	solid	-986	-1677				
$[\alpha\text{-SiMo}_{12}\text{O}_{40}]^{4-}$	dissolved	-274	-476				
	solid	-277	-487				
$[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$	dissolved	-720	-1071				
	solid	-713	-1062	-1578	-1939		
$[\alpha\text{-S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$	dissolved	390	272				
	solid	397	274				
$[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]^{4-}$	dissolved	20	-257	-720	-1005	-1373	-1628
	solid	30	-253	-714	-986	-1362	-1633

^a Results obtained on GC and Au electrodes are identical within the experimental error of ± 3 mV. ^b Peak potential for irreversible process.

$[\text{BMIM}][\text{PF}_6]$.^{24,29} The measured D values also decrease as the size (molecular weight) of the anion increases and increase as the $[\text{BMIM}][\text{PF}_6]$ temperature increases (viscosity decreases). All these observations are consistent with the Stokes–Einstein relationship.³⁴

Voltammetry of Adhered Microparticles of Polyoxometalate Salts in Contact with Locally Synthesized $[\text{BMIM}][\text{PF}_6]$. It is sometimes possible to obtain reversible potentials^{29,30,35} and the kinetics of first-order coupled homogeneous processes²⁴ of organometallic compounds adhered to an electrode in contact with an ionic liquid.^{14,15} Dissolution of polyoxometalates in $[\text{BMIM}][\text{PF}_6]$ is kinetically slow, so that if the one-electron-reduced forms dissolve rapidly on the voltammetric time scale, then the initial steps of the reaction scheme obtained from the adhered solid salt $[\text{Bu}_4\text{N}]_x[\text{POM}]$ will be as in eq 5.



This dissolution step may then facilitate detection of the expected series of one-electron-reduction processes in the ionic liquid phase and may also promote continuous dissolution of solid polyoxometalate. Cyclic voltammograms obtained in this manner from solid adhered to a GC electrode at 20 °C are shown in Figure 3. Voltammograms obtained in this way exhibit most of the characteristics associated with studies with dissolved polyoxometalate salts (Figure 1). However, processes are often better defined (more reversible) in the negative potential region. For example, although the presence of a surface-based process of unknown origin between reductions I and II was detected in the case of $[\text{Mo}_6\text{O}_{19}]^{2-}$ (Figure 3a), process II is now reversible, even at a scan rate of 0.1 V s⁻¹. In addition, a third reduction process can be detected at more negative potentials (labeled III in Figure 3a). This is attributed to the generation of much higher concentrations of dissolved $[\text{Mo}_6\text{O}_{19}]^{n-}$ ($n > 2$) at the electrode surface. Comparable peak currents were obtained even though reduction of microparticles occurs at

Table 3. E^0 Values (vs Fc^+/Fc) for Designated One-Electron-Reduction Processes Obtained from Cyclic Voltammetry for Solutions of $[\text{Bu}_4\text{N}]^+$ Salts (1.0 mM) Dissolved in Dry CH_3CN . $\nu = 100$ mV s⁻¹ ^a

polyoxometalate	E^0/mV vs Fc^+/Fc					
	I	II	III	IV	V	VI
$[\text{Mo}_6\text{O}_{19}]^{2-}$	-774	-1630 ^b				
$[\text{W}_6\text{O}_{19}]^{2-}$	-1310	-2260				
$[\alpha\text{-SiMo}_{12}\text{O}_{40}]^{4-}$	-710	-1103	-1789			
$[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$	-1116	-1623	-2309			
$[\alpha\text{-S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$	105	-138	-788	-1065		
$[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]^{4-}$	-245	-628	-1199	-1595	-2094	-2464

^a Results obtained on GC and Au electrodes are identical within the experimental error of ± 3 mV. ^b Peak potential for irreversible process.

