Influence of Charge Distribution on the Properties of Keggin- and Dawson-Type Heteropolyanions

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The cyclic voltammetric behavior of selected Keggin- and Dawson-type heteropolyanions has been studied as a function of electrolyte composition. The buffer capacity of the electrolyte is shown to be an important parameter that can be used to reveal the symmetry or dissymetry in charge distribution within each oxometalate. A fully symmetrical heteropolyanion like $[P_2W_{18}O_{62}]^{6-}$ exhibits a uniform protonability, while its α_1 and α_2 lacunary derivatives present a donor set of hard oxide ions with stepwise acid-base equilibria. The behavior of these sites is revealed readily in unbuffered or poorly buffered media at pH = 3, and is ascribed to the change in symmetry of charge distribution in the molecules. It is shown that cations other than the proton, even in very high excess, fail to give rise to the classical voltammograms of lacunary heteropolyanions. The same behavior also appears in $\alpha_2[Mo_2P_2W_{15}O_{61}]^{10-}$, $\alpha[PW_{11}O_{39}]^{7-}$, $\alpha[SiW_{11}O_{39}]^{8-}$, $[H_2P_2W_{12}O_{48}]^{12-}$, and, to a lesser extent, in $\alpha_2[Ni(H_2O)P_2W_{17}O_{61}]^{8-}$ and $\alpha_2[Zn(H_2O)P_2W_{17}O_{61}]^{8-}$. The analogy in the cyclic voltammograms of most dication-substituted heteropolyanions with those of the precursor lacunary species could thus be explained.

Introduction

Interest in the study of oxometalates remains at a high level due to their wide range of properties in several fields.[1−3] In particular, the main results from electrochemistry investigations by this group and from others, which establish unambiguously the existence of catalytic properties for heteropolyanions towards numerous chemicals in solution, have been reviewed recently.[4] New results concern the ability of one- and two-electron reduced heteropolyanions of the Keggin and Dawson series to convert quantitatively NO into N_2O in acidic aqueous media.[5] Unsubstituted and lacunary as well as transition metal cation substituted heteropolyanions of these two groups prove active for this purpose. Such achievements have stimulated our interest in the synthesis of heterometal-substituted heteropolyanions of these two families, with the aim of investigating their new electrocatalytic behavior.[6−10] Furthermore, the electrochemical characterization of these compounds reveals that most of them cannot be considered as "saturated" species and that the appropriate comparison remains between the cyclic voltammograms of the metal ion-substituted and the lacunary precursor oxometalates.[6,8−10] In the course of these comparisons, a strong sensitivity of the shapes, peak potential locations, and current intensities of the cyclic voltammograms to changes in the electrolyte was observed. On further scrutiny it was found that the influence appears to increase as the nominal charge of the heteropolyanion increases. Various lines of experimental evidence confirm the very low surface charge density, at least for symmetrical saturated Keggin- and Dawson-type heteropolyanions.[11−14] For example, a simple linear variation of the first reduction potentials of $\alpha[XW_{12}O_{40}]^{n-}$ with the anion charge is observed under conditions without protonation.[2] Extension of the preceding remarks to the corresponding lacunary species and to their first transition metal ion-substituted derivatives do not seem straightforward, possibly owing to the change in symmetry of the charge distribution in the molecules in conjunction with the increase in the overall negative charge. The lacunary heteropolyanions are known to exhibit "a donor set of hard oxide ions, while the adjacent d^0 (Mo^{VI}, W^{VI}) atoms provide acceptor orbitals".[1,15,16] In contrast, the classical symmetrical heteropolyacids like $H_6P_2W_{18}O_{62}$, $H_6Mo_3P_2W_{15}O_{62}$, $H_3PW_{12}O_{40}$, and $H_4SiW_{12}O_{40}$, which can be considered as the precursors of the species under investigation, are strong acids with a uniform acidity.[17]

The aim of the present paper is to illustrate the behavior, in cyclic voltammetry, of selected representative lacunary heteropolyanions and of the corresponding metal ion substituted species in the presence of various electrolytes.

Results

The Selection of Experimental Conditions

The following heteropolyanions were used: $\alpha[P_2W_{18}O_{62}]^{6-}$ (abbreviated as P_2W_{18}); α_1- and $\alpha_2[P_2W_{17}O_{61}]^{10-}$ (α_1- and $\alpha_2P_2W_{17}$); $\alpha[Mo_3P_2W_{15}O_{62}]^{6-}$ ($P_2W_{15}Mo_3$); α_2[Mo_2P_2-

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$W_{15}O_{61}]^{10-}$ ($\alpha_2P_2W_{15}Mo_2$); $\alpha[PW_{11}O_{39}]^{7-}$ (PW_{11}); $\alpha[SiW_{11}O_{39}]^{8-}$ (SiW_{11}); $[H_2P_2W_{12}O_{48}]^{12-}$ (P_2W_{12}); $\alpha_2[Zn(H_2O)P_2W_{17}O_{61}]^{8-}$ ($\alpha_2P_2W_{17}Zn$); $\alpha_2[Ni(H_2O)P_2W_{17}O_{61}]^{8-}$ ($\alpha_2P_2W_{17}Ni$). The preparation and characterization of these materials have already been described in detail.[6,8,9,18–21]

