# Co-solvent Effects on the Redox Potentials of Manganese-substituted α-Keggin-type Silicon Polyoxotungstate $K_6SiW_{11}O_{39}Mn(H_2O)$: First Electrochemical Generation of the Manganese(V) Redox System in an Aqueous Environment

Masahiro Sadakane[†] and Eberhard Steckhan[*]

Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Str. 1, D-53121 Bonn, Germany

**Dedicated to Professor Henning Lund on the occasion of his 70th birthday.**

Sadakane, M. and Steckhan, E., 1999. Co-solvent Effects on the Redox Potentials of Manganese-substituted α-Keggin-type Silicon Polyoxotungstate $K_6SiW_{11}O_{39}Mn(H_2O)$: First Electrochemical Generation of the Manganese(V) Redox System in an Aqueous Environment. – Acta Chem. Scand. 53: 837–841. © Acta Chemica Scandinavica 1999.

In the electrochemistry of the manganese-substituted α-Keggin silicon tungstate $[K_6SiW_{11}O_{39}Mn(II)(H_2O)]$ in phosphate buffer, co-solvents influence the redox potential of the manganese incorporated in the heteropolyanion. Thus, the redox potentials of $SiW_{11}O_{39}Mn(III/II)(H_2O)$ and $SiW_{11}O_{39}Mn[(IV)(OH)/(III)(H_2O)]$ shift to more negative potentials on increasing the amount of organic co-solvents. The organic solvents stabilize the more highly oxidized complex. By use of this stabilization, the generation of the pentavalent manganese-substituted silicon polyoxotungstate could be detected electrochemically for the first time.

Homogeneous catalytic oxidations have been one of the most interesting areas of chemical research. Numerous metalloporphyrin-based systems including iron, manganese, cobalt, chromium and ruthenium have been described.[1] Recently, considerable attention has been directed towards metal-substituted α-Keggin heteropoly-anions as stable analogues of metalloporphyrins.[2,3]

From α-Keggin heteropolyanions ($AB_{12}O_{40}$), so-called 'lacunary heteropolyanions' ($AB_{11}O_{39}$) are derived by removing one $BO_6$ unit. Many transition metals (Co, Cr, Fe, Mn, Ru, etc.) can fill this hole, giving rise to metal-substituted α-Keggin heteropolyanions such as $PW_{11}O_{39}Ru(H_2O)$. Similary to metalloporphyrins, metal-substituted α-Keggin heteropolyanions can work as oxygen carriers. These transition metals $M^{n+}$ accept oxygen from different oxygen donors (iodosylarenes, peroxides, etc.) and the thus formed oxometal species $M^{n+2}=O$ are able to oxidize various organic substrates such as hydrocarbons, alcohols and olefins.[2,3] The hetero-

polyanion ligands are robust under strongly oxidative conditions and thus have an important advantage over metalloporphyrin systems, which decompose under these conditions.

The electrochemical properties of the incorporated transition metal in the compounds $PW_{11}O_{39}Ru$,[4,5] $PW_{11}O_{39}Cr$,[6] $SiW_{11}O_{39}Fe$,[7–9] $SiW_{11}O_{39}Re$ and $PW_{11}O_{39}Re$[10] have been reported. The transition metal incorporated into the heteropolyanion resides in an octahedral environment with one coordination site occupied by a labile water molecule. On electrochemical oxidation in aqueous media, this water ligand works as an oxygen source. The transition metal aquo complex $M(III)(H_2O)$ ($M = Ru$, Cr and Re) has been oxidized to a transition metal oxo complex $M(V)=O$ by removal of two protons.[11]

We[12,13] and Pope's group[14–16] have investigated the electrochemical behavior of manganese-substituted α-Keggin heteropolyanions and their use as catalysts for oxidations of various organic compounds. In an aqueous solution, the bivalent manganese-substituted silicon polyoxotungstate $[K_6SiW_{11}O_{39}Mn(II)(H_2O)]$ first undergoes a pH-independent oxidation to the manganese(III)

---

[*] To whom correspondence should be addressed.
[†] Present address: Department of Chemistry, Georgetown University, Washington, DC 20057-1227, USA.

aquo complex $[SiW_{11}O_{39}Mn(III)(H_2O)]$ followed by a pH-dependent oxidation to the manganese(IV) hydroxy complex $[SiW_{11}O_{39}Mn(IV)(OH)]$.

In this paper, we report that the corresponding redox potentials can be controlled by using organic co-solvents. With increasing amounts of organic co-solvents they shift to a more negative potential.

## Experimental

*Material.* The potassium salts of the manganese-substituted Keggin heteropolyanion $K_6SiW_{11}O_{39}Mn(II)(H_2O)-6H_2O$ was prepared in the form of the α-isomer according to a procedure described previously.[17] The water content of the isolated salts was calculated from thermogravimetric measurements based on the total loss in weight up to 350 °C. Each solution was prepared from $KH_2PO_4$ (Ferak Berlin, analytical grade), KOH (Riedel–de Haën, reagent grade), 85% $H_3PO_4$ (Riedel–de Haën, reagent grade), an 1.0 M KOAc solution (Fluka) and water that had been purified by passage through a purification train. All organic solvents were used without further purification. The potassium concentration of all solutions was kept at 0.5 M.[12]

*Equipment and procedures.* Electrochemical measurements were conducted with a BAS100B/W computer-controlled electroanalytical system (Bioanalytical Systems Inc., West Lafayette, Indiana). A glassy carbon working electrode, a platinum wire counter electrode and a Ag/AgCl reference electrode (3 M KCl, Cypress System Inc., Lawrence, Kansas) were used. The glassy carbon working electrode (diameter 3 mm) was polished with silicon carbide (1000 mesh), washed with doubly distilled water before use without previous sonication.[7] The experiments were conducted at ambient temperature. $E_{1/2}$ values were calculated from cyclic voltammetry as the average of the cathodic and anodic peak potentials for the oxidative and reductive waves. Thermogravimetric analyses were obtained with an STA/QMS-System: 409/429-403 (Netzsch-Gerätebau GmbH, Selb).