a small fraction only of the electrode surface. Use of the adhered solid method appears to decrease the relative level of interference from adventitious impurities, that may accumulate during heating or extended periods of sonication to produce 5 mM solutions of dissolved polyoxometalate. In the case of $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$, four well-defined reversible one-electron-reduction processes, rather than only two, are now clearly detected (compare Figures 3d and 1d). As is the case with solution-phase studies, only the initial two reduction processes for reduction of $[\alpha\text{-SiMo}_{12}\text{O}_{40}]^{4-}$ and $[\alpha\text{-S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$ remain simple one-electron processes (Figure 3c, e) and six one-electron steps are again detected for the reduction of $[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]^{4-}$ (Figure 3f). E^0 values versus Fc^+/Fc for the readily identified primary one-electron-reduction processes obtained from dissolved and adhered microparticle studies are summarized in Table 2. Within experimental error, the data sets are identical.

Comparison with Voltammetry in Dry CH_3CN (0.1 M Bu_4NPF_6). Voltammograms obtained in dry CH_3CN (0.1 M Bu_4NPF_6) have similar characteristics to those obtained in locally synthesized $[\text{BMIM}][\text{PF}_6]$. For example, the reversible potentials of W polyoxometalate anions are always more negative than those of their Mo counterparts. However, the reversible potentials for designated one-electron-reduction processes (Table 3) are more negative ($-80 \rightarrow -400$ mV) than those found in $[\text{BMIM}][\text{PF}_6]$ (Table 2).

Detailed Studies on the Reduction of $[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]^{4-}$ in Ionic Liquids and Conventional Solvent (Electrolyte) Media. In view of its inherent simplicity in the voltammetric sense, the reduction of $[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]^{4-}$ was chosen for a

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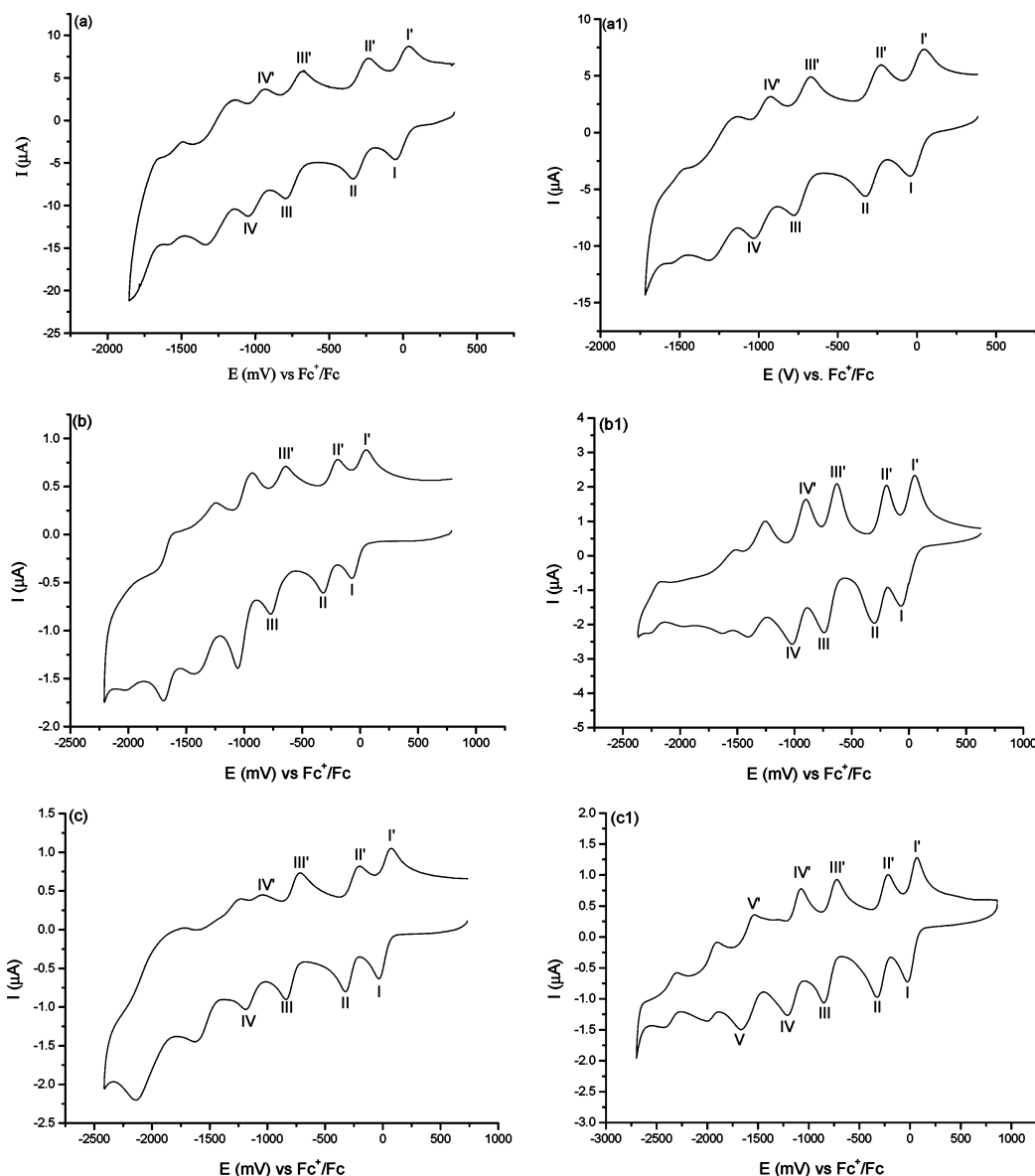