A priori, at least two antagonist influences due to the supporting electrolyte can be anticipated during the reduction of heteropolyanions: on the one hand, protonation and/or ion-pair formation with other cations, which might enhance the reduction kinetics; on the other hand, the anions of the electrolyte might counteract these reduction kinetics. It is desirable to maintain one of these influences constant for the study of the second one. First, sodium salts or, occasionally, lithium salts were used to maintain a constant cation concentration [M] = 0.4 M. In the cases in which the results are known, these two cations are not completely without action on the oxidized forms of several heteropolyanions; however, the stability constants of the corresponding complexes are rather small.[18] Even if a stronger association could be anticipated with the reduced forms of the heteropolyanions, the experiments described in the following pages indicate, as anticipated, that the interaction does not depend to an appreciable extent on the nature of these alkaline cations. This observation leaves room for the identification of other effects. Furthermore, the compounds under scrutiny in this work are sensitive to the concentration of protons. The corresponding saturated species react mostly by ECE- or EEC-type processes, with the C step usually being a protonation. Therefore, a constant pH = 3 value was selected throughout; in the present work we found this proton level high enough, in sulfate media, to favor the protonation of the reduced oxometalates over their ion-pairing with Na^+ or Li^+ cations, at least as far as the first redox system of the studied heteropolyanions is concerned. A detailed examination of the competition between protonation and ion-pairing of the reduced heteropolyanions is beyond the scope of this paper. Finally, our usual experimental conditions have been maintained in the present work, which is aimed first at confirming and expanding previous observations: This point essentially concerns the glassy carbon working electrode, which we have demonstrated to be suitable for the study of the electrochemical and electrocatalytic behaviors of heteropolyanions under a variety of experimental conditions.[5–10,22,23] Indeed, the present knowledge of the interfacial properties of glassy carbon is, at best, qualitative, even though several papers suggest that this electrode material could be used for kinetic studies.[11,24,25] Gold and platinum are well characterized but cannot be used throughout in experiments spanning a large potential domain in the relatively acidic media necessary for our studies.

Voltammetric Behavior of Selected Heteropolyanions in Several pH = 3 Media

Two lacunary heteropolyanions, $\alpha_2P_2W_{15}Mo_2$ and $\alpha_2P_2W_{17}$, were selected to illustrate the basic observations. Figure 1 (1A and 1B) shows the evolution of the corresponding cyclic voltammograms for $5 \cdot 10^{-4}$ M heteropolyanion in the presence of appropriate concentrations of Na_2SO_4, $NaClO_4$, $NaNO_3$, and NaCl as supporting electrolytes.

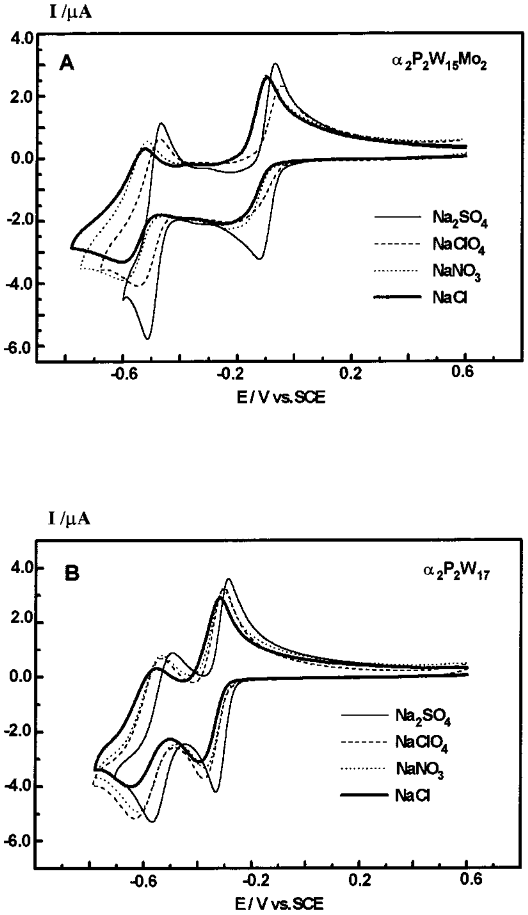

Figure 1. Cyclic voltammograms of a $5 \cdot 10^{-4}$ M solution of the relevant heteropolyanion in several pH = 3 media containing 0.4 M Na^+; scan rate: 10 mVs^{-1}; working electrode: glassy carbon

The potential domain is restricted to encompass the first two redox systems for each oxometalate. Figure 1 speaks for itself and only brief comments are necessary. However, the distortion is more marked in the cyclic voltammogram of $\alpha_2P_2W_{15}Mo_2$ than that of $\alpha_2P_2W_{17}$, even though qualitatively identical effects are observed. We note that the two waves are modified: taking the voltammogram in the sulfate medium as a reference, those in the presence of other salts show drawn out shapes, with smaller current intensities and peak potentials that are pushed in the negative direction. The concentration of Na^+ is 800 times that of the oxometalate. In this situation the ionic strength of the solution cannot be suspected to induce the observed phenomena. The nature of the anions of the supporting electrolyte is thus proposed as the relevant parameter. Furthermore, as these observations are made in the presence of a large excess of supporting electrolyte, it can be concluded that the effect of cations other than the proton is minimal in the reduction processes of these systems or largely counteracted by some anion effect. An attempt can be made to rationalize the difference in behavior between the two lacunary heteropolyanions by considering their respective basicities. The first two-electron wave for $\alpha_2P_2W_{15}Mo_2$ in the sulfate medium (taken as a reference) features Mo-centered redox processes while that for $\alpha_2P_2W_{17}$ is W-centered. A report in the literature[26] suggests the reduced Mo-substituted site to be the stronger base of the two compounds. As a consequence, protonation and/or ion-pairing are easier in Mo-substituted complexes. Correlatively, a higher sensitivity of the latter compound to possible anion effects is not expected, a situation in contrast to that actually observed. Provisionally, comparison between α_1 and $\alpha_2P_2W_{17}$ shows the two compounds to behave in exactly the same way. However, not much work was carried out with the α_1 isomer due to its known relative instability under most of the conditions used in the present investigation. Further discussion of this system is postponed until the main parameters of this study emerge clearly.

Figure 2 and Figure 3 are helpful in this issue. Figure 2 shows the observations pertaining to three other lacunary species and to a Zn-substituted Dawson-type complex in the two electrolytes that give the most contrasting behavior.

