Electrochemical and Computational Study of Ion Association in the Electro-Reduction of $\text{PW}_{12}\text{O}_{40}^{3-}$

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Abstract

Insights into ion pairing effects on the redox properties of the Keggin-type polyoxotungstate $\text{PW}_{12}\text{O}_{40}^{3-}$ are gained by combining electrochemical experiments and density functional theory (DFT) calculations. Such effects have been reported to affect the performance of these species as molecular electrocatalysts.

Experimental square wave voltammetry (SWV) of the two-electron reduction of $\text{PW}_{12}\text{O}_{40}^{3-}$ in acetonitrile evidences that the reduced forms $\text{PW}_{12}\text{O}_{40}^{4-}$ and $\text{PW}_{12}\text{O}_{40}^{5-}$ can be significantly stabilized by ion association. The strength and stoichiometry of the corresponding aggregates are estimated as a function of the nature of the cation (lithium, sodium and tetramethylammonium) and the oxidation state of the polyoxometalate. The results obtained in combination with DFT enable us to examine the roles of the cation solvation and the charge number and distribution of the polyanions.

1. Introduction

Polyoxometalates (POMs) are anionic metal-oxide clusters that show particular electronic properties of great interest in a large number of areas^{1–5}, specifically in electrocatalysis (water oxidation^{6,7}, epoxidation of alkenes⁸, bromate reduction⁹, hydrogen evolution reaction¹⁰, etc.)^{11,12}. POMs can undergo multiple electron transfers^{1,13,14} where the stability and reactivity of the different oxidation states are defined by their intrinsic electronic properties¹⁵ (structure^{16,17} and elemental composition^{18–20}) and also by 'environmental' factors²¹ (solvation, protonation...^{22–24}). Among the latter, ion pairing has been reported to affect the efficiency of molecular electrocatalysis of different systems even in aqueous media^{25,26} by decreasing the reactivity of the catalyst upon the ion association¹⁵; also, the catalytic pathway and turnover frequency²⁷ can be affected as a result of the change in the 'apparent' formal potential⁹ and the electron density distribution (see below). For the investigation of these effects, electrochemical methods are very valuable since they enable direct access to the redox behaviour of species under operational conditions, either dissolved in solution or surface-immobilized.

POMs have been reported to undergo ion association processes^{28–30} such that their redox behaviour and electrocatalytic activity will be affected by the ionic composition of the medium^{31–33}. In this work, ion pairing effects on the electrochemical properties of the Keggin-type polyoxotungstate $\text{PW}_{12}\text{O}_{40}^{3-}$ (PW^{3-}) will be investigated in detail via a joint electrochemical and quantum-chemical approach. As will be discussed, the 'apparent' relative stability in solution of PW^{3-} and the reduced forms PW^{4-} and PW^{5-} can be elucidated from voltammetric measurements in an aprotic media (acetonitrile). For this, the use of square wave voltammetry (SWV) in combination with microelectrodes provides important advantages for accurate quantitative analyses, mainly, well-defined, peak-shaped signals^{34,35} with reduced ohmic drop and capacitive distortions^{36–38}. As will be discussed, the variation of the position of the experimental SWV voltammograms corresponding to the first two electro-reductions of PW^{3-}

upon the addition of different monovalent cations (lithium, sodium and tetramethylammonium) clearly reflects the occurrence of ion association, which depends significantly on the nature of the cation and on the oxidation state of the polyoxometalate. Through the theory developed in a recent work for multi-electron transfers coupled with chemical equilibria³⁹ and with the assistance of density functional theory (DFT) calculations^{40–46}, a consistent picture is gained about the ion pairing of polyoxometalates, including the identification of the chief physicochemical factors (ion size, charge number and distribution, solvation and steric hindrance) and the determination of the anion:cation stoichiometries (which can be a difficult task³⁰) and the value of the association constants. The results can assist the optimization of operating conditions for the use of polyoxometalates as electrocatalysts.

2. Experimental

2.1. Chemical reagents

Anhydrous acetonitrile (MeCN, Sigma-Aldrich, 99.8%), ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$, Aldrich, 97%), tungstophosphoric acid sodium salt ($\text{Na}_3[\text{PW}_{12}\text{O}_{40}]$, Riedel-de-Haën, analytical reagent grade), tetrahexylammonium hexafluorophosphate (THAPF_6 , Sigma-Aldrich, 97%), tetramethylammonium hexafluorophosphate (TMAPF_6 , Sigma-Aldrich, 98%), sodium hexafluorophosphate (NaPF_6 , Sigma-Aldrich, 98%) and lithium hexafluorophosphate (LiPF_6 , Sigma-Aldrich, 98%) were all used as received without further purification.

2.2. Instrumentation

All electrochemical measurements were performed with a home-built potentiostat. A Pt wire was used as counter electrode, a silver wire as quasi-reference electrode and a carbon fiber (CF) microdisc electrode of 33 μm of diameter (ALS Co.) or a glassy carbon (GC) disc of 3 mm of diameter (CH Instruments) as working electrode. The electrodes were polished prior to the experiments using 1.0, 0.3 and 0.05 μm alumina–water slurry on soft lapping pads (Buehler, Illinois), and the electrode radius was calibrated via chronoamperometry^{37,38,47}.

