



In situ measurement of the Preyssler polyoxometalate morphology upon electrochemical reduction: A redox system with Born electrostatic ion solvation behavior

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ARTICLE INFO

Article history:

Received 2 June 2008

Received in revised form 21 October 2008

Accepted 24 November 2008

Available online 7 December 2008

Keywords:

Bulk electrolysis

Heteropolyanions

Polyoxometalate

Preyssler anion

Radius of gyration (R_g)

Small-angle X-ray scattering (SAXS)

ABSTRACT

SAXS (small-angle X-ray scattering) and controlled-potential bulk electrolysis were combined to probe the radius of gyration (R_g) of the molecular polyoxometalate (POM) cluster known as the Preyssler anion, $[\text{YP}_5\text{W}_{30}\text{O}_{110}]^{n-}$ dissolved in an aqueous mineral acid electrolyte, as a function of its charge, $n-$. The experimentally-determined R_g for the oxidized anion ($n = 12$) and its 2-, 4- and 10-electron reduced forms following the course of exhaustive electrolyses with a reticulated vitreous carbon electrode polarized at -0.145 , -0.255 , and -0.555 V vs. Ag/AgCl, respectively, is independent of reduction (and charge) under the solution conditions employed here. Within the limits of resolution and precision of our *in situ* measurements and analyses, ± 0.2 Å, we have found that the R_g is 5.8–6.0 Å, which is in agreement with R_g s calculated from the atomic coordinates of previously reported crystallographic structures for the solid-state salts of the fully-oxidized cluster, $[\text{Y}^3+\text{P}_5\text{W}_{30}\text{O}_{110}]^{12-}$ (abbreviated $[\text{YPA}]^{12-}$). The equivalence indicates that any modification of the P-W-O structure that may arise upon reduction of the Preyssler anion is too small to affect the R_g . Moreover, the identical, experimentally-determined R_g s (5.9 ± 0.1 Å) for the oxidized solution anions of $[\text{La}^{3+}\text{PA}]^{12-}$, $[\text{Ca}^{2+}\text{PA}]^{13-}$, $[\text{Sr}^{2+}\text{PA}]^{13-}$, and $[\text{Na}^+\text{PA}]^{14-}$ further demonstrate that the size of metal-ion-exchanged Preyssler anions, $[\text{M}^{n+}\text{PA}]^{n-15}$, is independent of the charge, n , on M and, hence, the overall cluster charge, $n-15$. This provides an ideal scenario with which to test the Born model of electrostatic ion solvation, wherein the electrochemical potential difference, ΔE_i° , between the first reduction couples of $[\text{M}^{n+}\text{PA}]^{n-15}$ anions that differ by a unit charge (for $\text{M}^{n+} \equiv \text{Na}^+$, Ca^{2+} , Sr^{2+} , Y^{3+} , La^{3+} , Th^{4+}) was used in a derivation of the original Born equation to calculate their Born radius, r . The result, 6.0(2) Å, is equivalent to the effective radius calculated for a charged ellipsoid in a dielectric medium ($r_{\text{eff}} = 5.9$ Å), thereby providing validation of the Born model.

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1. Introduction

The redox behavior of homogenous, monodisperse solution systems of nanomolecular clusters known as polyoxometalates (POMs), which have metal-oxygen framework architectures of remarkable variety [1–5], is of contemporary interest, both practical and fundamental [6–9]. Whereas the number and novelty of high-quality solid-state structures are on the rise [10], due to improving crystallographic capabilities, there are far fewer studies of solution structures, such as illustrated by the early X-ray scattering measurements of a 0.3095 M solution of the Keggin heteropolyoxoanion, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ [11], showing that the dissolution of the solid salt in water does not perturb the morphology of the

spherical anion illustrated in Fig. 1a. Such information about the shape and, particularly, the size of dissolved POMs with different overall charges (e.g., $[\text{AlW}_{12}\text{O}_{40}]^{5-}$ and $[\text{AlW}_{12}\text{O}_{40}]^{6-}$ as well as $[\text{PW}_{12}\text{O}_{40}]^{3-}$ and $[\text{PW}_{12}\text{O}_{40}]^{4-}$) is of pivotal importance in understanding aspects of the kinetics of electron-exchange and -transfer in terms of rate constants [6], reorganization energies [7], and reaction volumes [12].