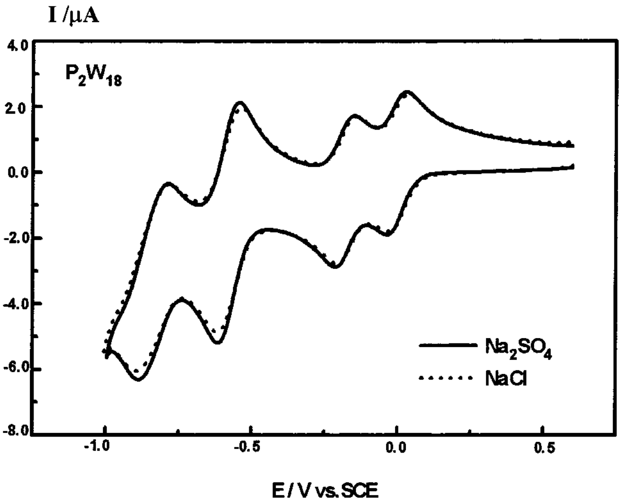

Figure 3. Cyclic voltammograms of a $5 \cdot 10^{-4}$ M $[P_2W_{18}O_{62}]^{6-}$ in two pH = 3 media containing 0.4 M Na^+; scan rate: 10 mVs^{-1}; working electrode: glassy carbon

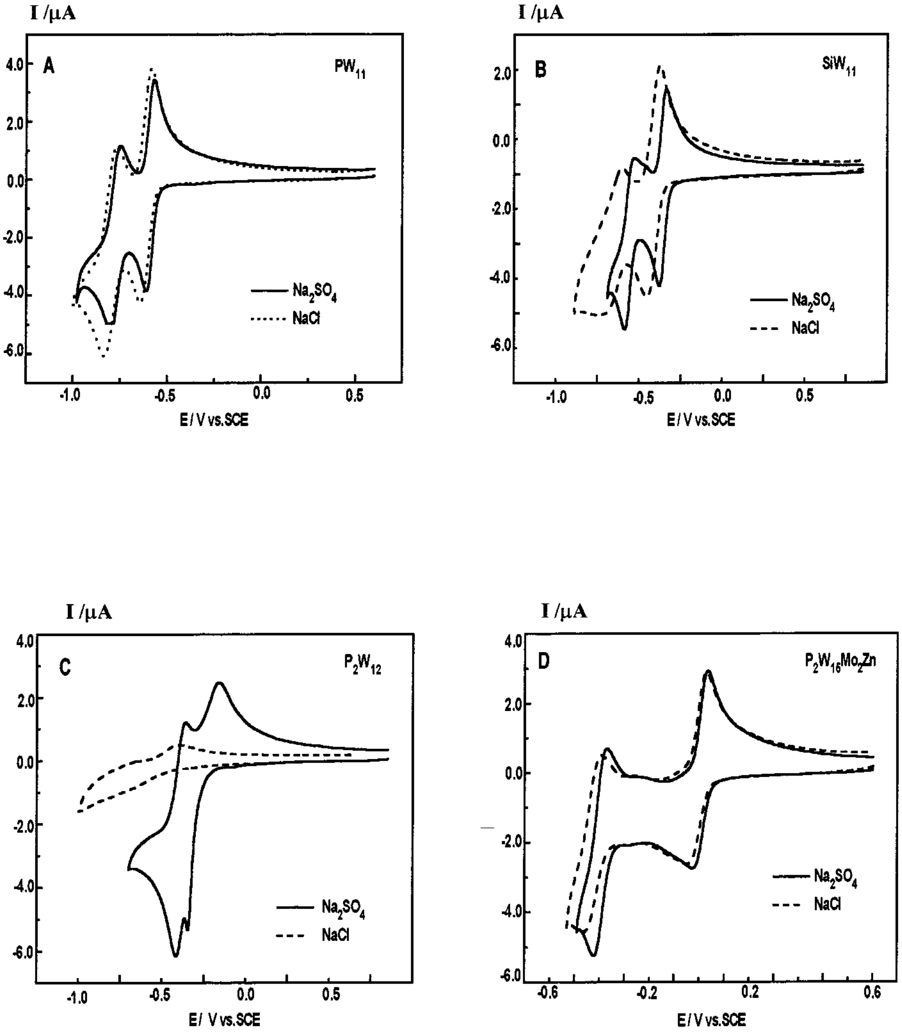

Figure 2. Cyclic voltammograms of a $5 \cdot 10^{-4}$ M solution of the relevant heteropolyanion in two pH = 3 media containing 0.4 M Na^+; scan rate: 10 mVs^{-1}; working electrode: glassy carbon

The previously observed effect also exists in this group, which contains two Keggin-type species. Even though the surface charge density varies from one component to the next, the structure of the heteropolyanion does not seem to constitute a relevant parameter. Strikingly, the intensity of the effect is greater as the nominal negative charge of the anion under scrutiny becomes larger. At least two details are worth noting and these will be elaborated in the following discussion: (i) the cyclic voltammogram of $[H_2P_2W_{12}O_{48}]^{12-}$ in NaCl solution vanishes almost completely; (ii) the behavior of $\alpha_2P_2W_{17}Zn$ also deserves emphasis in that as the volume increases, the nominal charge remains the same as SiW_{11} and a slightly smaller first peak potential shift is observed. Figure 3 compares the behaviors of P_2W_{18} in sulfate and chloride media and shows that no difference is observed. The same observation holds for $P_2W_{15}Mo_3$. This result is in agreement with the previously known behaviors of saturated heteropolyanions. Even though P_2W_{18} and $P_2W_{15}Mo_3$ are the less charged of the complexes in the present series, the main characteristic likely to bring about the difference in behavior in comparison with the others is the symmetry of the charge distribution in the saturated species.

The observations discussed above all converge to indicate the total nominal charge of each anion on the one hand and its distribution on the other, as two of the parameters that govern the shape and potential location of cyclic voltammetric waves. A second conclusion concerns the particular role of protons in the presence of large amounts of other cations, which failed to counteract the suggested anion effect. Could these observations be rationalized in the framework of the double layer theory? Some complementary experiments seem to contradict this possibility. For example, in a pH = 3 medium containing 0.1 M Na_2SO_4 + 0.2 M NaCl, the classical cyclic voltammograms known in sulfate media for $\alpha_2P_2W_{15}Mo_2$, $\alpha_2P_2W_{17}$, or P_2W_{12} are obtained almost exactly. More strikingly, upon addition of 0.1 M Na_2SO_4 to pH = 3 solutions containing 0.2, 0.3, or 1 M NaCl, the vanishingly small and drawn-out cyclic voltammogram of P_2W_{12} is immediately replaced by a well-defined pattern. In addition, the cyclic voltammograms depend on the concentration of the relevant heteropolyanion in solution. This behavior suggests a preeminent role for the proton and deserves further investigations, which are described in the following section.

