

## Influence of pH and Acetate on the Self-Assembly Process of $(\text{NH}_4)_{42}[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]\cdot\text{ca.}300\text{H}_2\text{O}$

C. V. Krishnan<sup>1,2,\*</sup>, M. Garnett<sup>1</sup> and B. Chu<sup>2</sup>

<sup>1</sup> Garnett McKeen Lab, Inc., 7 Shirley Street, Bohemia, NY 11716-1735, USA

<sup>2</sup> Department of Chemistry, Stony Brook University, Stony Brook, NY 11794-3400, USA

\*E-mail: [ckrishnan@notes.cc.sunysb.edu](mailto:ckrishnan@notes.cc.sunysb.edu)

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Cyclic voltammetry and electrochemical admittance and capacitance measurements were used to investigate the self-assembly process of the polyoxomolybdate, Müller's 'Mo<sub>132</sub>' cluster or  $(\text{NH}_4)_{42}[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]\cdot\text{ca.}300\text{H}_2\text{O}\cdot\text{ca.}10\text{CH}_3\text{COONH}_4$ . Cyclic voltammetry indicated that the self-assembly process could be detected in solutions below pH 4.5 and at total acetate/acetic acid concentrations above 1.5 M. Electrochemical admittance data showed that the molybdenum species in the  $\text{CH}_3\text{COONH}_4$ - $\text{CH}_3\text{COOH}$  buffer resembled the behavior of Müller's 'Mo<sub>132</sub>' cluster only at acetate buffer concentrations above 1.5 M and pH around 4.3 or lower. The behavior of molybdate species at higher pH values resembled those of non-protonated and/or protonated  $[\text{Mo}_7\text{O}_{24}]^{6-}$  and  $[\text{Mo}_8\text{O}_{26}]^{4-}$  anions. Detailed analysis of admittance as a function of pH and acetate/acetic acid concentration supported the existence of the molybdate species related to the  $\{\text{Mo}^{\text{VI}}\text{Mo}^{\text{VI}}_5\}$  fragment which is one of the components of Müller's 'Mo<sub>132</sub>' cluster. Admittance and capacitance results on the self-assembly process were more vivid than those from cyclic voltammetry. These data strongly suggested the critical need to control the pH value as well as the acetate/acetic acid concentration in order to affect the self-assembly process. We conclude with the suggestion that optimum acetate/acetic acid concentrations and pH values needed for the self assembly process of large Keplerate type structures could be monitored systematically by using admittance measurements.

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**Keywords:** Polyoxomolybdate, self-assembly, admittance, Keplerate-type clusters

### 1. INTRODUCTION

An important aspect of recent achievements in nanometer-scale chemistry has been elegantly summarized in the article on "The Beauty of Symmetry" by Achim Müller [1]. The beauty of symmetry is exemplified by the C<sub>60</sub> molecule that has icosahedral ( $I_h$ ) symmetry (with 20 hexagons and 12 pentagons), the highest possible symmetry for molecules [2]. Much more complicated units (which he termed as "clusters"), formed by self-assembly from simple ingredients, can also form

highly symmetric systems. Müller and his colleagues have reported several forms of polyoxomolybdates [3-11], including the very stable, easily accessible icosahedral 'Mo<sub>132</sub>' molybdenum clusters. The formation of highly symmetric clusters, with symmetry comparable to that of the Buckminsterfullerene C<sub>60</sub> is not limited to carbon or to Müller's 'Mo<sub>132</sub>' cluster, but also includes recent examples of phosphorus-copper [12] and nickel-arsenic [13] compounds. Clusters with more complex metal atom cores have also been reported [14]. The preference for highly symmetric objects with a spherical shape is the ability to have minimal surfaces that are more inert against destabilizing "attack" [15]. Thus the key factors for the formation of those interesting nanoscaled materials could be (1) the synthesis of those 'building' units and (2) the self-assembly of the 'building' units to form crystals of interest. The crystals are assembled, to our knowledge, from clusters (not molecules) that have fixed compositions and are not formed due to templates. However, the formation of clusters with fixed compositions does imply a demanding control of the redox potential that is required to dictate a specific ratio of the mixed oxidation states of molybdenum, together with the appropriate ingredients (e.g. acetate ions and pH), in order to produce the desired 'building' units or clusters.

Although Yamase and his collaborators have done experiments to understand the self-assembly processes of polyoxometalates in the photolysis reactions [16-20], few efforts have been made to investigate the self-assembly mechanism of polyoxometalates. The salt of polyoxomolybdate {Mo<sub>132</sub>} is ((NH<sub>4</sub>)<sub>42</sub>[Mo<sup>VI</sup><sub>72</sub>Mo<sup>V</sup><sub>60</sub>O<sub>372</sub>(CH<sub>3</sub>COO)<sub>30</sub>(H<sub>2</sub>O)<sub>72</sub>].ca.300H<sub>2</sub>O.ca.10CH<sub>3</sub>COONH<sub>4</sub>), as first published in 1998 by Müller and his collaborators [6]. Its anion has a beautiful hollow spherical structure, with an icosahedral symmetry, composed of 12 {Mo<sup>VI</sup><sub>6</sub>} pentagonal units of ((Mo)Mo<sub>5</sub>) linked by 30 {Mo<sup>V</sup><sub>2</sub>} spacers. However, no experiments have been focused on monitoring the self-assembly process of this type of inorganic clusters or how to arrive at the optimum conditions for their formation.

The complicated nature of the self-assembly process is obvious from the fact that other acetate compounds of molybdenum, such as Na<sub>10</sub>[H<sub>4</sub>Mo<sub>18</sub>O<sub>56</sub>(CH<sub>3</sub>COO)<sub>2</sub>] x ca. 36 H<sub>2</sub>O x 3 CH<sub>3</sub>COOH, (NH<sub>4</sub>)<sub>12</sub>Na<sub>12</sub>[Mo<sub>40</sub>O<sub>128</sub>] x ca. 70 H<sub>2</sub>O, (NH<sub>4</sub>)<sub>12</sub>Na<sub>20</sub>[H<sub>4</sub>Mo<sub>54</sub>O<sub>168</sub>(CH<sub>3</sub>COO)<sub>4</sub>] x ca. 64 H<sub>2</sub>O, Na<sub>32</sub>[H<sub>4</sub>Mo<sub>54</sub>O<sub>168</sub>(CH<sub>3</sub>COO)<sub>4</sub>] x ca. 128 H<sub>2</sub>O, Na<sub>32</sub>[H<sub>4</sub>Mo<sub>54</sub>O<sub>168</sub>(CH<sub>3</sub>COO)<sub>4</sub>] x ca. 98 H<sub>2</sub>O, [Mo<sub>48</sub>O<sub>128</sub>]<sup>28-</sup>, [Mo<sub>116</sub>O<sub>331</sub>](CH<sub>3</sub>COO)<sub>30</sub>(H<sub>2</sub>O)<sub>56</sub><sup>46-</sup> and (NH<sub>4</sub>)<sub>32</sub>[Mo<sup>VI</sup><sub>110</sub> Mo<sup>V</sup><sub>28</sub>O<sub>416</sub>H<sub>6</sub>(H<sub>2</sub>O)<sub>58</sub>(CH<sub>3</sub>COO)<sub>6</sub>] x H<sub>2</sub>O (x ~ 250), have been synthesized and characterized from aqueous molybdate solutions containing acetate at a pH of 3.5 - 4 using different reducing agents, as well as different amounts of the same reducing agent, to control the ratio of Mo<sup>VI</sup> and Mo<sup>V</sup> [21]. To vary the packing of the cluster units, reagents, such as sodium chloride and acetyl acetone, have also been used in the synthesis. The closing of the 20 "nanowindows" of the Mo<sub>132</sub> cluster achieved with guanidinium cations has resulted in producing well-structured and well defined H<sub>2</sub>O clusters *inside* the shell structure [5].

Previous work from our laboratory has demonstrated that electrochemical methods, especially cyclic voltammetry and admittance, would be very useful to analyze the self-assembly process of polyoxo and polyoxoperoxometalates [22-24]. Here we report our findings on the influence of pH and acetate on the formation of Mo<sup>V</sup><sub>2</sub>O<sub>4</sub><sup>2+</sup> that directs the formation of {Mo<sub>132</sub>} clusters by electrochemical analysis.