Figure 4. Cyclic voltammograms obtained for the reduction of $[\text{Bu}_4\text{N}]_4[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]$ at either a 3-mm diameter (a and a1) or a 1-mm diameter (b, b1, c, and c1) electrode with $\nu = 0.1$ (a and a1) or 0.2 (b, b1, c, and c1) V s^{-1} . (a) Solution (5 mM) in $[\text{BMIM}][\text{BF}_4]$; (a1) adhered solid in contact with $[\text{BMIM}][\text{BF}_4]$; (b) solution (2 mM) in $[\text{EMIM}][\text{tfsa}]$; (b1) adhered solid in contact with $[\text{EMIM}][\text{tfsa}]$; (c) 4 mM in $[\text{P1,4}][\text{tfsa}]$; and (c1) adhered solid in contact with $[\text{P1,4}][\text{tfsa}]$.

detailed study in a range of ionic liquids and other solvents (including water) and also to assess the possible influence of adventitious impurities on $E^{\circ'}$ values reported in ionic liquids.

Cyclic voltammograms obtained for the reduction of dissolved $[\text{Bu}_4\text{N}]_4[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]$ in $[\text{BMIM}][\text{BF}_4]$, $[\text{EMIM}][\text{tfsa}]$, and $[\text{P1,4}][\text{tfsa}]$ are displayed in Figure 4. In each ionic liquid, an extensive series of reduction steps are detected. Processes due to well-characterized one-electron steps are labeled as before.

$E^{\circ'}$ values measured in the low dielectric dichloromethane (0.1 M Bu_4NPF_6) medium are much more negative than that found in ionic liquids or in CH_3CN . Consequently, only four one-electron-reduction processes are detected within the available potential window (Figure 5).

Solvent Dependence of $E^{\circ'}$ Values. Reversible potentials obtained in This Work and in related work are summarized

in Table 4. They exhibit a very wide range of values. $E^{\circ'}$ -values for the first reduction process may be correlated with the solvent polarity (quantified by the Gutmann donor number^{1,18} or other methods¹⁸). Thus, $[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]^{4-}$ is the most difficult to reduce in the least polar solvent medium of examined dichloromethane (CH_2Cl_2 ; $E^{\circ'} = -0.437 \text{ V}$) and is the easiest to reduce in the most polar medium (H_2O ; $E^{\circ'} = 0.02 \text{ V}$). The polarity of CH_3CN is intermediate between those of CH_2Cl_2 and H_2O and the $E^{\circ'}$ value of -0.24 V lies between the values obtained in those solvents. The data in ionic liquid media are more akin to those found in the high dielectric medium, water. Ionic liquids are generally more polar than CH_3CN but less polar than H_2O ,³⁶ so their $E^{\circ'}$ -values appear to reflect their high polarity.