The conductivity measurements were performed with a conductimeter BASIC 30 (Crison) with built-in temperature correction.

2.3. Electrochemical measurements

The study of the electro-reduction of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ (PW^{3-}) was performed at different concentrations of hexafluorophosphate salts of the cations under study: LiPF_6 , NaPF_6 or TMAPF_6 . Acetonitrile solutions were deaerated prior to experiments and a nitrogen atmosphere was maintained in the cell meanwhile. A silver wire was employed to avoid any water contamination and uncertainties related to junction potentials, with the ferrocene-ferrocenium (Fc/Fc^+) redox couple as internal reference^{48–50}.

In order to fix the ionic strength in all solutions at 0.1 M, tetrahexylammonium hexafluorophosphate (THAPF_6) was employed, which can be expected to be fully dissociated given the large size of the THA^+ cation. For the same reason, ion association between the PW anions and THA^+ can be disregarded (see sections S.3 and S.4 of Supp. Info.). This was further verified with SWV experiments under different concentrations of THA^+ where the experimental

SWV curves did not show any dependence on the THA^+ concentration beyond that associated with the variation of the ionic strength.

2.4. Supporting electrolyte ion pairing

Possible association between the cations under study X^+ and their counterion in the supporting electrolyte (PF_6^-) will act as a competing chemical equilibrium reducing the actual concentration of 'free' cations in solution, $c_{\text{X}^+}^*$. In order to take this into account in the quantitative study (Section 3), the association constant (K_A^c) between the cations (Li^+ , Na^+ and TMA^+) and the anion PF_6^- were determined by conductivity:

The analysis of the decrease of the molar conductivity of LiPF_6 , NaPF_6 and TMAPF_6 in acetonitrile due to the formation of electroneutral ion pairs $\{\text{X}^+\text{PF}_6^-\}$ was analyzed in the range of concentrations 0.05-5 mM with the Fuoss-Hsia-Fernandez-Prini equation^{51,52} (see Section S.2. of the Supp. Info). The experimental values obtained for the association constant and the limiting molar conductivity are given in Table 1; note that in all cases the Λ_0 -value agrees satisfactorily with the data reported in the literature.

Electrolyte	K_A^c (this work) (M^{-1})	Λ_0 (this work) ($\text{Scm}^2\text{mol}^{-1}$)	$\Lambda_0^{48,53-55}$ ($\text{Scm}^2\text{mol}^{-1}$)
LiPF_6	21±4	169.4±0.2	169.75±0.05
NaPF_6	29±3	174.3±0.2	178.6±0.02
TMAPF_6	33±4	204.9±0.2	196.75

Table 1. Values of the ion association constant (K_A) and limiting molar conductivity (Λ_0) between the ions of the supporting electrolytes obtained via conductivity with the Fuoss-Hsia-Fernandez-Prini equation^{51,52}. $T = 298 \pm 2$ K. Error bars correspond to the standard deviation obtained from three different sets of measurements.

2.5. Computational Details

Gaussian-09 Revision D.01 package programme⁵⁶ was employed in all the quantum-chemical computations performed. All the density functional theory (DFT) calculations were carried out with the B3LYP functional^{57,58} and the 6-31+G(d) basis set. In the case of the PW species, quasi-relativistic pseudopotentials of the W atoms proposed by Hay and Wadt⁵⁹ were employed and the LANL2DZ basis sets associated with the pseudopotential were adopted. For the rest of the elements, the 6-31+G(d) was employed as the basis set.

For optimizations, the SCF convergence criteria was set to 10^{-7} . An ultrafine integration grid was considered for the Density Functional Theory (DFT) calculations and a fine one to solve the Coupled Perturbed Hartree-Fock (CPHF) equations. Frequency calculations were performed at the same level of theory as the geometry optimisations to characterize the stationary points as local minima (equilibrium structures). No scaling procedures were considered. Also, the effect of the solvent was taken into account by using the CPCM solvation model (conductor like polarizable continuum model)⁶⁰⁻⁶².

3. Results and Discussion

3.1. Theoretical treatment of the electrochemical SWV response

Given that species PW^{3-} and the reduced forms PW^{4-} and PW^{5-} are bulky and highly-charged, the possibility of association with multiple cations can be envisaged. Hence, the general reaction Scheme 1 will be considered for the study of the first two electro-reductions of PW^{3-} in the presence of the cation X^+ :

Scheme 1. Extended rectangular scheme of $3 \times (n+1)$ – members. $E_h^{0'}$ (V) are the formal potentials of the (free-ligand) redox couple involved in the h -th electron transfer ($h=1$ or 2), whereas $K_{i,j}$ correspond to the *apparent* chemical equilibrium constants of the j -th association ($j=1, 2, \dots, n$) of the i -th oxidation state ($i=3-, 4-$ or $5-$). All the chemical and electrochemical steps are assumed to be in equilibrium.