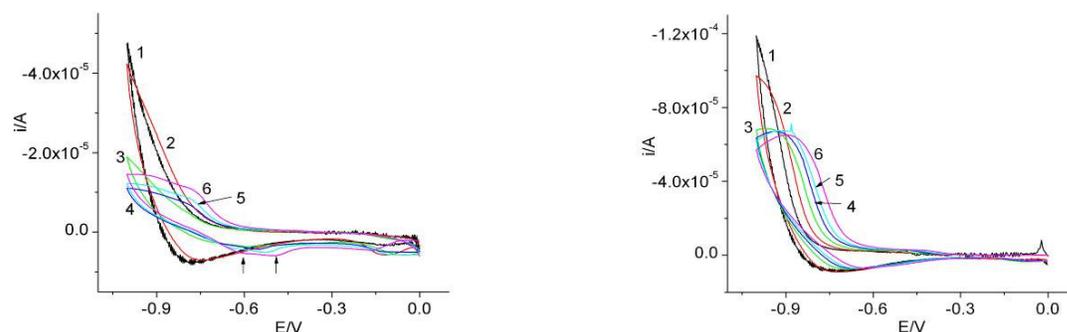
## 2. EXPERIMENTAL PART

An EG & G PARC Model 303A SMDE tri-electrode system (mercury working electrode, platinum counter electrode and Ag/AgCl (3.5M KCl, reference electrode) along with Autolab eco chemie was used for cyclic voltammetric and electrochemical admittance measurements at 298 K. All the chemicals ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, CH<sub>3</sub>COONH<sub>4</sub>, acetic acid and HCl) used in the experiments were of analytical grade. Distilled water was used to prepare all solutions. The solutions were purged with N<sub>2</sub> for about 10 minutes before each experiment. Admittance and impedance measurements were carried out using about 7 mL solutions in the frequency range 1,000 Hz to 50 mHz. The amplitude of the sinusoidal perturbation signal was 10 mV.

## 3. RESULTS AND DISCUSSION

### 3.1. Cyclic Voltammetry

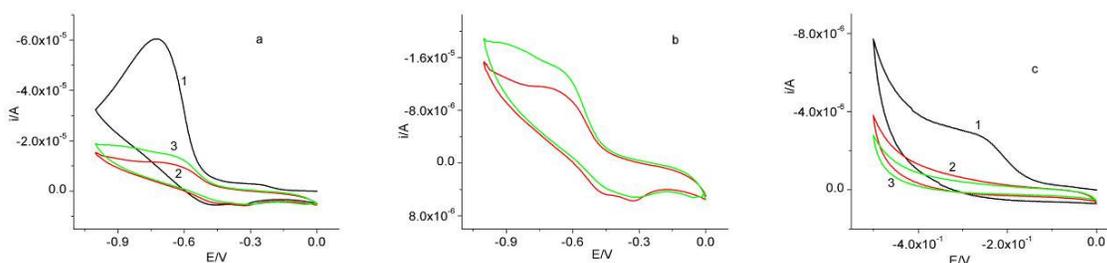
Three scans at 0.1 V/s were measured of solutions containing 0.014 M (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> and differing concentrations of ammonium acetate and acetic acid (with a total concentration of 2 M acetate) in order to obtain differing pH values. The details of the concentrations and pH are included in the figure captions. Of the three scans, scans two and three gave nearly identical results and the results of the third scan are shown in Figure 1 (Left). At pH values greater than about 5, no obvious reduction peak and one oxidation peak were observed. At constant total acetate concentration, as the pH value was further lowered, the nature of the graph changed and one reduction peak with indications of a second peak and two oxidation peaks appeared. There was one obvious reduction peak and two shoulders for oxidation peaks, coming probably from two types of reduced molybdenum species. These two oxidation peak shoulders were more evident in the pH range 4.4 to 4.0, the pH range where Müller's 'Mo<sub>132</sub>' clusters were formed. We had observed these peaks before in our previous studies [24].



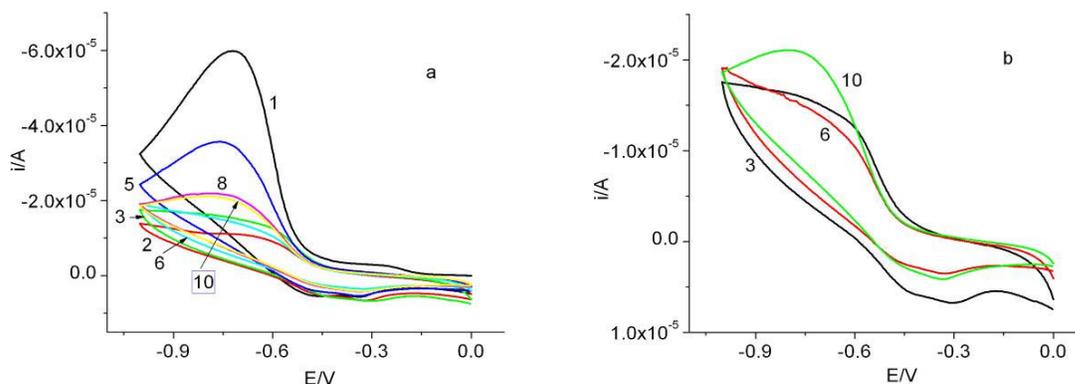
**Figure 1.** Left: Cyclic voltammetry of 0.014 M (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> (scan 3) with 1) 2.0 M CH<sub>3</sub>COONH<sub>4</sub>, 0.0 M CH<sub>3</sub>COOH, pH 6.23; 2) 1.6 M CH<sub>3</sub>COONH<sub>4</sub>, 0.4 M CH<sub>3</sub>COOH, pH 5.57; 3) 1.2 M CH<sub>3</sub>COONH<sub>4</sub>, 0.8 M CH<sub>3</sub>COOH, pH 5.06; 4) 0.8 M CH<sub>3</sub>COONH<sub>4</sub>, 1.2 M CH<sub>3</sub>COOH, pH 4.62; 5) 0.6 M CH<sub>3</sub>COONH<sub>4</sub>, 1.4 M CH<sub>3</sub>COOH, pH 4.36; 6) 0.4 M CH<sub>3</sub>COONH<sub>4</sub>, 1.6 M CH<sub>3</sub>COOH, pH 4.00; The arrows indicate the oxidation shoulders; Right: all of the above, scan 1.

For comparison, the cyclic voltammetric data for the first scan are shown in Figure 1(Right). The behavior was mostly similar except that the two oxidation peak shoulders were not evident. This could probably be due to insufficient formation of the reduced species and also insufficient time for the formation of the self-assembled species. It took 4 days of waiting to prepare the crystals of this Müller's 'Mo<sub>132</sub>' cluster [6]. It should also be pointed out that at the end of the first scan, there could still be some adsorbed species on the working electrode. This observation was also evident from the much lower current observed during scans 2 and 3.

Figure 2 gives the cyclic voltammetric data for the first three scans for a total acetate-acetic acid concentration of 2.23 M at a pH of 4.15. The scans 2 and 3 are again shown in Figure 2b on an expanded scale. These results are consistent with the results in Figure 1. However, a shoulder cathodic peak around -0.25 V was also seen in this figure which was masked in Figure 1 due to the higher current at higher pH. The peak was more obvious during the first scan, as shown more clearly in Figure 2c when the scan was carried out in the potential range 0 to -0.5V.