Influence of the Purity of Ionic Liquids on $E^{\circ'}$. Perusal of the data for $[\text{Bu}_4\text{N}]_4[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]$ in Table 4 reveals that, while potentials for the initial 4-/5-/6-/7- processes are similar

Table 4. Reversible Potentials^a for Designated One-Electron Processes Obtained for the Reduction of [Bu₄N]₄[α -S₂W₁₈O₆₂] in Ionic Liquids, CH₂Cl₂, CH₃CN (100%), CH₃CN/H₂O (95:5 v/v), and Aqueous Electrolyte Media

			E^0/V vs Fc^+/Fc						
solvent/electrolyte (0.1 M)	working electrode	state	4-/5-	5-/6-	6-/7-	7-/8-	8-/9-	9-/10-	reference
[BMIM][PF ₆]	GC or Au	dissolved	0.020	−0.257	−0.720	−1.005	−1.373	−1.628	This Study
		solid	0.030	−0.253	−0.714	−0.986	−1.362	−1.633	
[EMIM][tfsa]	GC or Au	dissolved	−0.001	−0.249	−0.701				
		solid	0.000	−0.252	−0.700	−0.986			
[P1,4][tfsa]	GC or Au	dissolved	0.023	−0.263	−0.778	−1.120			
		solid	0.020	−0.262	−0.777	−1.130	−1530		
[BMIM][BF ₄]	GC or Au	dissolved	−0.010	−0.287	−0.736	−1.000			
		solid	0.001	−0.280	−0.728	−0.978			
DCM/Bu ₄ NPF ₆	GC	dissolved	−0.437	−0.802	−1.357	−1.745			6
CH ₃ CN/Bu ₄ NPF ₆	GC	dissolved	−0.245	−0.628	−1.199	−1.595	−2.094	−2.464	
CH ₃ CN/Bu ₄ NPF ₆	GC	dissolved	−0.24	−0.62	−1.18	−1.57	−2.02	−2.32	
H ₂ O/Et ₄ NCl ^b	GC	solid	0.02	−0.20	−0.64	−0.89	−1.08	−1.20	
	Au	solid	0.02	−0.19	−0.63	−0.90			
CH ₃ CN/Bu ₄ NClO ₄	GC	dissolved	−0.24	−0.62	−1.18	−1.57			11b
CH ₃ CN/H ₂ O (95:5)/Bu ₄ NClO ₄	GC	dissolved	−0.23	−0.59	−1.12	−1.42			

^a Calculated as (*E*_p^{red} + *E*_p^{ox})/2 from cyclic voltammograms. ^b The *E*⁰ values (vs Ag/AgCl) are converted (small temperature difference neglected) to the Fc^{+/}Fc scale using the Ag/AgCl and Fc/Fc⁺ standard potentials in aqueous media of 0.212¹⁸ and 0.44⁴⁰ vs NHE, respectively, at 25 °C.

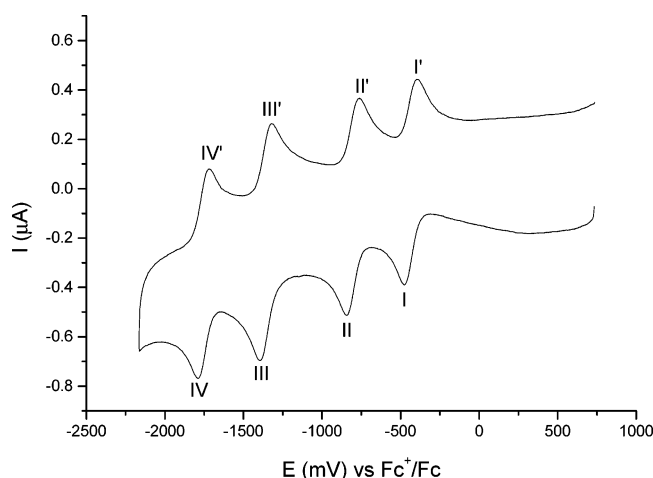

Figure 5. Cyclic voltammogram obtained with 1-mm diameter GC electrode for the reduction of 0.2 mM [α -S₂W₁₈O₆₂]^{4−} in CH₂Cl₂ (0.1 M Bu₄NPF₆). *v* = 0.2 V s^{−1}.