According to Scheme 1, PW^{3-} undergoes two electro-reductions and, in principle, all the redox species can associate with X^+ ($X^+ \equiv TMA^+, Li^+$ or Na^+) forming ion pairs, including aggregates of three (two X cations and a single anion), four or even more ions.

Attending to the large size of the polyoxometalate with respect to cations X^+ , we will assume that the diffusivity of the ion associates $\{X(PW)\}$ is similar to that of species PW such that they all have the same value of the diffusion coefficient: D . Also, as ion pairing processes generally show very fast kinetics^{63,64}, it can be assumed that chemical equilibrium conditions hold at any point in solution (q) and time of the experiment (t)^{65,66}:

$$\forall q, t: \quad K_{i,j}^c = \frac{c_{X_jPW^i}^{eq}(q, t)}{c_{X_{j-1}PW^i}^{eq}(q, t) \cdot c_X^{eq}(q, t)} \quad \begin{cases} i = 3-, 4- \text{ or } 5- \\ j = 1, 2, \dots, n \end{cases} \quad (2)$$

where $K_{i,j}^c$ is the ion association constant based on concentrations. The modelling of the electrochemical response of Scheme 1 greatly simplifies by working under conditions where the concentration of species X^+ can be assumed as constant: $c_X(q,t) = c_X^*$. Thus, in the voltammetric experiments, the effective concentration of species X^+ is in excess (at least 20 times) with respect to the polyoxotungstate and the following *apparent* (or *conditional*) equilibrium constant $K_{i,j}$ can be defined:

$$\forall q,t: \quad K_{i,j} = K_{i,j}^c c_X^* = \frac{c_{X_jPW^i}^{eq}(q,t)}{c_{X_{j-1}PW^i}^{eq}(q,t)} \quad \begin{cases} i = 3-, 4- \text{ or } 5- \\ j = 1, 2, \dots, n \end{cases} \quad (3)$$

c_X^* is the effective bulk concentration of species X^+ [†].

Under the conditions above-discussed, the superposition principle can be applied and the expression of the current-potential response is given by the sum of products of a potential-dependent function and a function dependent on time and on the electrode geometry^{67,68}, whatever the electrode geometry (G) and the voltammetric technique considered. Thus, for a certain y -th cycle of the SWV perturbation (with $y = 1, 2, \dots, N/2$), the corresponding forward ($I_G^{[y],F}$) and backward ($I_G^{[y],B}$) components of the SWV signal are³⁹:

$$\begin{aligned} I_G^{[y],F} &= FA_G D \left\{ \sum_{m=1}^{2y-1} \left[(W^{m-1,s} - W^{m,s}) f_G(q_G, (2y-m)\tau) \right] \right\} \\ I_G^{[y],B} &= FA_G D \left\{ \sum_{m=1}^{2y} \left[(W^{m-1,s} - W^{m,s}) f_G(q_G, (2y-m+1)\tau) \right] \right\} \end{aligned} \quad \left. \vphantom{\sum_{m=1}^{2y-1}} \right\} y = 1, 2, \dots, (N/2) \quad (4)$$

and the net square wave current of the y -th cycle ($\Delta I_G^{[y],SWV}$) is given by the difference

$\Delta I_G^{[y],SWV} = I_G^{[y],F} - I_G^{[y],B}$, which can be expressed in a normalized form as follows:

$$\Psi_G^{[y],SWV} = \frac{\Delta I_G^{[y],SWV} \sqrt{\tau}}{FA_G c_T^* \sqrt{D}} \quad (5)$$

[†] In this case, after taking into account the weak ion pairing between X^+ and the salt counterion PF_6^- (see Section 2.4).

where A_G is the electrode area. The function $f_G(q_G, t)$ depends on time and on the shape and size of the electrode, being given exactly for a macroelectrode ($f_p(x, t)$) and approximately to within 0.6% for all times for a disc-microelectrodes ($f_d(r_d, t)$) by:

$$\left. \begin{aligned} f_p(x, t) &= \frac{1}{\sqrt{\pi D t}} \\ f_d(r_d, t) &= \frac{4}{\pi} \frac{1}{r_d} \left(0.7854 + 0.44315 \frac{r_d}{\sqrt{D t}} + 0.2146 \exp\left(-0.39115 \frac{r_d}{\sqrt{D t}}\right) \right) \end{aligned} \right\} \quad (6)$$

The potential-dependent function ($W^{m-1,s} - W^{m,s}$) for the reaction Scheme 1 when the chemical and electrochemical processes are at equilibrium take the form:

$$\begin{aligned} W^{[m],S} &= c_{PW}^* \left(\frac{2e^{\eta_{app,1}^{[m]}} e^{\eta_{app,2}^{[m]}} + e^{\eta_{app,2}^{[m]}}}{1 + e^{\eta_{app,1}^{[m]}} e^{\eta_{app,2}^{[m]}} + e^{\eta_{app,2}^{[m]}}} \right); \quad m=1, 2, \dots, p \\ W^{[0],S} &= W^* = 2c_{PW}^* \end{aligned} \quad (7)$$

where c_{PW}^* is the bulk concentration of electroactive species and:

$$\eta_{app,h}^{[m]} = \frac{F}{RT} (E^{[m]} - E_{app,h}^{0'}); \quad h=1 \text{ or } 2 \quad (8)$$

with $E_{app,h}^{0'}$ being the *apparent* formal potentials that depend on the values of the ion association constants as follows^{39,50,69,70}:

$$\begin{aligned} E_{app,1}^{0'} &= E_1^{0'} + \frac{RT}{F} \ln \left[\frac{1 + \sum_{j=1}^n (\beta_{(4-),j})}{1 + \sum_{j=1}^n (\beta_{(3-),j})} \right] \quad (a) \\ E_{app,2}^{0'} &= E_2^{0'} + \frac{RT}{F} \ln \left[\frac{1 + \sum_{j=1}^n (\beta_{(5-),j})}{1 + \sum_{j=1}^n (\beta_{(4-),j})} \right] \quad (b) \end{aligned} \quad (9)$$

where $\beta_{i,j}$ are the *conditional* overall association constant:

$$\beta_{i,j} = \prod_{a=1}^j K_{i,a} = \frac{c_{O,X_j}^{eq}(q, t)}{c_{O_i}^{eq}(q, t)} = \prod_{a=1}^j K_{i,a}^c c_X^* \quad (10)$$

From the above expressions, it can be inferred that the association of the polyoxometalate anions with X^+ will result in the change of the apparent formal potentials $E_{app,1}^{0'}$ and $E_{app,2}^{0'}$ according to Eqs. (9). By determining their values from the SW signal as detailed in ^{50,71} for different values of c_X^* , the association constants and stoichiometries can be investigated as discussed in the following sections ³⁹.

3.2. Electrochemical study of the ion association between TMA⁺ and PW anions

Ion pairing between PW anions and tetramethylammonium (TMA⁺) was first investigated. The effective concentration of TMA⁺ ($C_{TMA^+}^*$) was always in excess with respect to the initial concentration of PW³⁻ ($C_{TMA^+}^* \geq 20C_{PW}^*$) according to the value of the association constant obtained from conductivity measurements (see Section 2.4 and sections S.2 and S.3 of the Supp. Info. ⁵²).

In Figure 1, representative experimental square wave voltammograms at the highest and lowest concentrations of TMA⁺ assayed are shown, as obtained at a carbon fiber microdisc (Figure 1a) and at a glassy carbon macroelectrode (Figure 1b). The square wave voltammograms show two well-defined peaks that correspond to two reversible, one-electron reductions as can be inferred from the values of the half-peak width (see below). The first peak is ascribed to the reduction of PW³⁻ to PW⁴⁻ while the second peak to the reduction of PW⁴⁻ to PW⁵⁻ ^{14,72}. For both peaks, the experimental values of the half-peak width ($W_{1/2}$) are very close to the theoretical value predicted for reversible one-electron transfers for the square wave amplitudes employed: $W_{1/2}^{Exp} = 90-94\text{ mV}$ for $E_{SW} = 10\text{ mV}$ (vs $W_{1/2}^{theor} = 92\text{ mV}$) and $W_{1/2}^{Exp} = 96-105\text{ mV}$ for $E_{SW} = 25\text{ mV}$ (vs $W_{1/2}^{theor} = 99\text{ mV}$) ^{34,35,73}. The second peak at the microelectrode is broader and smaller than the first one ($W_{1/2}^{Exp,2^{nd}-micro} = 98-115\text{ mV}$), which is likely related to the quasi-reversible character of the electron transfer, since the influence of the electrochemical kinetics is more significant at microelectrodes due to the enhanced diffusion mass transport ^{35,36,38}.

Nevertheless, these electrode kinetic effects do not affect significantly the peak position of the second peak, as proven from the good agreement between the experimental $E_{2,peak}$ -value obtained at micro and at macroelectrodes (<5mV, not shown)⁷⁴.

Figure 1. Influence of the concentration of TMA⁺ cation on the SWV curves corresponding to the two first electroreductions of the PW^{3-} at CF microdisc electrode of 33 μm of radius **(a)** and at a GC macroelectrode **(b)** with $c_{PW^{3-}}^* = 50 \mu M$. Baseline-corrected experimental square wave voltammograms obtained with $E_{sw} = 25$ mV (CF microdisc electrode, **a**) and $E_{sw} = 10$ mV (GC macroelectrode, **b**). For both electrodes: $f_{sw} = 10$ Hz, $|\Delta E| = 5$ mV, Ionic strength set at 0.1M; T=298±2K.

As can be seen in Figure 1, when the concentration of TMA⁺ is increased, the positions of the two peaks shift towards less negative values, which reveals the occurrence of ion associations between the polyoxometalate anions and TMA⁺. The shift is more obvious in the second peak such that it can be concluded that the strength of the association follows the order $PW^{5-} > PW^{4-} > PW^{3-}$. This behaviour is that predicted by electrostatic-only considerations, being also in agreement with the results of quantum-chemical calculations with DFT methods (see below). Figure 2 shows the Electrostatic Potential Mapped Electron Density Surface (ESP) of the different PW anions. As could be expected, the ‘outer shell’ of the PW species is negatively charged and it becomes more negative as the PW species gets further reduced. The minimum ESP-value is located at the holes defined by four octahedrals of two different M_3O_{13} triads (see red regions in Fig. 2 and section S.5 of the Supp. Info).