**Figure 2.** a) Cyclic voltammetry of 0.014 M  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ , 0.50M  $\text{CH}_3\text{COONH}_4$ , 1.73 M  $\text{CH}_3\text{COOH}$ , pH 4.15; potential scan 0 to -1 V and back, a, 1) scan 1, 2) scan 2, 3) scan 3; b, expanded scale for scans 2 and 3 and c, potential scan 0 to -0.5 V and back, 1) scan 1, 2) scan 2, 3) scan 3



**Figure 3** Cyclic voltammetry of 0.014 M  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ , 0.50M  $\text{CH}_3\text{COONH}_4$ , 1.73 M  $\text{CH}_3\text{COOH}$ , pH 4.15; potential scan 0 to -1 V and back, a, The numbers indicate the scan number; b, expanded scale for scans 3, 6, and 10

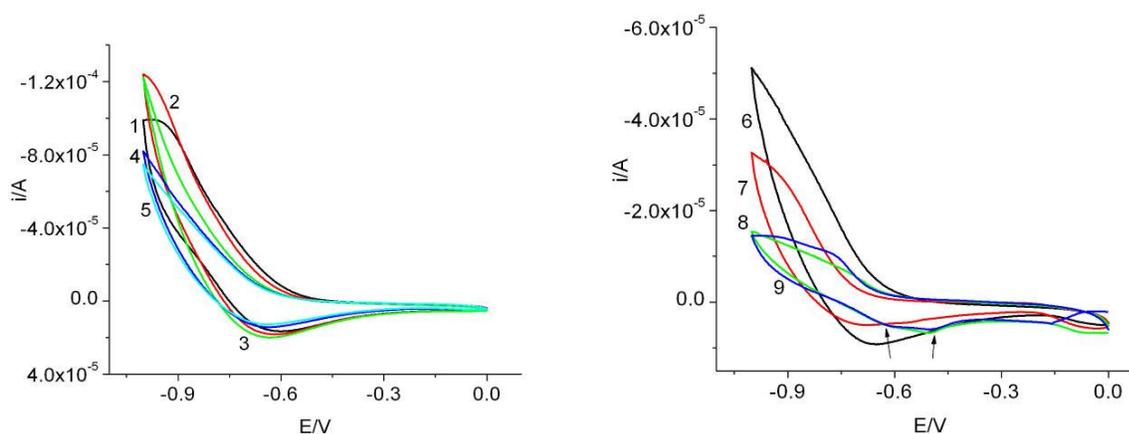
These results, the shoulders of the two oxidation peaks and two cathodic peaks with the more negative one around  $-0.8\text{V}$  dominating the current, could indicate the involvement of more than one redox process in the self-assembly process of the formation of Müller's 'Mo<sub>132</sub>' cluster.

The results of increasing the number of scans to 10 at the total acetate concentration of 2.23 M and pH 4.15 are shown in Figure 3. From these figures, it was evident that there were two cathodic and two anodic processes taking place during the scan. The cathodic process at about  $-0.25\text{V}$  was the most sensitive and could mostly be observed during the first scan.

A comparison of the data in Figures 1, 2, and 3 suggested that the self-assembly process could be detected in solutions below pH 4.5 and at a total acetate/acetic acid concentration above 1.5 M.

In Figure 4, the cyclic voltammetric data at nearly the same pH of around 4.2 but with varying concentrations of total acetate/acetic acid are given. The double anodic peaks, characteristic of Müller's 'Mo<sub>132</sub>' cluster, began to appear at a total acetate/acetic acid concentration of greater than 1.30 M (see curves 7, 8, and 9 in Figure 4).

It is evident that the pH value as well as the total acetate/acetic acid concentration are critical factors that influence the self-assembly process of Müller's 'Mo<sub>132</sub>' cluster. Our data confirm the suggestion that "the equilibria (the dynamics of aggregation reactions) are mostly characterized by the degree of acidity" [21].



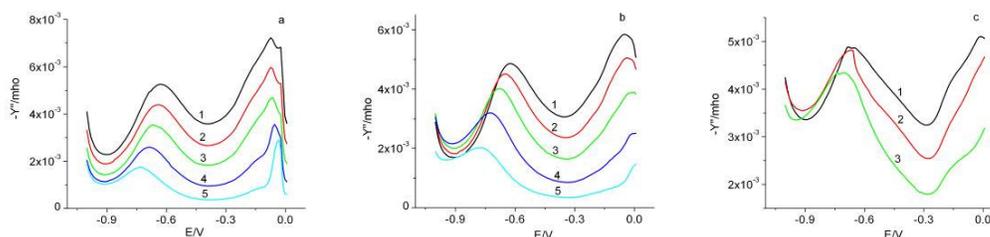
**Figure 4.** Cyclic voltammetry of 0.014 M  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  with 1) 0.0 M  $\text{CH}_3\text{COONH}_4$ , 0.04 M  $\text{CH}_3\text{COOH}$ , pH 4.21; 2) 0.02 M  $\text{CH}_3\text{COONH}_4$ , 0.06 M  $\text{CH}_3\text{COOH}$ , pH 4.26; 3) 0.10 M  $\text{CH}_3\text{COONH}_4$ , 0.14 M  $\text{CH}_3\text{COOH}$ , pH 4.36; 4) 0.15 M  $\text{CH}_3\text{COONH}_4$ , 0.21 M  $\text{CH}_3\text{COOH}$ , pH 4.36; 5) 0.20 M  $\text{CH}_3\text{COONH}_4$ , 0.28 M  $\text{CH}_3\text{COOH}$ , pH 4.28; 6) 0.30 M  $\text{CH}_3\text{COONH}_4$ , 0.44 M  $\text{CH}_3\text{COOH}$ , pH 4.35; 7) 0.52 M  $\text{CH}_3\text{COONH}_4$ , 0.80 M  $\text{CH}_3\text{COOH}$ , pH 4.54; 8) 0.40 M  $\text{CH}_3\text{COONH}_4$ , 1.13 M  $\text{CH}_3\text{COOH}$ , pH 4.17; 9) 0.40 M  $\text{CH}_3\text{COONH}_4$ , 1.6 M  $\text{CH}_3\text{COOH}$ , pH 4.00

### 3.2. Admittance

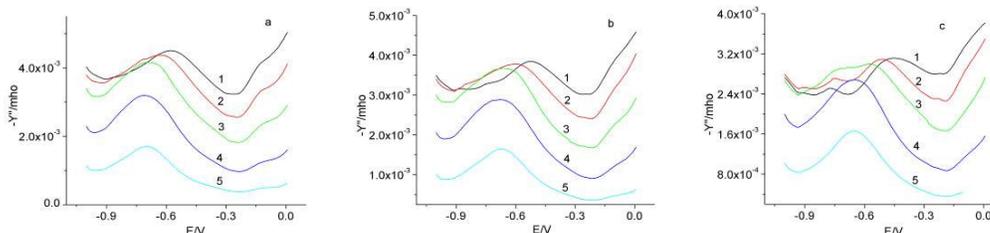
The relationship between admittance ( $Y$ ) and impedance ( $Z$ ) is as follows.  $Y \equiv Z^{-1} \equiv Y' + jY''$ . Admittance-plane plotting for the determination of accurate conductivity of solid electrolytes [25] was first introduced by Bauerle in 1969. We have explored this plot extensively and have discovered that this technique is a powerful tool for understanding solute-solvent interactions near the electrode double

layer [22-24, 26-31] and may be used for monitoring the self-assembly process of Keplerate-type clusters.

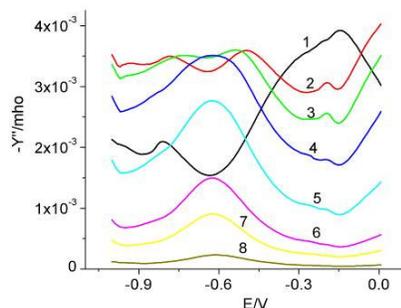
The admittance data for 0.014 M ammonium molybdate and a total acetate/acetic acid concentration of 2.0 M but differing pH are shown in Figures 5 and 6. Figure 7 also includes admittance data for the same ammonium molybdate concentration but with a total acetate/acetic acid concentration of 2.55 M, a concentration similar to that used for the synthesis of Müller's 'Mo<sub>132</sub>' cluster [6].