Influence of the Proton to Heteropolyanion Concentration Ratio

To highlight the influence of this parameter, the following experiments were carried out with a proton to heteropolyanion concentration ratio from 4 down to 0.22 in most cases. Typically, the pH = 3 supporting electrolyte contains 0.2 M Na_2SO_4 and the concentration of the appropriate heteropolyanion varied from $0.25 \cdot 10^{-3}$ to $4.5 \cdot 10^{-3}$ M. Figure 4 and Figure 5 pertain to $\alpha_2P_2W_{15}Mo_2$ and $\alpha_2P_2W_{17}$, respectively. For the sake of clarity each figure is split into three parts.

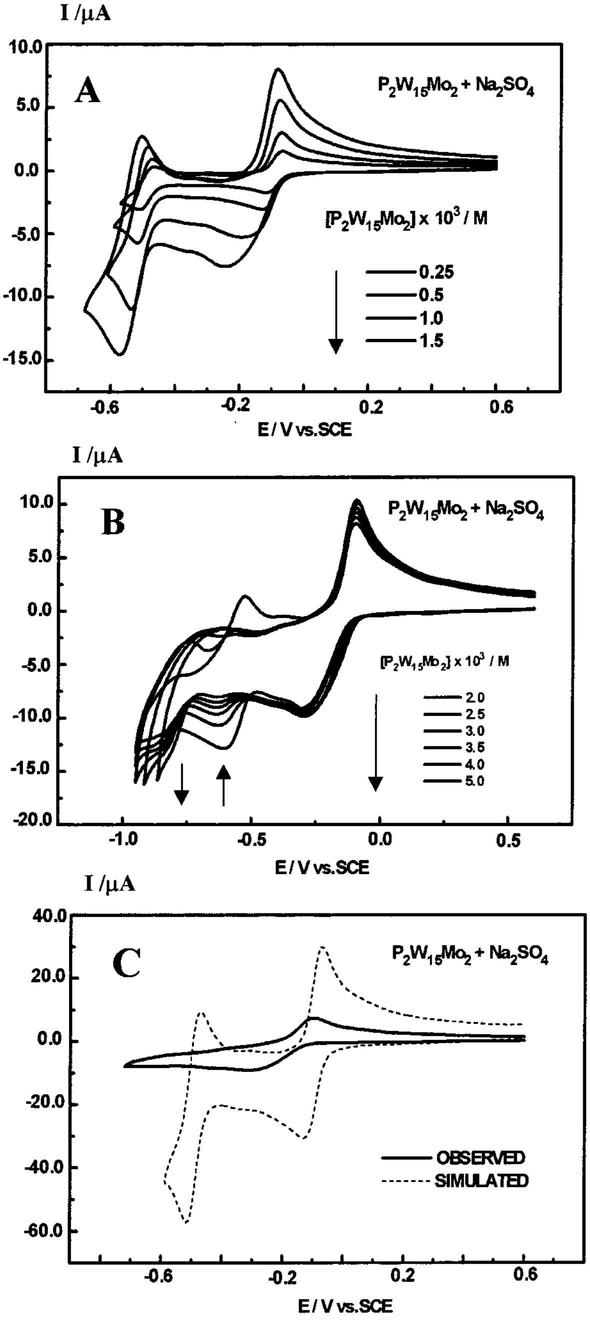

Figure 4. Cyclic voltammograms of several increasing concentrations of $\alpha_2[Mo_2P_2W_{15}O_{61}]^{10-}$ in 0.2 M Na_2SO_4 + H_2SO_4 (pH = 3 before addition of heteropolyanion); scan rate: 10 mVs^{-1}; working electrode: glassy carbon; A and B: the appropriate concentrations are indicated in the sketches; C: observed and simulated cyclic voltammograms for a concentration of $4.5 \cdot 10^{-3}$M $\alpha_2[Mo_2P_2W_{15}O_{61}]^{10-}$ in the initially pH = 3 medium; scan rate: 10 mVs^{-1}; working electrode: glassy carbon; for further details, see text

In Figure 4A the peak current intensities are strictly proportional to the analytical concentration of the heteropolyanion. This concentration domain is narrow, despite the presence of a high concentration of cations in the solution. Details in Figure 4B deserve particular attention. Upon in-