Figure 2. Electrostatic potential on the 0.001 au molecular surface of PW^{3-} (top), PW^{4-} (centre) and PW^{5-} (bottom) species, computed with the B3LYP functional as indicated in Section 2.5. Optimized structures were obtained with Td symmetry constraint (α -isomer) and considering the CPCM approach to take into account solvent effects.

Next, as indicated previously (Section 3.1) and as detailed in ³⁹, the elucidation of the ion pairing mechanism and the determination of the association constants and stoichiometries of the different PW_{12} species were performed by the analysis of the variation of the *apparent* formal potentials with the concentration of TMA^+ (Eq.(9)), with the corresponding equilibrium constants as adjustable parameters. Given that the first and second peaks are well-separated

$(\Delta E_{p-p} = E_{p,2} - E_{p,1} \leq -436\text{mV})$, the electron transfers can be treated separately and the SW peak potential coincides with the *apparent* formal potential ($E_{\text{peak,h}} \equiv E_{\text{app,h}}^{0'}$, see Eqs.(9)) whatever the electrode size and shape considered ⁷⁵.

The mechanistic analysis is not straightforward since multiple ion associates of different stoichiometries can be envisaged given the high negative charge and large size of the PW anions. In order to establish realistic and consistent mechanisms and thermodynamic parameters, the fitting procedure was carried out under the following considerations:

- The values of the formal potentials of the redox couples $\text{PW}^{3-}/\text{PW}^{4-}$ and $\text{PW}^{4-}/\text{PW}^{5-}$ were obtained from independent SWV experiments in 0.1M THAPF₆ solutions (in the absence of TMA⁺): $E_1^{0'} = -703 \pm 3\text{mV}$ and $E_2^{0'} = -1216 \pm 2\text{mV}$. The values obtained point out that the two SWV peaks correspond to the α -isomer ⁷².
- Where necessary, the cation:anion stoichiometry was increased up to achieving satisfactory fits of experimental data ($R^2 \geq 0.99$).
- The values of the equilibrium constants were constraint to be positive values, performing several independent fittings with different initial values with a perfect coincidence
- The equilibrium constants obtained with a value of the dependency parameter ⁷⁶ close to 1 (>0.85) were not considered.

In addition to the above, a '*purely electrostatic* model' for the ion association was initially considered. Thus, ion desolvation and anion-cation coulombic interactions are the main forces involved in the ion pair formation. In the case of low dielectric-constant media and highly charged species, one could expect that electrostatic interactions will prevail over desolvation. Accordingly, the value of the association constants can be presumed to be determined by the charge number of the cation and anion taking part in the ion pairing process; for example, the following equilibria:

where all the starting anions have the same charge number ($z=3-$) would have the same value of the association constant K_{z_a} : $K_{3-,1} = K_{4-,2} = K_{5-,3} \equiv K_{3-}$. Assuming this, Eqs. (9) become:

$$\begin{aligned}
E_{\text{peak},1} &= E_1^{0'} + \frac{RT}{F} \ln \left(\frac{1 + K_{4-}^c c_L^* + K_{3-}^c K_{4-}^c (c_L^*)^2 + \dots}{1 + K_{3-}^c c_L^* + \dots} \right) \\
E_{\text{peak},2} &= E_2^{0'} + \frac{RT}{F} \ln \left(\frac{1 + K_{5-}^c c_L^* + K_{4-}^c K_{5-}^c (c_L^*)^2 + K_{3-}^c K_{4-}^c K_{5-}^c (c_L^*)^3 \dots}{1 + K_{4-}^c c_L^* + K_{3-}^c K_{4-}^c (c_L^*)^2 + \dots} \right)
\end{aligned} \tag{12}$$

The fittings of the experimental data of the peak potentials with the ‘electrostatic model’ (Eq.(12)) were not satisfactory in any case ($R^2 \leq 0.90$). To shed some light on this issue, ESP surfaces of PW^{3-} and $[\text{Li}^+ \text{PW}^{4-}]^{3-}$ (i.e., two PW species with the same charge number) were calculated and they are shown in Figure 3. Note that the localized sites of electron density differ between both of them, the species $[\text{Li}^+ \text{PW}^{4-}]^{3-}$ having a region with higher electron density at the ‘outer shell’ than PW^{3-} . Hence, both the electrochemical and computational results support the idea that the *overall* charge of the anion species is not the only key parameter that determines the strength of ion pairing in this system.

It is also important to notice that the association of a cation with PW breaks down the symmetry of the electron density distribution as can be inferred from the ESP surfaces shown in Figure 2 (and in Figure 3a). Thus, the association of a single lithium cation at one of the sites of highest electron density (Figure 3b) leads to higher density at the opposite one. Hence, a statistical theoretical treatment as frequently-used for macromolecules⁷⁷ does not seem to be not suitable in this case.