**Figure 5.** Admittance of 0.014 M  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  at 1) 1000 Hz 2) 750 Hz 3) 500 Hz 4) 250 Hz 5) 100 Hz; a) 2.0 M  $\text{CH}_3\text{COONH}_4$ , 0.0 M  $\text{CH}_3\text{COOH}$ , pH 6.23; b) 1.6 M  $\text{CH}_3\text{COONH}_4$ , 0.4 M  $\text{CH}_3\text{COOH}$ , pH 5.57; c) 1.2 M  $\text{CH}_3\text{COONH}_4$ , 0.8 M  $\text{CH}_3\text{COOH}$ , pH 5.06



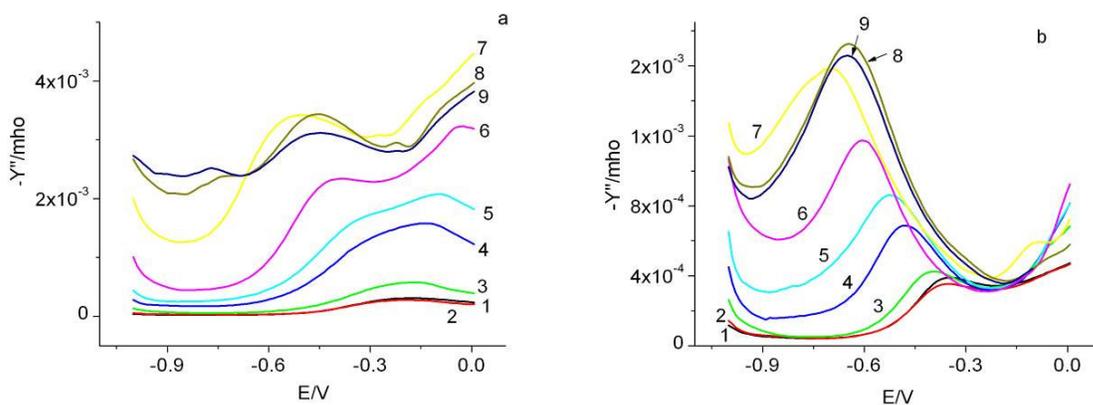
**Figure 6.** Admittance of 0.014 M  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  at 1) 1000 Hz 2) 750 Hz 3) 500 Hz 4) 250 Hz 5) 100 Hz; a) 0.8 M  $\text{CH}_3\text{COONH}_4$ , 1.2 M  $\text{CH}_3\text{COOH}$ , pH 4.62; b) 0.6 M  $\text{CH}_3\text{COONH}_4$ , 1.4 M  $\text{CH}_3\text{COOH}$ , pH 4.36; c) 0.4 M  $\text{CH}_3\text{COONH}_4$ , 1.6 M  $\text{CH}_3\text{COOH}$ , pH 4.00.



**Figure 7.** Admittance of 0.014 M  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ , 0.47 M  $\text{CH}_3\text{COONH}_4$ , 2.08 M  $\text{CH}_3\text{COOH}$ , pH 3.84 1) 5000 Hz 2) 1000 Hz 3) 750 Hz 4) 500 Hz 5) 250 Hz 6) 100 Hz 7) 50 Hz 8) 10 Hz

For a constant total concentration of acetate/acetic acid, a slight cathodic shift in the peak admittance was observed around  $-0.7$  V with decreasing frequencies. On the other hand, when the pH value was lowered, there was a slight anodic shift in the admittance maximum. The cathodic shift on decreasing frequencies was somewhat similar to that observed with polyoxomolybdate without any acetate/acetic acid. We had attributed the anodic shift on lowering the pH as due to the influence of condensation of molybdate to form hepta and octamolybdates and their protonated forms and the cathodic shift at lower frequencies due to the orientation effects of water on the protonated species at or near the double layer [22]. At  $\text{pH} = 4.36$ , we observed the formation of the double peak in admittance which was similar to that observed by us for Müller's 'Mo<sub>132</sub>' cluster [24]. The formation of these double peaks became more pronounced at  $\text{pH} = 4.00$ , as seen in Figure 6c, and was still more obvious at  $\text{pH} = 3.84$  and a total acetate/acetic acid concentration of 2.55 M, the one used to synthesize Müller's 'Mo<sub>132</sub>' cluster.

In these measurements the only reduction taking place was due to the electrochemical reduction during the scan and in that sense we were only making a very minute amount of Müller's 'Mo<sub>132</sub>' cluster. These data clearly indicate the need to control the pH value precisely for obtaining the Müller's 'Mo<sub>132</sub>' cluster.

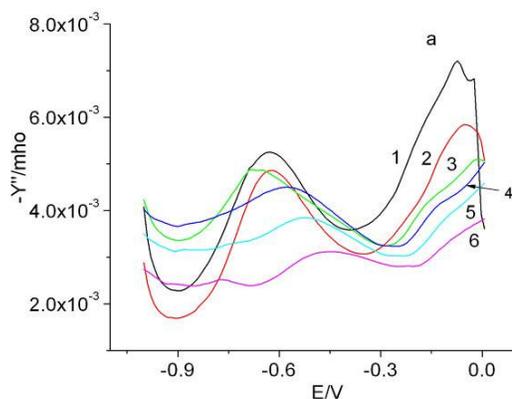


**Figure 8.** Admittance comparison at (a) 1000 Hz and (b) 100 Hz for 0.014 M  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  with 1) 0.0 M  $\text{CH}_3\text{COONH}_4$ , 0.04 M  $\text{CH}_3\text{COOH}$ ,  $\text{pH} 4.21$ ; 2) 0.02 M  $\text{CH}_3\text{COONH}_4$ , 0.06 M  $\text{CH}_3\text{COOH}$ ,  $\text{pH} 4.26$ ; 3) 0.10 M  $\text{CH}_3\text{COONH}_4$ , 0.14 M  $\text{CH}_3\text{COOH}$ ,  $\text{pH} 4.36$ ; 4) 0.15 M  $\text{CH}_3\text{COONH}_4$ , 0.21 M  $\text{CH}_3\text{COOH}$ ,  $\text{pH} 4.36$ ; 5) 0.20 M  $\text{CH}_3\text{COONH}_4$ , 0.28 M  $\text{CH}_3\text{COOH}$ ,  $\text{pH} 4.28$ ; 6) 0.30 M  $\text{CH}_3\text{COONH}_4$ , 0.44 M  $\text{CH}_3\text{COOH}$ ,  $\text{pH} 4.35$ ; 7) 0.52 M  $\text{CH}_3\text{COONH}_4$ , 0.80 M  $\text{CH}_3\text{COOH}$ ,  $\text{pH} 4.54$ ; 8) 0.40 M  $\text{CH}_3\text{COONH}_4$ , 1.13 M  $\text{CH}_3\text{COOH}$ ,  $\text{pH} 4.17$ ; 9) 0.40 M  $\text{CH}_3\text{COONH}_4$ , 1.6 M  $\text{CH}_3\text{COOH}$ ,  $\text{pH} 4.00$

In Figure 8, the admittance data at 1000 Hz (Left) and at 100 Hz (Right) are compared as a function of acetate/acetic acid concentration but at nearly a constant pH value of around 4.3. The results clearly indicate that we need a critical total acetate/acetic acid concentration of at least 1.5 M for the formation of Müller's 'Mo<sub>132</sub>' cluster (curves 8, 9 in Figure 8).

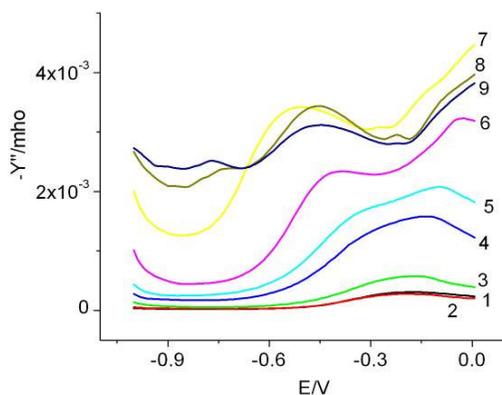
To have a comparative view of all the data in Figures 5 and 6, the data at 1000 Hz are plotted as a function of pH but at a total constant concentration of acetate/acetic acid and the results are shown

in Figure 9. It is clear that the appearance of the double admittance maxima were observed only at pH 4.36 and below. This observation is also consistent with the cyclic voltammetric data.



**Figure 9.** Admittance comparison at 1000Hz for 0.014 M  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  with 1) 2.0 M  $\text{CH}_3\text{COONH}_4$ , 0.0 M  $\text{CH}_3\text{COOH}$ , pH 6.23; 2) 1.6 M  $\text{CH}_3\text{COONH}_4$ , 0.4 M  $\text{CH}_3\text{COOH}$ , pH 5.57; 3) 1.2 M  $\text{CH}_3\text{COONH}_4$ , 0.8 M  $\text{CH}_3\text{COOH}$ , pH 5.06; 4) 0.8 M  $\text{CH}_3\text{COONH}_4$ , 1.2 M  $\text{CH}_3\text{COOH}$ , pH 4.62; 5) 0.6 M  $\text{CH}_3\text{COONH}_4$ , 1.4 M  $\text{CH}_3\text{COOH}$ , pH 4.36; 6) 0.4 M  $\text{CH}_3\text{COONH}_4$ , 1.6 M  $\text{CH}_3\text{COOH}$ , pH 4.00

The admittance data at nearly the same pH but varying concentrations of total acetate/acetic acid concentrations are compared at 100 Hz and these are given in Figure 10. The results again clearly indicated that the self-assembly process of Müller's 'Mo<sub>132</sub>' cluster could only occur at fairly high concentrations of total acetate/acetic acid of 1.5 M.