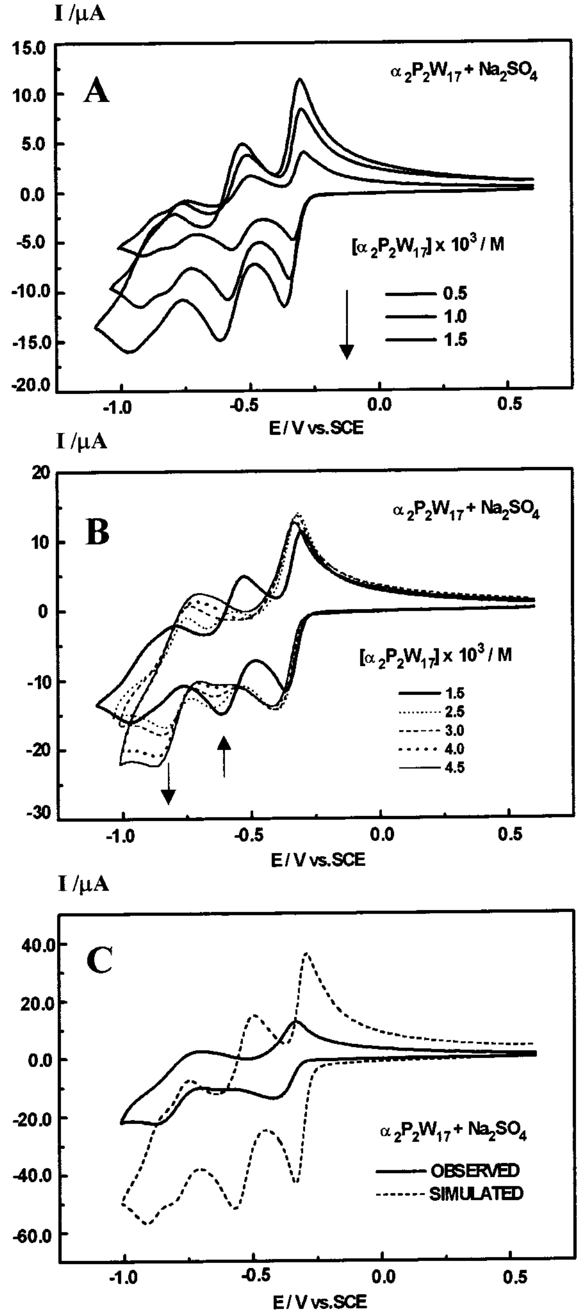

Figure 5. Cyclic voltammograms of several increasing concentrations of $\alpha_2[P_2W_{17}O_{61}]^{10-}$ in 0.2 M Na_2SO_4 + H_2SO_4 (pH = 3 before addition of heteropolyanion); scan rate: 10 mVs^{-1}; working electrode: glassy carbon; A and B: the appropriate concentrations are indicated in the sketches; C: observed and simulated cyclic voltammograms for a concentration of $4.5\cdot10^{-3}$ M $\alpha_2[P_2W_{17}O_{61}]^{10-}$ in the initially pH = 3 medium; scan rate: 10 mVs^{-1}; working electrode: glassy carbon; for further details, see text

creasing the heteropolyanion concentration, the first wave becomes roughly constant in intensity and the peak potential continues its slight shift in the negative direction; the current intensity of the second wave decreases until it becomes vanishingly small; concomitantly, a new wave appears at a more negative potential than the former second wave and grows at its expense. Figure 4 C shows a comparison between the final voltammogram observed for $4.5\cdot10^{-3}$ M $\alpha_2P_2W_{15}Mo_2$ and the voltammogram simulated from that corresponding to the lowest concentration of complex on the assumption that the peak current intensities maintain the expected proportionality and peak potentials remain constant. Figure 5 shows analogous observations for $\alpha_2P_2W_{17}$. Apart from the difference in wave shapes, which is the incentive for showing both Figure 4 and 5, exactly the same comments are applicable to the two complexes and will not be repeated.

In contrast, the addition of potassium hydrogen phthalate, which increases the buffer strength of the sulfate solution, improves drastically the observed phenomena. Figure 6 compares the observed and simulated cyclic voltammograms for $\alpha_2P_2W_{15}Mo_2$ and $\alpha_2P_2W_{17}$, respectively, under these experimental conditions.

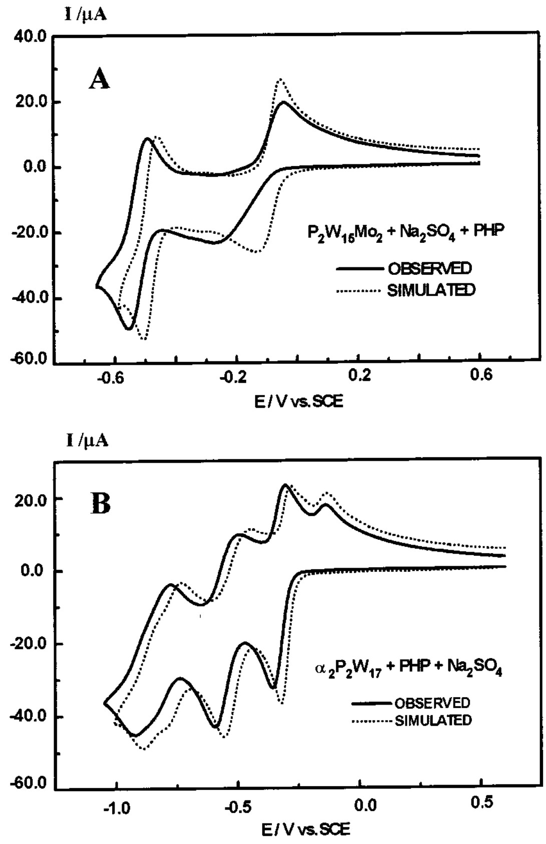

Figure 6. Observed and simulated cyclic voltammograms for $5\cdot10^{-3}$ M of the relevant heteropolyanion in 0.175 M Na_2SO_4 + $5\cdot10^{-2}$ M PHP (initial pH = 3); scan rate: 10 mVs^{-1}; working electrode: glassy carbon; for further details, see text; A: $\alpha_2[Mo_2P_2W_{15}O_{61}]^{10-}$; B: $\alpha_2[P_2W_{17}O_{61}]^{10-}$

Even with modest concentrations of the phthalate, the "expected" cyclic voltammograms are almost completely restored, as can be seen in Figure 6. Such an observation underscores the influence of the buffer capacity of the electrolyte and the special participation of the proton in the electrochemistry of the selected oxometalates. Also, comparison of the behavior of the two complexes in the same medium confirms the difference in basicity between their reduced forms.

Finally, complementary experiments were carried out. Figure 7 indicates for two metal ion substituted heteropolyanions, $\alpha_2P_2W_{17}Ni$ and $\alpha_2P_2W_{17}Zn$ selected as representative examples, the same trends as obtained for the precursor lacunary species, albeit to a lesser extent.

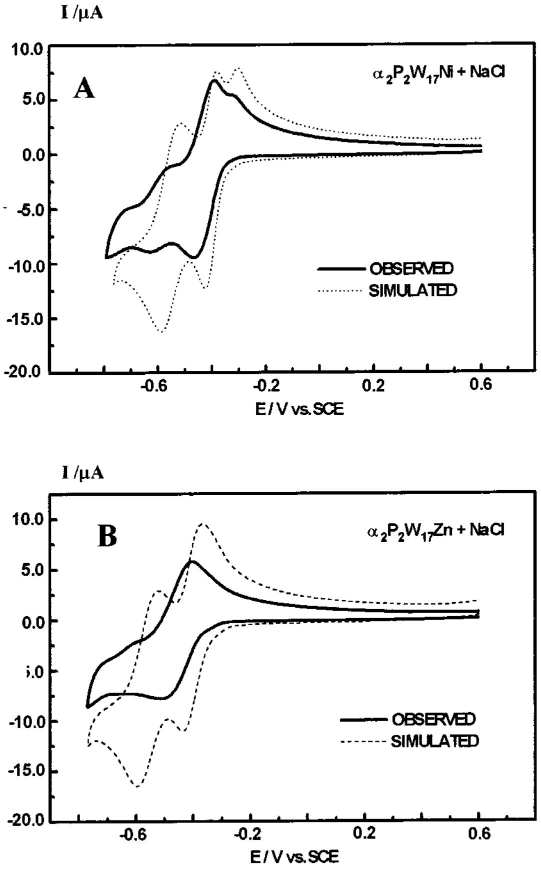

Figure 7. Observed and simulated cyclic voltammograms for $5\cdot10^{-3}$ M of the relevant heteropolyanion in 0.4 M NaCl + HCl (initial pH = 3); scan rate: 10 mVs^{-1}; working electrode: glassy carbon; for further details, see text; A: $\alpha_2[NiP_2W_{17}O_{61}]^{8-}$; B: $\alpha_2[ZnP_2W_{17}O_{61}]^{8-}$