Figure 3. Electrostatic potential mapped surface of PW_3^{3-} (a, left side) and $[\text{Li}(\text{PW}_4^-)]^{3-}$ species (b, right side) at the same conditions as in Figure 2. Position of the lithium cation indicated with a yellow arrow.

Figure 4. Experimental variation of the peak positions with the concentration of TMA^+ (points). Best-fit theoretical curve (black solid line, Eqs.(9)). Error bars of the peak potentials correspond to the standard deviation calculated from three independent SWV experiments and those of the estimated equilibrium constants to the asymptotic standard error.

In view of the above results, the fitting of the experimental $E_{app,h}^{0'}$ vs c_X^* data was carried out with arbitrary, adjustable values of all the association constants. As shown in Figure 4, for the satisfactory description of the experimental variation of both peak potentials ($R^2 > 0.99$), it is necessary to include the formation of triple ions for PW^{4-} and quadruple ions in the case of PW^{5-} (Scheme 2). The formation of multiple ion associates with the TMA^+ cations can be explained by the large size and high negative charge of the PW_{12}^{4-} and PW_{12}^{5-} anions such that a very high coulombic attraction towards the cations is expected to take place without significant steric effects between the associated cations.

Scheme 2. Ion pairing between the PW species and TMA+ as elucidated from SWV experiments.

The values obtained for the chemical equilibrium constants obtained follow the order $K_{5-j}^c > K_{4-j}^c > K_{3-j}^c$, which is consistent with the ESP surfaces (Figure 2). Also, it is quite remarkable that the most oxidized species PW^{3-} undergoes no ion association in spite of its high negative charge. This is in line with the very high acid character of this form of the polyoxometalate reported in the literature^{15,78}.

3.2.2. Effect of the size of the ions: Cation desolvation vs Coulombic attraction

The electroreduction of PW^{3-} in acetonitrile was also studied in the presence of two different alkaline cations (lithium (Li^+) and sodium (Na^+)) in order to gain insight into the effects of the nature and size of the cations on the ion association. As in the case of TMA^+ , the effective concentration of these cations (c_{Li^+/Na^+}^* , as calculated from the value of the association constant

obtained in Section 2), was always in excess with respect to the bulk concentration of PW^{3-} (i.e., $c_{\text{Li}^+/\text{Na}^+}^* \geq 20c_{\text{PW}^{3-}}^*$).

Figure 5. Influence of the concentration of Li^+ and Na^+ cations on the SWV curves corresponding to the two first electroreductions of the PW^{3-} at CF microelectrode of $33\mu\text{m}$ of radius (a-c) and at a GC macroelectrode of 3mm of radius (b-d) with $c_{\text{PW}^{3-}}^* = 50\mu\text{M}$. SWV experimental parameters and other conditions as in Figure 1.

In Figure 5, representative experimental SWV curves at the carbon fiber microelectrode (Figure 5a, 5c) and the glassy carbon macroelectrode (Figure 5b, 5d) are shown for the highest and lowest $c_{\text{Li}^+/\text{Na}^+}^*$ -values assayed. As in the experiments with TMA^+ , two well-defined and separate peaks are observed that shift towards less negative potentials when the concentration

of Li^+ or Na^+ is increased. At the highest concentration of Li^+ (Figures 5a and 5b), a third peak is also observed that corresponds to the two-electron reduction of species PW^{5-} to PW^{7-} .

The shift of the first peak is significantly smaller than in the experiments with TMA^+ , which can be explained either by the ion association of species PW^{3-} and PW^{4-} being of similar strength (see Eq. (8a)), or by the absence of ion pairing with species PW^{3-} and PW^{4-} . The latter is consistent with results obtained by Himeno *et al.*^{22,23,28} that indicated the negligible formation of ion associates between Li^+ and the phosphopolyoxomolibdates $[\text{PMo}_{12}\text{O}_{40}]^{3-/4-}$ by combined cyclic voltammetry and ^7Li NMR.

According to the above, only the shift of the second peak was considered in the quantitative analysis (Figure 6). The shift is clearly more significant when the size of the cation decreases in spite of the larger desolvation energy (see below); for example, the shift of the second peak in the case of TMA^+ is of *ca.* 120mV at 50mM, whereas in the case of lithium at 30mM of *ca.* 290mV. This simple preliminary analysis suggests that the coulombic attraction prevails over cation desolvation for PW^{5-} ion associates.

Figure 6. Experimental variation of the peak positions with the concentration of Li^+ (a, points), Na^+ (b, points) and best-fit theoretical curves (black solid lines, Eqs.(9)). Error bars of the peak potentials correspond to the standard deviation calculated from three independent SWV experiments and those of the estimated equilibrium constants to the asymptotic standard error.