**Figure 10.** Admittance comparison at 100Hz for 0.014 M  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  with 1) 0.0 M  $\text{CH}_3\text{COONH}_4$ , 0.04 M  $\text{CH}_3\text{COOH}$ , pH 4.21; 2) 0.02 M  $\text{CH}_3\text{COONH}_4$ , 0.06 M  $\text{CH}_3\text{COOH}$ , pH 4.26; 3) 0.10 M  $\text{CH}_3\text{COONH}_4$ , 0.14 M  $\text{CH}_3\text{COOH}$ , pH 4.36; 4) 0.15 M  $\text{CH}_3\text{COONH}_4$ , 0.21 M  $\text{CH}_3\text{COOH}$ , pH 4.36; 5) 0.20 M  $\text{CH}_3\text{COONH}_4$ , 0.28 M  $\text{CH}_3\text{COOH}$ , pH 4.28; 6) 0.30 M  $\text{CH}_3\text{COONH}_4$ , 0.44 M  $\text{CH}_3\text{COOH}$ , pH 4.35; 7) 0.52 M  $\text{CH}_3\text{COONH}_4$ , 0.80 M  $\text{CH}_3\text{COOH}$ , pH 4.54; 8) 0.40 M  $\text{CH}_3\text{COONH}_4$ , 1.13 M  $\text{CH}_3\text{COOH}$ , pH 4.17; 9) 0.40 M  $\text{CH}_3\text{COONH}_4$ , 1.6 M  $\text{CH}_3\text{COOH}$ , pH 4.00

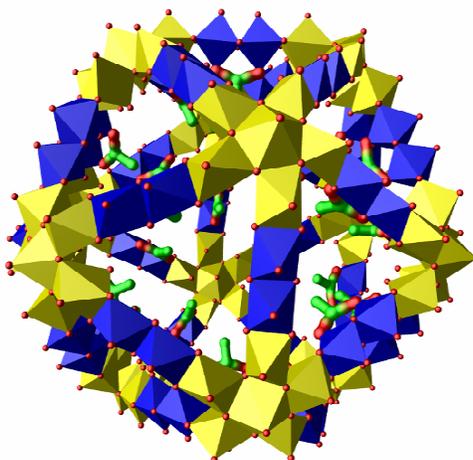
These results obtained by varying the pH values and at a fixed high concentration of total acetate/acetic acid and by varying the total acetate/acetic acid concentration at nearly the same pH value clearly demonstrated the critical need to control both the pH value and the total acetate/acetic acid concentration for optimizing the formation of Müller's 'Mo<sub>132</sub>' cluster. It is not clear from the literature how this optimum concentration and pH were arrived at. However, our data indicated that we could utilize the techniques of cyclic voltammetry, and even more so, of admittance to monitor the self-assembly process and to determine the optimum acetate/acetic acid concentration and the pH value.

During admittance measurements, the potential was changed gradually from -1.0V to +0.5V. During this process the orientation of the water molecules could change from one or two hydrogens pointing towards mercury to oxygen pointing towards mercury. Also the free positively charged ammonium ions would be pointing towards mercury during the scan at negative potentials and the negatively charged acetate ions pointing towards mercury during the scans at positive potentials. This change-over may be carried out cooperatively through ion pair formation between ammonium ions and acetate ions with or without a water molecule in between the ions [29]. The shift from hydrogen to oxygen as well as from ammonium ions to acetate ions pointing towards the electrode could be gradual and should be decided by the changes in the scanning potential. Moreover, in the extreme anodic region, one should consider the passivation of mercury and the exact potential at which passivation begins to appear could depend on the nature of the ions and their concentrations in solution.

It is known that the electrolyte concentration at or near the double layer is about ten times that of the bulk concentration [32]. To understand the admittance data of simple electrolytes, such as NaCl, we had introduced a new type of ion-pair formation, "potential induced water-structure enforced ion-pairs".

Along with the changes mentioned above, one should also consider the orientation changes of water molecules near the highly charged (negatively) polyoxomolybdate with or without coordinating acetate ligands. Significant amounts of ions, such as Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup>, HMo<sub>7</sub>O<sub>24</sub><sup>5-</sup>, H<sub>2</sub>Mo<sub>7</sub>O<sub>24</sub><sup>4-</sup>, Mo<sub>8</sub>O<sub>26</sub><sup>4-</sup>, HMo<sub>8</sub>O<sub>26</sub><sup>3-</sup>, and H<sub>2</sub>Mo<sub>8</sub>O<sub>26</sub><sup>2-</sup>, exist at the pH of our measurements along with possible acetate complexes of these species. Also under similar conditions, complexes such as Na<sub>10</sub>[H<sub>4</sub>Mo<sub>18</sub>O<sub>56</sub>(CH<sub>3</sub>COO)<sub>2</sub>] x ca. 36 H<sub>2</sub>O x 3 CH<sub>3</sub>COOH, (NH<sub>4</sub>)<sub>12</sub>Na<sub>12</sub>[Mo<sub>40</sub>O<sub>128</sub>] x ca. 70 H<sub>2</sub>O, (NH<sub>4</sub>)<sub>12</sub>Na<sub>20</sub>[H<sub>4</sub>Mo<sub>54</sub>O<sub>168</sub>(CH<sub>3</sub>COO)<sub>4</sub>] x ca. 64 H<sub>2</sub>O, Na<sub>32</sub>[H<sub>4</sub>Mo<sub>54</sub>O<sub>168</sub>(CH<sub>3</sub>COO)<sub>4</sub>] x ca. 128 H<sub>2</sub>O, Na<sub>32</sub>[H<sub>4</sub>Mo<sub>54</sub>O<sub>168</sub>(CH<sub>3</sub>COO)<sub>4</sub>] x ca. 98 H<sub>2</sub>O, [Mo<sub>48</sub>O<sub>128</sub>]<sup>28-</sup>, [Mo<sub>116</sub>O<sub>331</sub>](CH<sub>3</sub>COO)<sub>30</sub>(H<sub>2</sub>O)<sub>56</sub><sup>46-</sup> and (NH<sub>4</sub>)<sub>32</sub>[Mo<sup>VI</sup><sub>110</sub> Mo<sup>V</sup><sub>28</sub>O<sub>416</sub>H<sub>6</sub>(H<sub>2</sub>O)<sub>58</sub> (CH<sub>3</sub>COO)<sub>6</sub>] x H<sub>2</sub>O (x ~ 250) have been prepared [21]. Even if we were to ignore all these ions and complexes and to consider only the Müller's 'Mo<sub>132</sub>' cluster, we should consider the following additional complications arising from the orientation changes of water molecules inside the spherical polyoxomolybdate, as shown in Figure 11. The building block of this molecule is {Mo<sup>V</sup><sub>2</sub>}<sub>30</sub>{(Mo<sup>VI</sup>)Mo<sup>VI</sup><sub>5</sub>}<sub>12</sub>. It is formulated as [{Mo<sup>V</sup><sub>2</sub>O<sub>4</sub>(CH<sub>3</sub>COO)]<sub>30</sub>{(Mo)Mo<sub>5</sub>O<sub>21</sub>(H<sub>2</sub>O)<sub>6</sub>}<sub>12</sub><sup>42-</sup>. In this molecule, there are 132 oxygen atoms of the type M=O outside and pointing away from the sphere, 72 oxygen atoms from water molecules bonded to the Mo inside the sphere and pointing towards the center of the sphere, and the rest of the oxygen atoms on the surface of the sphere, with an overall charge of - 42 for the ion. Also the existence of several disordered water molecules inside the sphere has been suggested [6]. Thus, the

competition for the water orientation between the negatively charged mercury and the ion must be considerable. The interaction may be cooperative with one hydrogen of the water oriented towards the negatively charged mercury and the other one towards the oxygen of the M=O or the surface oxygen. During admittance measurements, when the voltage of the electrode is changed from negative to less negative and finally to zero, the orientation of water molecules should also change correspondingly in all the environment mentioned above, whether it is free water molecules near the double layer or bound water molecule of hydration around the ion or inside the spherical cluster. With such a large negative charge around the polyoxomolybdate, there must be competing influences of orientation of water towards the electrode or the surface charge of the spherical ion.