Substitution of Na^+ by Li^+ in the supporting electrolyte does not change the general behavior observed for lacunary as well as for metal cation substituted heteropolyanions. Figure 8 summarizes the evolution, with the heteropolyanion concentration, of the current intensity ratio of the observed and simulated first voltammetric waves as defined previously.

It is also clear from Figure 8 that there is a slower decrease of this ratio when the ionic strength of the electrolyte increases.

With a proton-to-heteropolyanion ratio smaller than 2, all the observations suggest a reaction pathway in which two main species are in equilibrium in the solution, with their reduction featured respectively by the first and the second voltammetric waves. In this issue, it can be hypothesized that the first wave should correspond to the reduction of a protonated form of the heteropolyanion and the second wave to another protonated or to an unprotonated form.

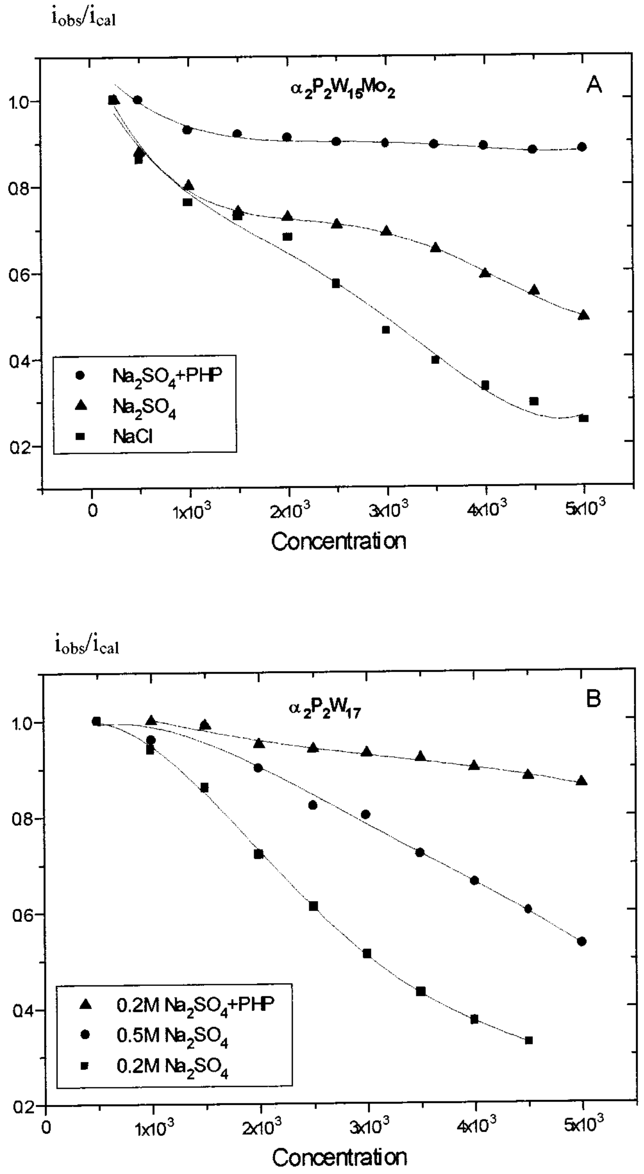

Figure 8. Normalized first reduction peak current intensity as a function of heteropolyanion concentration [M], using the calculated diffusion current as a reference; for further details, see text; A: $\alpha_2[Mo_2P_2W_{15}O_{61}]^{10-}$; B: $\alpha_2[P_2W_{17}O_{61}]^{10-}$

This distinction stems from the failure of large amounts of sodium or lithium cation to assume the role of protons and from the known polybasic behavior of $\alpha_2P_2W_{17}$,[18] which is also anticipated for $\alpha_2P_2W_{15}Mo_2$.

Acid−Base Equilibria

An attempt to rationalize the observations discussed above demands complementary experiments that can support or invalidate the basic hypothesis. The study is restricted to $\alpha_2P_2W_{15}Mo_2$ and $\alpha_2P_2W_{17}$.

Typically, several experiments were performed by starting the measurements with a pH = 3 solution containing the appropriate concentration of Na_2SO_4 + PHP, Na_2SO_4, or NaCl, which are the most representative supporting electrolytes used in this work. The pH of such solutions was then monitored accurately as a function of the added concentra-