We are interested in the effects of electrochemical reduction and oxidation upon the structure of POMs, wherein, for example, the addition of charge to the M-O ($\text{M} \equiv \text{Mo}^{6+}$, W^{6+}) framework, such as resulting in the formation of heteropoly blues [13–18], produces some degree of bond elongation and cluster expansion [19,20]. In a similar fashion, the spherical cage-structure of C_{60}^{3-} experiences a charge-induced bond-distortion upon reduction to C_{60}^{4-} , resulting in an oblate spheroid morphology [21]. To address the issue of electronic deformation of molecular structure in POM solution chemistry, we have combined electrochemical and SAXS methods to investigate variations of POM morphology that

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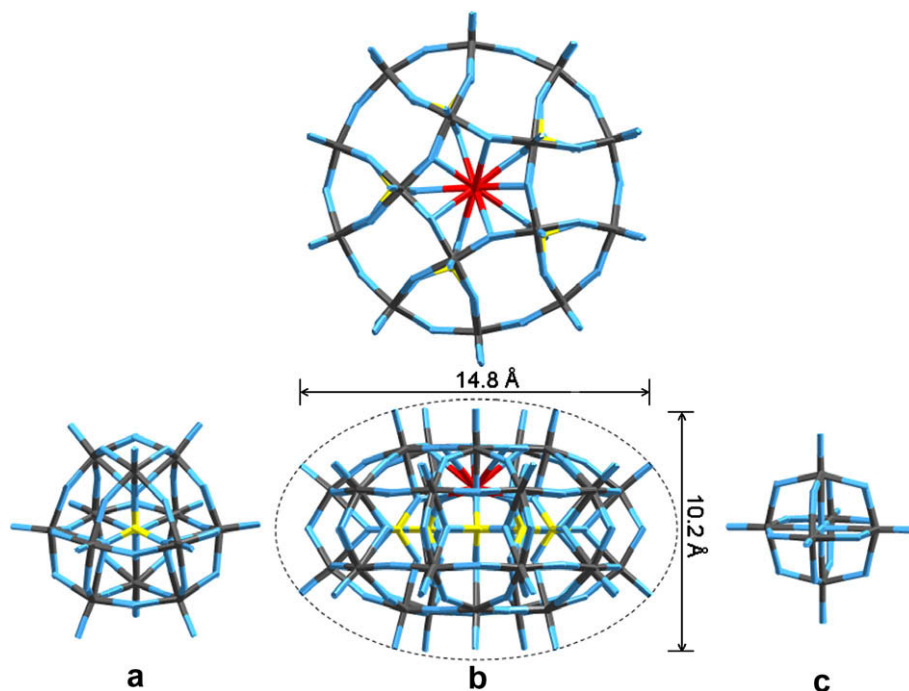


Fig. 1. Stick models of the eponymous: (a) Keggin; (b) Preyssler; and (c) Lindqvist POMs. In these, O atoms are blue, W atoms are gray, and P atoms are yellow. The $[\text{YP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ molecular anion, shown along orthogonal projections in (b) [38] wherein the centrally-encapsulated Y^{3+} ion is red, has a 14.8 Å diameter and 10.2 Å depth. The dashed line represents the ellipsoid model of Eq. (3). The average crystallographic radii, 5.2 and 4.0 Å, of the effectively spherical Keggin and Lindqvist anions, respectively, illustrated here in (a) [77] and (c) [80] were determined as the average distance between the central atoms (P for Keggin, O for Lindqvist) and the terminal-oxo atoms (12 for Keggin, 6 for Lindqvist). (For interpretation of color in Fig. 1 readers are referred to the web version of this article.)

are driven by the controlled polarization of an electrode. Although SAXS has been applied to elucidate POM morphology [22–27], there have been no reports of *in situ* experiments on solutions of POMs to probe the influence of charge on size. The *in situ* approach facilitates the targeted production and stabilization of a single, charge-specific species, which may be otherwise prone to either oxidation or reduction, while probing its R_g [28], in any solution electrolyte, including aqueous, organic, and ionic media. As a redox reagent, electrons are particularly useful because they produce no interferences, such as might arise through the addition of conventional reagents, e.g., chemical oxidants and reductants. As such, *in situ* SAXS finds routine use in providing structural insights into solid-state electrochemical reactions of operating battery [29–31] and fuel cell [32–34] electrodes as well as polymer films [35].