**Figure 11.** Polyhedral representation of  $(\text{NH}_4)_{42}[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}] \cdot \text{ca.}300\text{H}_2\text{O} \cdot \text{ca.}10\text{CH}_3\text{COONH}_4$  [6].

The admittance data at higher concentrations of acetic acid/acetate with a pH value of around 4.2 indicated that there were two admittance maxima in the frequency range 1000-500 Hz and thereafter there was only one maximum. This finding was consistent with the observations we had reported earlier [24]. While the admittance maximum around -0.7 V shifted to *less* negative potentials with decreasing frequency from 1000 to 500 Hz, the admittance maximum around -0.1V shifted to *more* negative potentials with decreasing frequency from 1000 to 500 Hz. Thus, at frequencies below 500 Hz, the admittance maxima merged somewhat and exhibited only one maximum. We had attributed the admittance maximum near -0.1 V to that of the pure molybdates with or without acetate, the second admittance maxima around - 0.7 V to the self-assembled Müller's 'Mo<sub>132</sub>' cluster. Inside the sphere, some water molecules were coordinated with the molybdenum atoms so that the sheet-like {Mo<sup>VI</sup><sub>6</sub>} fragments could give the water molecules nearby two different orientations. Thus, the two peaks could probably come from the two sides of the {Mo<sup>VI</sup><sub>6</sub>} fragments. The admittance maximum at least negative potentials had been attributed to the oxygen double-bonded with the molybdenum and had similar tendency on increasing frequency with the [Mo<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> anions. The admittance maximum at

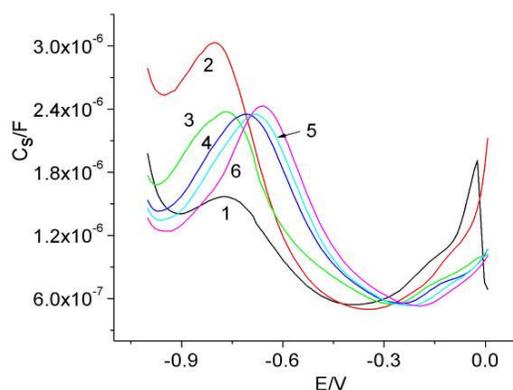
the most negative potential could be attributed from the hydrogen bonding effects of water molecules with the coordinated water molecules of molybdenum on the inside surface of the  $\{\text{Mo}^{\text{VI}}_6\}$  fragments and thus accounting for the differences in the observed behavior of shifts of admittance maxima in opposite directions with decreasing frequency.

Our recent data with L-cysteine and molybdate-L-cysteine have indicated that different orientation effects of water near oppositely charged ions such as  $\text{Na}^+$  and  $-\text{COO}^-$  as well as  $\text{Na}^+$  and  $-\text{S}^-$  can give rise to opposing cathodic and anodic shifts in admittance on decreasing frequency. A similar effect, observed earlier, was attributed to the effects of water inside and outside the Keplerate type cluster [24]. However, close proximity of opposing charges such as  $\text{NH}_4^+$  and acetate of the Müller's 'Mo<sub>132</sub>' cluster or  $\text{NH}_4^+$  and the oxygen bonded to the molybdenum in the Müller's 'Mo<sub>132</sub>' cluster could account for these two opposing cathodic and anodic shifts in admittance on decreasing frequency.

### 3.3. Double layer capacitance

Double layer capacitance,  $C_{\text{dl}}$ , is generally obtained from differential capacitance measurements when ohmic resistance is compensated. In such a case,  $C_{\text{dl}}$  should be independent of frequency.

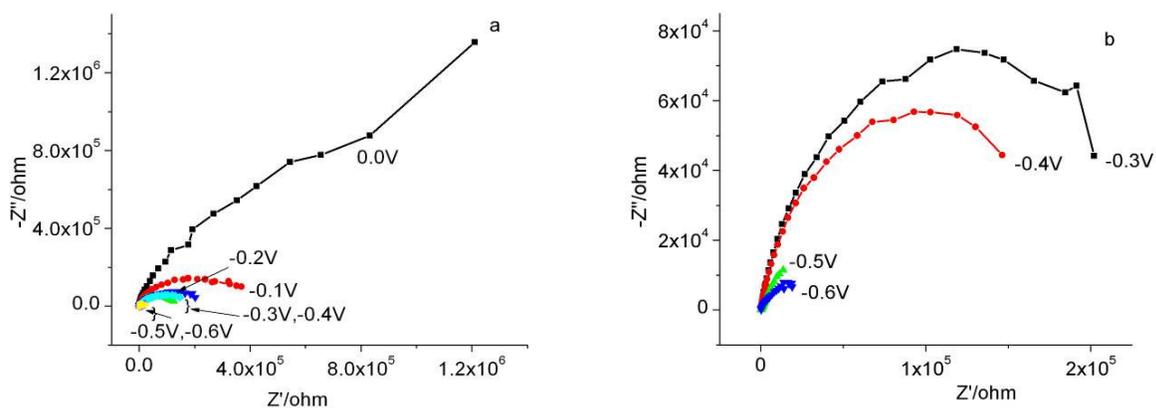
The capacitance data at 1000 Hz for 0.014 M  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  as a function of pH but fixed total concentration of acetate/acetic acid of 2.0 M are shown in Figure 12. These data indicate a major capacitance peak at highly cathodic potentials and a small one around -0.25 V. The result is consistent with that observed in the cyclic voltammetric data. The slight shift in the capacitance peak to less cathodic potentials with decreasing pH is consistent with that observed in admittance data. However there was only an extremely small shoulder and a good peak for the capacitance data corresponding to the two observed admittance maxima.



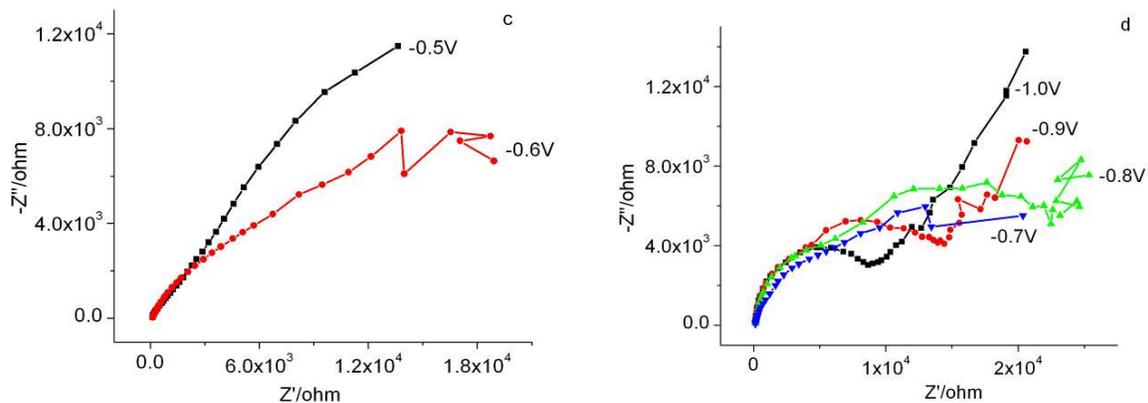
**Figure 12.** Capacitance comparison at 1000Hz for 0.014 M  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  with 1) 2.0 M  $\text{CH}_3\text{COONH}_4$ , 0.0 M  $\text{CH}_3\text{COOH}$ , pH 6.23; 2) 1.6 M  $\text{CH}_3\text{COONH}_4$ , 0.4 M  $\text{CH}_3\text{COOH}$ , pH 5.57; 3) 1.2 M  $\text{CH}_3\text{COONH}_4$ , 0.8 M  $\text{CH}_3\text{COOH}$ , pH 5.06; 4) 0.8 M  $\text{CH}_3\text{COONH}_4$ , 1.2 M  $\text{CH}_3\text{COOH}$ , pH 4.62; 5) 0.6 M  $\text{CH}_3\text{COONH}_4$ , 1.4 M  $\text{CH}_3\text{COOH}$ , pH 4.36; 6) 0.4 M  $\text{CH}_3\text{COONH}_4$ , 1.6 M  $\text{CH}_3\text{COOH}$ , pH 4.00

## 3.4. Nyquist and Bode Plots

In order to complete the characterization of the self-assembly process of Müller's 'Mo<sub>132</sub>' cluster, we have investigated the impedance data. The Nyquist plots for a solution of 0.014 M (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>, 0.50M CH<sub>3</sub>COONH<sub>4</sub>, 1.73 M CH<sub>3</sub>COOH, pH 4.15 at different potentials from 0 to -1.0 V are given in Figures 13 and 14 and the Bode plots are given in Figures 15 and 16. For the sake of clarity, the modulus of impedance and phase angle are plotted separately.