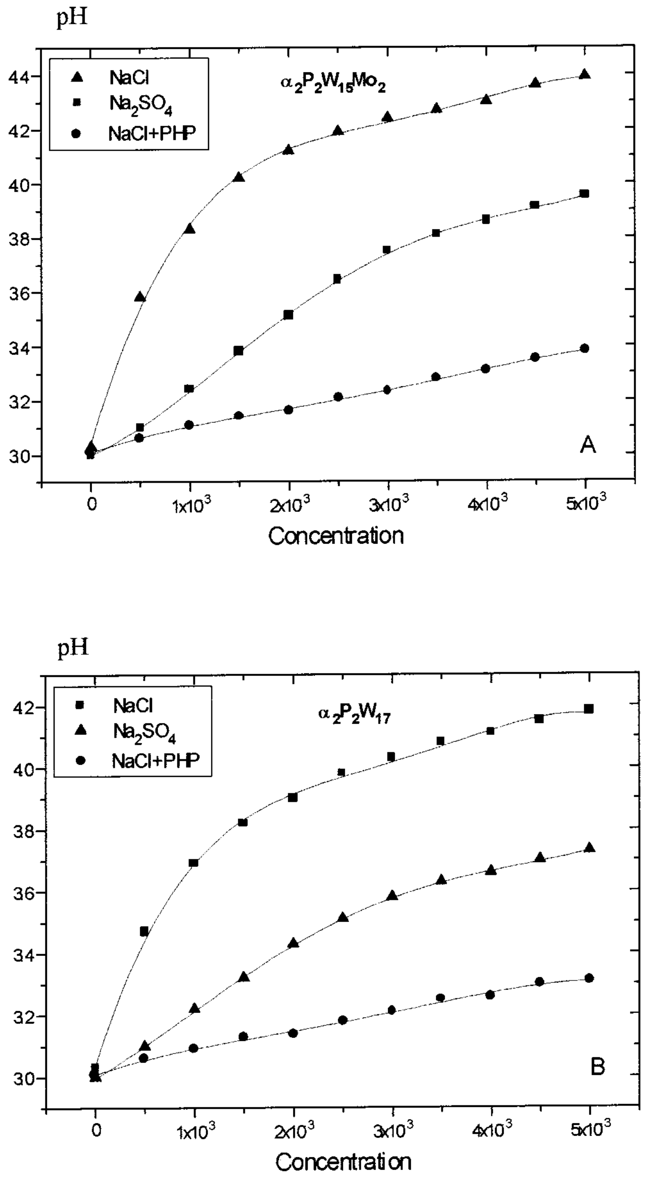

Figure 9. Variation of pH as a function of the concentration of heteropolyanion added to an initially pH = 3 solution; the composition of the electrolyte is indicated on each curve; A: $\alpha_2[Mo_2P_2W_{15}O_{61}]^{10-}$; B: $\alpha_2[P_2W_{17}O_{61}]^{10-}$

tion of the relevant heteropolyanion. The results are shown in Figure 9 and are enlightening.

Even with the smallest concentration of oxometalate used in this work, proton consumption occurs. Clearly, for both heteropolyanions, at least one of their pK_a values falls in the pH domain of the supporting electrolyte. The differences observed between the various media are easily explained in terms of their buffer capacity. The chloride medium has no buffer capacity and the consumption of protons by the heteropolyanion results in a rapid increase in the pH value. In the pure sulfate medium, $[HSO_4]^-$ is a proton donor, the presence of which confers some buffer capacity to the electrolyte. By following a literature procedure,[27] the initial concentration of hydrogen sulfate in the pH = 3 solution containing 0.2 M Na_2SO_4 can be evaluated and was found to be roughly $1.54 \cdot 10^{-2}$ M. Incidentally, it is worth noting that the increase of hydrogen sulfate species in 0.5 M Na_2SO_4 ($3.85 \cdot 10^{-2}$ M) and, to a lesser extend, the increase of cations, participate in the observed influence of ionic strength in Figure 8A. Finally, two proton donors are present in the mixture of sulfate and PHP, which can explain the small variation of pH with the concentration of heteropolyanion in that medium.

As far as the acid-base equilibria of the heteropolyanions are concerned, each of the present Dawson-type lacunary compounds is theoretically expected to fix ten protons. In fact, previous work on $\alpha_2P_2W_{17}$[18] and the present experiments on the two species under investigation indicate that the consumption of only three protons occurs. A detailed account of the accurate pK_a determinations for these compounds, as well as for several other species in the Dawson and Keggin series, under various experimental conditions will be given elsewhere along with the distribution of the various possible species in equilibrium at a given pH value.[28]

Discussion

The classical picture encountered so far in our studies for the reduction of lacunary heteropolyanions in pH = 2 or 3 media with a large enough proton-to-heteropolyanion ratio,[6−10,29] begins with two two-electron waves. At least the first peak current intensity is proportional to the analytical concentration of the oxometalate. Most, but not all, first transition metal ion substituted heteropolyanions behave similarly and show a system of two-electron waves at practically the same potential locations as those of the precursor lacunary species.[6−10,29] Hence the conclusion that most of these systems cannot actually be considered as "saturated" compounds.

Several observations in the experiments described above deserve further specific discussion. Emphasis will be placed on an attempt at the rationalization of the influence of the overall negative charge of the heteropolyanion, the partial localization of this charge, and the role of various counterions present in the solution, with particular attention paid to the remarkable behavior of the proton.

In the pH domain explored and with the heteropolyanion concentrations used in this work, the lacunary as well as the substituted compounds are stable. As a matter of fact, regardless of the starting situation, addition of acid to obtain a large proton-to-heteropolyanion ratio restores immediately the classical cyclic voltammograms with a first two-electron wave, the current intensity of which is proportional to the analytical concentration of the oxometalate. The extremely high speed of this restoration might rule out association phenomena as the origin of the observed behavior.

We consider first the situation in Figure 1 through 3. With the sulfate medium chosen as a reference, the electrolyte composition seems suitable to ensure classical behavior for the oxometalates described in this work. For this same pH but in the presence of other anions, a general negative shift in the peak potential locations is obtained with a concomitant decrease of the peak currents. Such behavior spans a large potential domain, roughly from +0.6 to −1 V in the present experiments. Provisionally, it must be noted that this domain encompasses two two-electron waves of the fully symmetrical heteropolyanion P_2W_{18}, and that the whole cyclic voltammogram for this compound remains unaltered by the change in anion in the supporting electrolyte. On the reasonable assumption that the added electrons are delocalized in the equatorial region or that the charge distribution remains symmetrical in the first few reduced forms of P_2W_{18}, this cyclic voltammogram would indicate that the overall charge by itself is not a main parameter in the observed behavior. In contrast, substituted heteropolyanions are sensitive to the change of anions, which lends support to the conclusion that they behave much like the precursor lacunary species. The idea emerges that charge localization is of prime importance to induce the behaviors of lacunary and lacunary-like species. The larger this charge localization, the larger the effects. It has also been confirmed by UV/Vis spectroscopy that decomposition of the oxometalates does not occur. Given this information we are left with an explanation involving anion effects and/or local pH effects. The most striking or complex behaviors are encountered with $\alpha_2P_2W_{15}Mo_2$ and P_2W_{12}. Work is still in progress on the latter compound. Therefore, focus is placed on the first compound. The anion effect in electrochemistry has been known for some time and is rationalized in terms of adsorption and double layer effects.[30−35] More specifically, the anion effect in the reduction of chromate ions has been described in detail by Gierst and co-workers.[36,37]

However, examination of Figure 8A. and Figure 9A, indicates that $\alpha_2P_2W_{15}Mo_2$ and its reduced species should fix protons irreversibly, thus raising the pH value in the reaction layer. As a consequence, the peak current intensity could be lowered and the peak potential driven in the negative direction. This possibility might appear difficult to separate from the pure double layer effect, but the present observations rule out any preeminent anion effect.