Both for Na^+ and Li^+ , the first and second peaks are well-separated ($\Delta E_{p-p}^{\text{Exp}} = E_{p,2} - E_{p,1} \leq -240\text{mV}$) for the concentration range considered^{II} so that the peak potentials coincide with the apparent formal potentials given by Eq.(2). With respect to PW^{5-} , the experimental data are consistent with the formation of quadruple ions (as in the case of TMA^+) with the overall ion pairing constant increasing as the size of the cation decreases: $\text{Li}^+ > \text{Na}^+ > \text{TMA}^+$. This contrasts with the ordering observed for the strength of the association between hexafluorophosphate and the same cations (Li^+ , Na^+ , TMA^+) via conductimetry (Section 2.4), pointing out that there is a significant competition between ion solvation and electrostatics in this medium.

Scheme 3. Ion pairing between the PW species and Li^+/Na^+ as elucidated via SWV. Association between species PW^{3-} and PW^{4-} with Li^+ and Na^+ was initially considered in the model (grey colour), although the analysis of the experimental SWV results suggest that such ion pairing is negligible under the present conditions.

In order to shed some light on this, as well as to corroborate the experimental results, a DFT-based computational study was performed to estimate the ‘strength’ of (1) the solvation of cations X^+ in acetonitrile as well as of (2) the ion pairing of cations X^+ with PF_6^- and (3) with the PW anions.

^{II} In the case of the highest concentration of Li^+ , the difference between the second and the third peak is also sufficiently negative for the square wave amplitudes employed as to enable the assumption of addressing both electron transfers as independent ($\Delta E_{p-p}^{\text{Exp}} = E_{p,3} - E_{p,2} \leq 170\text{mV}$, see Ref. ⁷⁵).

(1) In Table 2, the solvation of cations X^+ in acetonitrile is studied through the acetonitrile nitrogen-cation distance and the specific ($\Delta G_{\text{Sp.Solv.}}^{0,\text{gas}}$) and global ($\Delta G_{X,\text{TSolv.}}^0$) solvation Gibbs energy calculated according to the following thermodynamic cycle:

Scheme 4. The first step corresponds to the specific solvation of the X cations which has been employed previously to measure the interaction strength between the acetonitrile groups and the X cations⁴⁵, whereas the second step represents the non-specific solvation of the cluster which is given by the difference between the electronic energy obtained with the CPCM model (s) and in vacuum (g).

For the three cations under study, a tetrahedral four-coordinated solvation shell is predicted (Figure 7) and the value of the solvation energy is significant (see Table 2), in agreement with that reported in^{45,79}. As expected, solvation becomes stronger as the size of the cation decreases such that the nitrogen-X distance and the solvation Gibbs energy decrease.

Figure 7. Optimised structure for $[\text{Na}(\text{ACN})_4]^+$ (left side) and $[\text{TMA}(\text{ACN})_4]^+$ (right side) computed at B3LYP/6-31+G(d) level as indicated in Section 2.5. Optimized structures were obtained with Td symmetry constraint.

X^+ cations	d_{N-X} (pm)	Specific Solvation (g) $\Delta G_{Sp.Solv.}^{0,gas}$ (KJ / mol)	Non-Specific Solvation (s, CPCM) $\Delta E_{N-Sp.Solv.}$ (KJ / mol)	Total Solvation $\Delta G_{X,TSolv.}^0$ (KJ / mol)
<i>Li+</i>	205	-369	-154	-523
<i>Na+</i>	239	-277	-158	-434
<i>TMA+</i>	385	-60	-157	-216

Table 2: Summary of the parameters of interest of the solvation of the X cations in acetonitrile media at the B3LYP/6-31+G(d) level of theory.

(2) The DFT study of the ion pairing strength between the PF_6^- and X^+ was performed according to the following scheme:

where the possibility of ion pairing including part of the cation solvation shell is considered; specifically, the cation is assumed to maintain three molecules of acetonitrile of the first solvation upon ion association according to⁴⁶. Given the number of possibilities of ion pairing between PF_6^- and the different cations X^+ (see Refs.^{46,80}), the study was restricted to contact ion pairs involving a single cation and one anion.

Figure 8. Optimized structures of TMA(PF_6) (left side) and Li(PF_6) (right side), both at computed at B3LYP/6-31+G(d) level as indicated in Section 2.5.

Coordination opposite to a single fluorine atom (see Figure 8) was found to be the most favorable and the ordering of the ion pairing strength predicted theoretically agrees with that obtained experimentally by conductimetry: $TMA^+ > Na^+ > Li^+$ (see Table 3). Hence, both DFT and

conductivity data indicate that the ordering of the ion pairing strength between hexafluorophosphate and the cations under study is determined by the cation desolvation.

X^+ cations:	Relative Ion Pairing Energies^{III} (KJ/mol):
	$\Delta(\Delta G_{XPF_6}^{0, Tot. IP})$
Li^+	0
Na^+	-9.4
TMA^+	-13.6

Table 3. Summary of ion pairing between the X^+ cations with the PF_6^- anion at the B3LYP/6-31+G(d). Structures shown in Figure 8.

(3) Finally, a DFT-study of the association of the anions PW^{3-} and PW^{5-} with the alkaline cations was performed in order to examine whether the strength of the ion association is predicted to be defined by the coulombic attraction (as suggested by the experimental data for PW^{5-}) or by the cation desolvation as found with the less charged anion PF_6^- . The association with the first cation was considered according to the following scheme:

where, for the sake of simplicity and given the demand of the DFT calculations, the first solvation shells were not considered.