Table 5. *E*⁰ (vs Fc^{+/}Fc) Values Measured for the Reduction of [α -S₂W₁₈O₆₂]^{4−} in Locally Synthesized and Commercially Supplied [BMIM][PF₆]^a

process	<i>E</i> ⁰ /mV vs Fc ^{+/} Fc			
	locally synthesized [BMIM][PF ₆]		commercial [BMIM][PF ₆]	
	adhered solid	dissolved	adhered solid	dissolved
4-/5-	30	20	10	9
5-/6-	−253	−257	−255	−260
6-/7-	−714	−720	−690	−691
7-/8-	−986	−1005	−870	−875
8-/9-	−1362	−1373	−1110	−1115
9-/10-	−1633	−1628	−1380	−1370

^a *E*⁰ values obtained at GC and Au electrodes are identical within experimental error (±3 mV).

in all studies in CH₃CN, the reversible potential for processes 8-/9- and 9-/10- obtained in extensively purified CH₃CN (see Experimental Section) are, respectively, 74 and 144 mV more

negative than reported previously in nominally the same solvent (electrolyte) but where purification was confined to drying with basic alumina.⁶ This difference indicates that very careful purification of solvent/electrolyte media may be crucial for measurement of the reversible potentials of extensively reduced (highly negatively charged) polyoxometalate anions. In principle, a more negative *E*⁰ value obtained for the reduction process is likely to be the more reliable value (less influence from impurity) as coupled homogeneous reactions between the reduced form and a trace cationic impurity is predicted to shift the potential in the positive direction.

In the absence of purification procedures,⁷ nonvolatile ionic liquids may contain significant levels of impurities.³⁷ Noting the importance of the purity of CH₃CN media discussed above, the potentials of the reversible one-electron processes of highly reduced forms of [α -S₂W₁₈O₆₂]^{4−} were studied as an indicator of ionic liquid purity. Cyclic voltammograms obtained with commercially supplied [BMIM][PF₆] (quoted as 99.3%) are shown in Figure 6. It can be seen immediately that the negative potential window is significantly lower than in the locally synthesized form discussed above (−1.5 vs −2.3 V). Water and acid are two obvious impurities that may be present at elevated levels which could have this effect. Table 5 summarizes the *E*⁰ data obtained from the commercial ionic liquid and the locally synthesized [BMIM][PF₆] used in this work (see Experimental Section). The *E*⁰ values obtained for the first two processes [S₂W₁₈O₆₂]^{4−/5−} and [S₂W₁₈O₆₂]^{5−/6−} are not significantly influenced by the origin of the medium. However, significant differences are observed for subsequent processes, increasing to 250 mV for [S₂W₁₈O₆₂]^{9−/10−}. Further experiments demonstrated that deliberate introduction of 1% water into locally synthesized [BMIM][PF₆] had no noticeable influence on the measured *E*⁰ values of any of the reduction processes, even though the solvent potential window was decreased signifi-