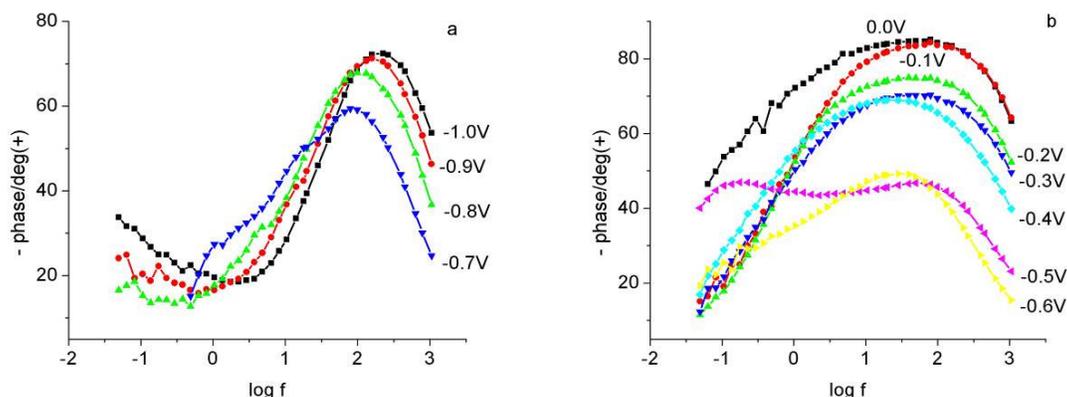


**Figure 13.** Nyquist plots for 0.014M (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>, 0.50M CH<sub>3</sub>COONH<sub>4</sub>, 1.73 M CH<sub>3</sub>COOH, pH 4.15 at different potentials

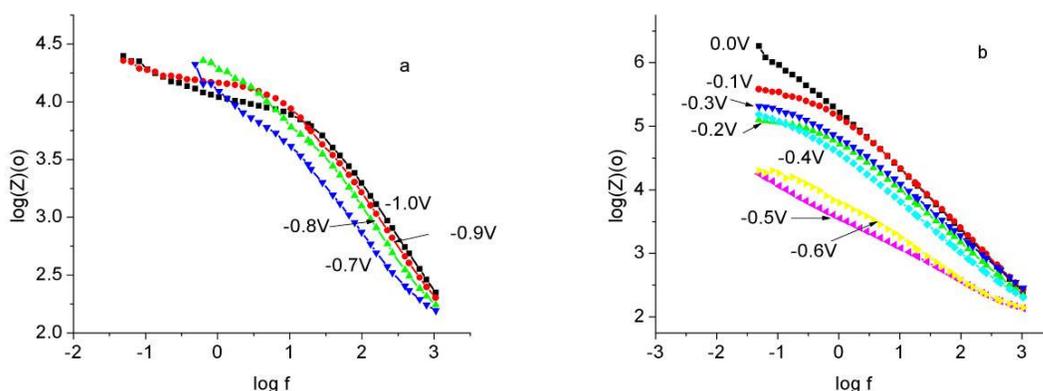


**Figure 14.** Nyquist plots for 0.014M (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>, 0.50M CH<sub>3</sub>COONH<sub>4</sub>, 1.73 M CH<sub>3</sub>COOH, pH 4.15 at different potentials

With increasing cathodic potential from 0 V, the impedance becomes less and less (Figure 13a). For the sake of continuity and clarity the data from Figure 13a are expanded and shown in Figure 13 b and 14c.



**Figure 15.** Bode plots (phase angle) for 0.014M  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ , 0.50M  $\text{CH}_3\text{COONH}_4$ , 1.73 M  $\text{CH}_3\text{COOH}$ , pH 4.15 at different potentials



**Figure 16.** Bode plots (impedance modulus) for 0.014M  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ , 0.50M  $\text{CH}_3\text{COONH}_4$ , 1.73 M  $\text{CH}_3\text{COOH}$ , pH 4.15 at different potentials

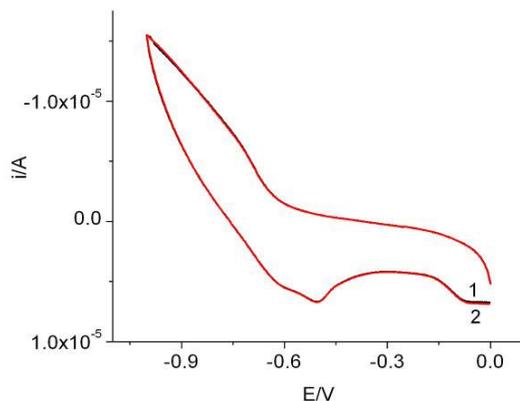
A close examination of the phase angle data showed two relaxation phenomena at potentials close to -0.5 and -0.6 V. This is consistent with the cyclic voltammetric and admittance data.

The impedance data in Figures 13-16 suggest that Nyquist and Bode plots are not powerful enough to monitor the assembly process of Keplerate-type clusters when compared with that of cyclic voltammetry, admittance and capacitance.

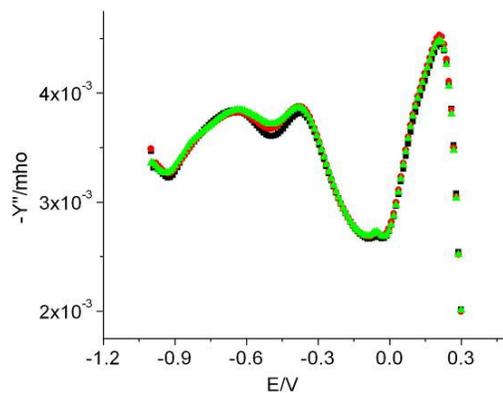
### 3.5. Stability of experimental data

We have checked the reproducibility of the cyclic voltammetry, admittance, and impedance data and the results of are shown in Figure 17 a, 17b and 17c. Considering the complexity of the system, the reproducibility of the data is excellent. We had pointed out earlier that one could manipulate the visual observation of the scatter by carefully selecting the type of data for reproducibility [18]. The purpose of our experiment was to demonstrate that the two anodic peaks as

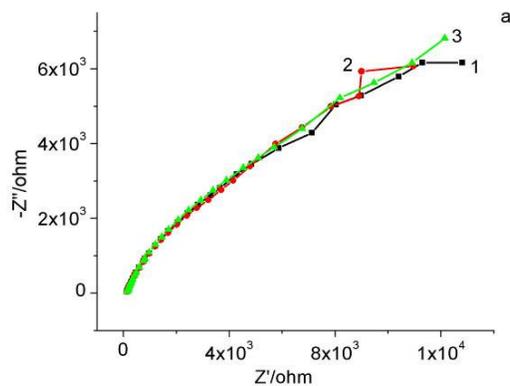
well as two admittance maxima observed for the self-assembled Müller's 'Mo<sub>132</sub>' cluster were real and reproducible.



**Figure 17a.** Cyclic voltammetry, reproducibility of data for 0.014M (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>, 0.40M CH<sub>3</sub>COONH<sub>4</sub>, 1.13 M CH<sub>3</sub>COOH, pH 4.17, two sets of data



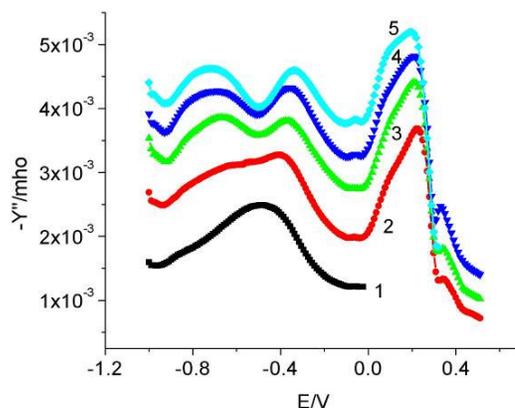
**Figure 17b.** Admittance, reproducibility of data for 0.014M (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>, 0.50M CH<sub>3</sub>COONH<sub>4</sub>, 2.02 M CH<sub>3</sub>COOH, pH 4.05 at 1000Hz; three sets of data



**Figure 17c.** Nyquist plot, reproducibility of data for 0.014M (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>, 0.50M CH<sub>3</sub>COONH<sub>4</sub>, 1.73 M CH<sub>3</sub>COOH, pH 4.15 at -0.6V; 1 and 2 are data from same solution and data for 3 are from another stock solution of another day.