We have chosen to study the yttrium(III)-exchanged Preyssler heteropolyoxoanion, $[\text{YP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ for the following three reasons: it exhibits multi-electron redox activity in aqueous solution [36,37] that is independent of Y and, therefore, the charge on the P-W-O framework can be manipulated by electrode potential; its high-Z molecular framework provides excellent contrast in the aqueous electrolyte (1 M HCl) for the *in situ* SAXS measurements; its molecular structure has been determined through X-ray crystallographic investigations [38]. In two solid-state salts, the fully-oxidized anion, $[\text{YP}_5\text{W}_{30}\text{O}_{110}]^{12-}$ containing W^{6+} , is an oblate ellipsoid with a tunnel through its center, wherein the Y^{3+} cation is encapsulated, as depicted in Fig. 1b. The radius of the tunnel pentagon is 2.18 Å as calculated from the 5 O atom positions that bridge the 5 W atoms [39]. In addition, besides Y^{3+} , all of the lanthanoid(III) ions [36,39], except Pm, as well as selected actinoid[40] and alkaline earth [39,41] ions are similarly encapsulated as $[\text{M}^{n+}\text{P}_5\text{W}_{30}\text{O}_{110}]^{n-15}$, abbreviated $[\text{M}^{n+}\text{PA}]^{n-15}$. Results from X-ray crystallography [38,41,42] demonstrate that the P-W-O framework structures of $[\text{Na}^+\text{PA}]^{14-}$, $[\text{Ca}^{2+}\text{PA}]^{13-}$, $[\text{Eu}^{3+}\text{PA}]^{12-}$, and $[\text{U}^{4+}\text{PA}]^{11-}$, are identical to that shown in Fig. 1b, and are independent of the cluster charge.

From SAXS measurements, we have determined the R_g values of the solution species, $[\text{YP}_5\text{W}_{30}\text{O}_{110}]^{n-}$, maintained in four different states of formal charge, $n-$: the fully-oxidized (colorless) anion, $n = 12$, as well as its heteropoly blues of the 2-, 4-, and 10-electron reduced anion. In the absence of protonation, which can accompany reduction, these three reductions correspond to cluster anions with 14-, 16-, and 22- formal charges. The experimental results are evaluated with respect to the R_g s calculated by using the crystallographically-determined atomic coordinates [38,42] of a selection of oxidized $[\text{M}^{n+}\text{PA}]^{n-15}$ anions, including $\text{M}^{n+} \equiv \text{Na}^+$, Ca^{2+} , Y^{3+} , Eu^{3+} , U^{4+} . Comparisons are also drawn with the oxidized and reduced forms of other POM salts, including Keggin and Lindqvist anions (illustrated in Fig. 1a and c, respectively), for which R_g s were calculated from the atomic coordinates of single-crystal X-ray diffraction studies reported elsewhere [43–50]. We also show that results previously obtained [37] from cyclic voltammetry measurements of the first reduction potentials of $[\text{M}^{n+}\text{PA}]^{n-15}$ anions that differ by 1 unit of charge, i.e., $(n-15)$ and $(n-15) \pm 1$, can be used to calculate the Born radius, r , of the Preyssler anion. The application of this electrochemical approach is based upon the Born model of electrostatic ion solvation by use of a formalism developed beforehand by Maeda et al. [51].

2. Experiments

2.1. Electrochemical system design

The system design for the simultaneous combination of electrochemical and SAXS measurements is illustrated in Fig. 2. It consists of three principal, commercially-available components: (A) BASI bulk electrolysis cell (MF-1056) with a reticulated vitreous carbon working electrode (MF-2077), Ag/AgCl reference electrode with a porous Vycor[®] tip (MF-2052), and a 6.15 mm dia. graphite rod auxiliary electrode (Alfa, 14739); (B) Masterflex[®] peristaltic pump

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