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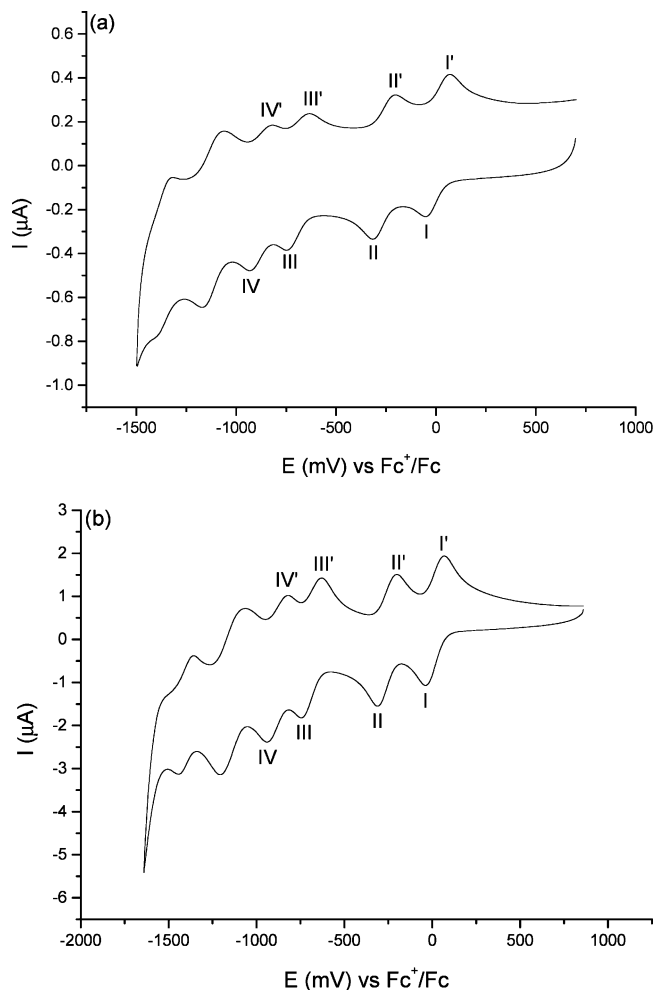


Figure 6. Cyclic voltammograms obtained with a GC electrode (d, 1 mm) for reduction of $[\text{Bu}_4\text{N}]_4[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]$ in commercial $[\text{BMIM}][\text{PF}_6]$ for (a) dissolved $[\text{Bu}_4\text{N}]_4[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]$ (5 mM); (b) $[\text{Bu}_4\text{N}]_4[\alpha\text{-S}_2\text{W}_{18}\text{O}_{62}]$ micro-particles adhered to electrode surface ($\nu = 0.2 \text{ V s}^{-1}$).

cantly (note that addition of 5% water to CH_3CN also has a relatively small influence on E^0 data; see Table 4). In addition, introduction of a 1:1 molar ratio of acid (5 mM trifluoroacetic acid) into locally synthesized $[\text{BMIM}][\text{PF}_6]$

significantly influences the fourth (7-/8-) and following reduction processes (also decreases the potential window). Thus, trace levels of acid impurity play a significant role in the voltammetry of highly reduced polyoxometalates. The influence of metal ion impurities such as Na^+ or K^+ and concomitant ion pairing also could be important.³⁸ It is known that a trace of water in PF_6^- ionic liquids leads to the slow production of HF;³¹ hence, adventitious water in the commercial $[\text{BMIM}][\text{PF}_6]$ may be related to its conversion to HF during the months between production and use. However, the nature of the impurities which affects the voltammetric data has not been unambiguously identified.

Conclusions

The reduction of a range of Mo and W polyoxometalate anions has been investigated in both ionic liquid and conventional solvent (electrolyte) media. The results show that (1) the Mo polyoxometalates are always much easier to reduce than their W counterparts and reduced W polyoxometalates are more stable than their isostructural Mo analogues (these difference are possibly associated with the higher electron affinity of Mo(VI) sites and higher proton affinity of $-\text{O}-$ sites in Mo polyoxometalates³⁹ which makes the Mo moieties easier to reduce and also more prone to attack by protons than their W counterparts); (2) the polarity of the solvent plays a key role in determining the reversible potential; and (3) adventitious impurities in ionic liquids may have a significant influence on the reversible potential found for the reduction of highly reduced polyoxometalate anions.

Acknowledgment. The authors acknowledge the Australian Research Council for financial support of this project.

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