### 3.6. Surface area

There are several advantages of using mercury as a working electrode. First, it is easy to have a fresh clean surface of mercury for each experiment. Also the surface area of the mercury can be easily controlled by use of the dispense button in the 303A electrode system. We have studied the influence of surface area on the electronic properties of the self-assembled Müller's 'Mo<sub>132</sub>' cluster and the results are shown in Figure 18.



**Figure 18.** Influence of surface area on the impedance of 1.0 M NaCl at 0.087 V. Surface area in cm<sup>2</sup>, 1) 0.011 2) 0.017 3) 0.022 4) 0.027 5) 0.031

It is interesting to note that the full admittance behavior was not obvious with very low surface area. However, there was consistent behavior with increased surface area. Further increase in surface area did not change the nature of the admittance curve but only increased the absolute value of the admittance.

### 3.7. Color oscillations

During the electrochemical investigation of isopolyoxomolybdates as a function of pH using frequency response analysis, we have observed that the color of the mercury drop often changed, depending on the pH, or potential or frequency. Quite often the mercury drop retained the color of the adsorbed species even after allowing the drop to fall into the bulk solution. During admittance and impedance measurements, the color changed at least 4 times in the beginning from yellow to gold to copper to blue and finally stayed as dark blue on the mercury. We had briefly described the nature of these oscillations and similar color variations in other systems [22].

We have observed similar color oscillations above pH 4.5 in the present system but not below pH 4.3 at constant high concentrations of acetate/acetic acid. Also there was color oscillation around pH 4.2 when the acetate/acetic acid concentration was less than 1.3 M. But we could not observe any color oscillation when the pH as well as total acetate/acetic acid concentration were close to that used for the self-assembly of Müller's 'Mo<sub>132</sub>' cluster. However during admittance and cyclic voltammetry measurements, the mercury retained the copper or brass color at the end of the scan in solutions with

high acetate/acetic acid buffer and pH = 4.15. The different cluster anions of acetate with mixed-valent polyoxomolybdate containing 18, 40, and 54 Mo atoms had colors of red and red lozenge [21].

#### 4. CONCLUSIONS

Cyclic voltammetry and electrochemical admittance and capacitance measurements were used to characterize the self-assembly process of the polyoxomolybdate, Müller's 'Mo<sub>132</sub>' cluster or (NH<sub>4</sub>)<sub>42</sub>[Mo<sup>VI</sup><sub>72</sub>Mo<sup>V</sup><sub>60</sub>O<sub>372</sub>(CH<sub>3</sub>COO)<sub>30</sub>(H<sub>2</sub>O)<sub>72</sub>].ca.300H<sub>2</sub>O.ca.10CH<sub>3</sub>COONH<sub>4</sub>). Cyclic voltammetry indicated that the self-assembly process could be detected in solutions below pH = 4.5 and at total acetate/acetic acid concentrations of above 1.5 M. Electrochemical admittance data showed the molybdenum species in the CH<sub>3</sub>COONH<sub>4</sub>-CH<sub>3</sub>COOH buffer resembled the behavior of Müller's 'Mo<sub>132</sub>' cluster only at acetate buffer concentrations above 1.5 M and pH around 4.3 and lower. The behavior of molybdate species at higher pH values resembled those of non-protonated and/or protonated [Mo<sub>7</sub>O<sub>24</sub>]<sup>6-</sup> and [Mo<sub>8</sub>O<sub>26</sub>]<sup>4+</sup> anions. Detailed analysis of admittance as a function of pH and acetate/acetic acid concentration supported the existence of the molybdate species related to the {(Mo<sup>VI</sup>)Mo<sup>VI</sup><sub>5</sub>} fragment which is one of the components of Müller's 'Mo<sub>132</sub>' cluster. Admittance and capacitance results on the self-assembly process were more vivid than those from cyclic voltammetry. These data suggested the critical need to control the pH value and the acetate/acetic acid concentration to control the self-assembly process. We conclude with the suggestion that optimum concentrations needed for the self assembly process of large Keplerate-type structures could be monitored systematically using admittance measurements.

#### ACKNOWLEDGEMENTS

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#### References

1. A. Müller, *Science*, 300 (2003) 749
2. M. O'Keeffe, B.G. Hyde, *Crystal Structures, I. Patterns and Symmetry*, Mineralogical Society of America, Washington DC, (1996)
3. L. Cronin, E. Diemann, A. Müller, *Inorganic Experiments*, D. Woollins, Ed., Wiley-VCH, Weinheim, Germany, 2<sup>nd</sup> ed. (2003) 340
4. A. Müller, E. Beckmann, H. Bögge, M. Schmidtman, A. Dress, *Angew. Chem. Int. Ed.*, 41 (2002) 1162
5. A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, S. Roy, A. Berkle, *Angew. Chem. Int. Ed.*, 41 (2002) 3604
6. A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, F. Peters, *Angew. Chem. Int. Ed.*, 37 (1998) 3360
7. A. Müller, V.P. Fedin, C. Kuhlmann, H. Bögge, M. Schmidtman, *Chem. Commun.*, (1999) 927
8. A. Müller, S. Roy, *Coord. Chem. Rev.*, 245 (2003) 153
9. A. Müller, P. Kogerler, A.W.M. Dress, *Coord. Chem. Rev.*, 222 (2001) 193

10. A. Müller, S.Q.N. Shah, H. Bögge, M. Schmidtman, *Nature*, 397 (1999) 48
11. A. Müller, C. Serain, *Acc. Chem. Res.*, 33 (2000) 2
12. J. Bai, A.V. Virovets, M. Scheer, *Science*, 300 (2003) 781
13. M.J. Moses, J.C. Fetting, B.W. Eichhorn, *Science*, 300 (2003) 778
14. A. Schnepf, H. Schnöckel, *Angew. Chem. Int. Ed.*, 41 (2002) 3532
15. J. Glanz, *Science*, 276 (1997) 678
16. T. Yamase, *J. Chem. Soc., Dalton Trans.*, 3055 (1991)
17. T. Yamase, E. Ishikawa, *Langmuir*, 16 (2000) 9023.
18. T. Yamase, P.V. Prokop, *Angew. Chem. Int. Ed.*, 41 (2002) 466.
19. T. Yamase, P. Prokop, Y. Arai, *J. Mol. Struct.*, 656 (2003) 107.
20. T. Yamase, Y. Yano, E. Ishikawa, *Langmuir*, 21 (2005) 7823.
21. A. Müller, C. Kuhlmann, H. Bögge, M. Schmidtman, M. Baumann, E. Krickemeyer, *Eur. J. Inorg. Chem.*, (2001) 2271
22. C.V. Krishnan, M. Garnett, B. Hsiao, B. Chu, *Int. J. Electrochem. Sci.*, 2 (2007) 29
23. C.V. Krishnan, M. Garnett, B. Chu, *Int. J. Electrochem. Sci.*, 2 (2007) 444
24. C.V. Krishnan, Q. Li, B. Chu, *Electrochimica Acta*, 53 (2007) 975
25. J. E. Bauerle, *J. Phys. Chem. Solids*, 30 (1969) 2657
26. C.V. Krishnan, M. Garnett, *Electrochim. Acta*, 51 (2006) 1541.
27. C.V. Krishnan, M. Garnett, *Int. J. Electrochem. Sci.*, 1 (2006) 215
28. C.V. Krishnan, M. Garnett, *Int. J. Electrochem. Sci.*, 1 (2006) 283
29. C.V. Krishnan, M. Garnett, B. Chu, *Int. J. Electrochem. Sci.*, 2 (2007) 958
30. C.V. Krishnan, M. Garnett, B. Chu, *Int. J. Electrochem. Sci.*, 3 (2008) 854
31. C.V. Krishnan, M. Garnett, B. Chu, *Int. J. Electrochem. Sci.*, 3 (2008) 873
32. B.E. Conway, *J. Electroanal. Chem.*, 123 (1981) 81