The regions with the minimum values of the ESP mapped surface ('ESP-H' in Table 4) shown in Fig. 2 and in section S.3. of the Supp. Info. which are the most probably sites for ion pairing since these regions show the highest 'exposed' electron density. Also, the association through the terminal oxygens (O_T in Table 4) of PW^{5-} was considered attending to previous computational studies on proton affinity^{15,40}. In Figure 9, one of the optimized structures at the two positions considered are shown and the ΔG_{XPW}^0 - values are given in Table 4.

^{III}Given that our interest is to compare the strength of the interaction between the cations X^+ with PF_6^- , relative energies have been considered assigning a value of zero to $\Delta G(LiPF_6)$.

Figure 9. Optimized structures of $\text{Li}(\text{PW}^{3-})_2$ with lithium cation directed towards a region with the highest electron density (ESP-H, left side) and a terminal oxygen (O_t , right side), both at computed as indicated in Section 2.5.

X^+ position:	$\Delta(\Delta G_{\text{XPW}}^0)$ (KJ/mol) : PW^{3-}	$\Delta(\Delta G_{\text{XPW}}^0)$ (KJ/mol): PW^{5-}
Li^+		
O_t	-10.6	-25.2
ESP-H	0	-58.1
Na^+		
O_t	-14.8	-24.6
ESP-H	-12.8	-30.5

Table 4. Summary of the ion pairing between the PW species (PW^{3-} and PW^{5-}) with the alkaline cations with the CPCM model as indicated in Section 2.5.

In the case of species PW^{3-} the most favourable position for the interaction is the oxygen terminal (as indicated by previous authors ^{15,40}), whereas in the case of the PW^{5-} species the association is predicted to be more stable at the here-called ‘ESP-H’ sites. As expected, the interaction of the alkaline cations in terms of Gibbs energy with the PW^{5-} species is always stronger than in the case of PW^{3-} .

Comparing the data obtained for both cations, the interaction between lithium and the PW anion is more favoured than for sodium in the case of the most reduced species (PW^{5-}) which is in accordance with the results obtained in the experimental electrochemical study. The opposite trend is observed in the case of PW^{3-} species, this behaviour being comparable with that obtained for the ion pairing with PF_6^- .

4. Conclusions

Ion pairing effects on the electrochemical behaviour of the Keggin-type polyoxometalate $\text{PW}_{12}\text{O}_{40}^{3-}$ have been investigated through a joint electrochemical and computational approach including square wave voltammetry (SWV) experiments and density functional theory (DFT) calculations. The main outcomes provide insights into the magnitude and nature of such effects that can affect the reactivity and turnover frequency of these well-known electrocatalysts.

The stoichiometry and strength of the ion associations have been evaluated in acetonitrile via SWV for three different oxidation states of the polyoxotungstate ($\text{PW}_{12}\text{O}_{40}^{3-}$, $\text{PW}_{12}\text{O}_{40}^{4-}$ and $\text{PW}_{12}\text{O}_{40}^{5-}$) and three different cations (lithium, sodium and tetramethylammonium). The SWV study points out that the ion pairing in aprotic media is stronger as the polyanion is further reduced and that its charge distribution plays an important role. Thus, the polyanion $\text{PW}_{12}\text{O}_{40}^{5-}$ has been found to form triple and quadruple ions with alkaline cations (lithium and sodium) as well as with tetramethylammonium.

Opposite effects of the size of the cation on the strength of the ion pairing are observed experimentally between PW^{5-} and $\text{PW}^{3-/4-}$, being in consistency with DFT calculations. This can be ascribed to the different magnitude of the coulombic attraction with respect to the cation desolvation. In the case of $\text{PW}_{12}\text{O}_{40}^{5-}$, the strength of the ion associations follows the trend established by electrostatic considerations indicating that the coulombic attraction prevails; thus, the smaller the cation is, the stronger the ion pairing. On the other hand, the cation desolvation predominates in the case of the less charged anions (species $\text{PW}^{3-/4-}$ and also PF_6^-) so that the association with TMA^+ is more favoured than with Li^+ and Na^+ that show stronger interaction with their solvation shell.

Supporting Information

The Supporting Information is available including: glossary; estimation of ion pairing constants of the supporting electrolytes considered via conductimetry; experimental verification of the absence of ion pairing between the polyoxometalate anions and the tetrahexylammonium cation; experimental verification of the negligible influence of the counterion (sodium) of the polyoxometalate salt in this study; enlarged electrostatic mapped potential surface of the isolated polyoxometalate

Acknowledgments

The authors greatly appreciate the financial support provided by the Fundación Séneca de la Región de Murcia (Project 19887/GERM/15) as well as by the Ministerio de Economía y Competitividad (Project CTQ-2015-65243-P). JMGG thanks the Ministerio de Educación, Cultura y Deporte for the fellowship 'Ayuda de Formación de Profesorado Universitario 2015'. EL thanks the Ministerio de Economía y Competitividad for the fellowship "Juan de la Cierva-Incorporación 2015".

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