The second issue of importance concerns the role of counter cations in the reaction mixture. Even though they are active in ensuring the overall electroneutrality of the solutions, their behavior is particularly prominent when the proton to heteropolyanion ratio is low. In these circumstances, it is observed that the high cation-to-heteropolyanion ratio cannot counteract the pH variation effect. This conclusion is confirmed in Figure 4 and 5, in which it can be seen that cations other than the proton also fail to give rise to the classical cyclic voltammograms of lacunary heteropolyanions. In contrast, the efficiency of protons in these circumstances is clearly highlighted, in particular through the buffer capacity of the supporting electrolyte. The facts in this particular case are clear although their complete rationalization seems difficult at present. Therefore, the following discussion represents an attempt to sum up the main questions raised by the present observations, with an indication of the tentative ways in which these questions could be solved. At least two questions arise: (i) the extent, if any, of ion-pairing of cations with the outer surface of heteropolyanions, more specifically in the reduced states; (ii) the compensation by cations of the localized charges of the vacancy corresponding to the missing moiety. Complexation and/or ion-pairing of the lacunary[18] and the substituted[18,38,39] heteropolyanions with alkali metal cations were demonstrated and seem to be associated with the dissymetry of the molecules.[12,40] This remark suggests charge localization to some extent. As a consequence, we focus on the atoms in and around the vacancy. The complexation stability constants, in the cases in which they were measured,[18,28] have sizeable values. It can be assumed that the corresponding reduced species should be even more strongly complexed by alkali metal cations. Then, the particular role played by protons should be tentatively attributed to either or both of the following possibilities: the very fast protonation kinetics, in agreement with the p*K* values, and/or some restricted accessibility of protonable/complexable sites. This last assumption might be supported by the known bulkiness of solvated alkali metal cations:[41,42] the ionic radii are 2.35 Å for solvated Na^+, 2.08 Å for solvated Li^+, while the value of 0.74 Å for W^{6+} is generally accepted to represent also the radius of the vacancy. A new problem now arises concerning the actual state (i.e. whether they are solvated, partially solvated or unsolvated) of the cations that participate in the neutralization of the charges around the vacancy. It is known[18,28] that, among the five protonable sites, only the four outer sites have a good accessibility and that three are protonable. It is likely that solvated cations can only complex these sites in a fairly loose manner. Work in progress is aimed at clarifying several of these problems.

Concluding Remarks

The observations made for the electrochemical behavior of the oxometalates studied in this work show evidence for the influence of electrolyte composition. Despite the variety of Dawson- and Keggin-type structures, the conclusion emerges that lacunary as well as their divalent cation substituted species are sensitive mainly to the buffer capacity of the electrolytes. This influence pushes the peak potentials in the negative direction and, as a whole, increases the reduction overvoltage of the oxometalate. The intensity of the influence decreases smoothly from the lacunary species to their divalent cation substituted derivatives, and vanishes completely in the precursor-saturated compound. Furthermore, the importance of this influence turns out to follow smoothly the nominal negative charge borne by each molecule. This observation confirms and reinforces the conclusion that most divalent cation substituted heteropolyanions are not actually "saturated" compounds and that their electrochemistry should be compared with that of the corresponding lacunary species. This behavior reveals, in fact, some dissymmetry in the charge distribution in the molecules, as evidenced by the comparative study with P_2W_{18} or $P_2W_{15}Mo_3$. The possible further interference of local pH changes during reduction processes must also be considered. Thus, one remarkable outcome of this work is the possibility that electrochemical behavior governed by electrolyte composition can serve as probes of charge distribution in oxometalates.

Another issue of interest concerns the very modest role played by cations other than the proton in the electrochemical behavior of oxometalates. The series of questions raised by this observation can be partly answered by considering qualitatively the charge localization on hard oxide ions around the vacancy and the bulkiness of solvated alkali cations in competition with proton hopping. Also, the pK_a value of the various sites in the oxidized as well as in the reduced forms must be considered. These explanations cannot be extended to the known specificity of several cations in the synthesis of lacunary heteropolyanions. Work in progress aims at answering several such questions.

Experimental Section

Pure water from a Milli-RO_4 unit followed by a Millipore Q purification set was used throughout. All chemicals were of high-purity grade and were used as received. H_2SO_4, Li_2SO_4, Na_2SO_4, LiCl, NaCl, HCl, $NaClO_4$, $NaNO_3$, $C_8H_5O_4K$ (potassium hydrogen phthalate, abbreviated as PHP), CH_3COOH, CH_3COONa (Prolabo) were commercial products. In the present comparative study, only pH = 3 media were used. The heteropolyanions used in this work have been cited previously, along with appropriate abbreviations and preparations.[6,8,9,18–21] The stability of these compounds was checked in a 0.2 M Na_2SO_4 + H_2SO_4 medium (pH = 3) by UV/Vis spectroscopy over a period of at least 24 h. The solutions were deaerated thoroughly for at least 30 min with pure argon and kept under a positive pressure of this gas during the experiments.

The source, mounting and polishing of the glassy carbon (GC, Le Carbone Lorraine, France, 3 mm diameter) have been described.[5,6] The electrochemical set-up was an EG & G 273 A driven by a PC with the corresponding 270 software. Potentials are quoted against a saturated calomel electrode (SCE) in a compartment separated from the test solution by a fine-porosity glass frit. The counter electrode was platinum gauze of large surface area in a separated compartment with a medium-porosity glass frit. The UV/Vis spectra were recorded with a Perkin−Elmer Lambda 19 spectrophotometer. Experiments were performed at 23 ± 1 °C.

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