In a previous paper,[12] we reported that well-defined redox waves of the $SiW_{11}O_{39}Mn(III/II)(H_2O)$ and $SiW_{11}O_{39}Mn[(IV)(OH)/(III)(H_2O)]$ redox processes can be obtained after an oxidative pretreatment. Therefore, all cyclic voltammograms were measured after keeping the working electrode potential at 1.25 V for 30 s. The concentration of the complex was ca. 1.0 mM and the scan rate was 20.0 mV s$^{-1}$.

## Results and disscussions

*Effect of pH on the redox potentials of the manganese incorporated into the heteropolyanion in phosphate solution and in acetate solution.* Figure 1 shows the dependence of $E_{1/2}$ on the pH for the $SiW_{11}O_{39}Mn(III/II)$ and $SiW_{11}O_{39}Mn(IV/III)$ redox processes in phosphate buffer and acetate buffer. As shown in the previous



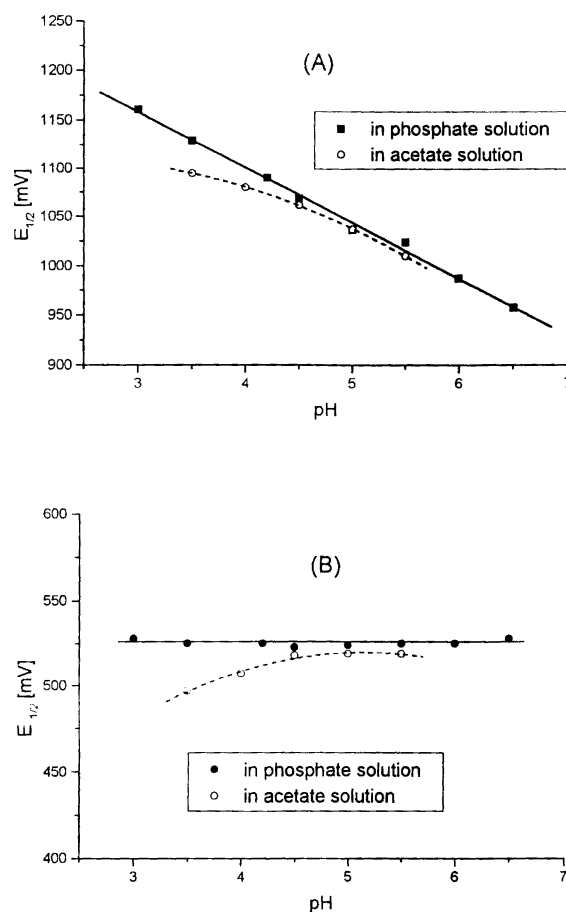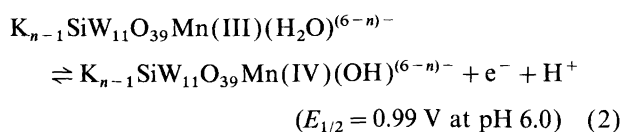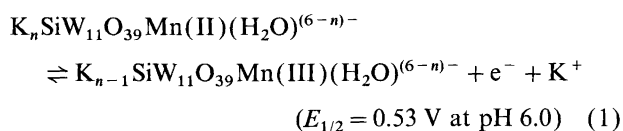*Fig. 1.* pH dependence of the $E_{1/2}$ values for the $SiW_{11}O_{39}Mn(IV/III)$ (A) and the $SiW_{11}O_{39}Mn(III/II)$ (B) redox couples in phosphate buffer (●) and in acetate buffer (○).

paper,[12] the $E_{1/2}$ of the $SiW_{11}O_{39}Mn(IV/III)$ redox system shows a clear linear dependence on the pH, with a slope of 57 mV per pH unit, and the $E_{1/2}$ of the $SiW_{11}O_{39}Mn(III/II)$ redox system is independent of the pH in phosphate solution. This means that one proton is included in the $SiW_{11}O_{39}Mn(IV/III)$ redox step, clearly indicating the generation of the hydroxymanganese complex $SiW_{11}O_{39}Mn(IV)(OH)$ [eqn. (2)]. The oxidation of the divalent manganese complex to the trivalent one is accompanied by the loss of one potassium cation [eqn. (1)]. Therefore, the $E_{1/2}$ of the $SiW_{11}O_{39}Mn(III/II)(H_2O)$ redox couple does not depend on the pH but on the potassium cation concentration.

$$K_n SiW_{11}O_{39}Mn(II)(H_2O)^{(6-n)-}$$

$$\rightleftharpoons K_{n-1} SiW_{11}O_{39}Mn(III)(H_2O)^{(6-n)-} + e^- + K^+$$

$$(E_{1/2} = 0.53 \text{ V at pH } 6.0) \quad (1)$$

$$K_{n-1} SiW_{11}O_{39}Mn(III)(H_2O)^{(6-n)-}$$

$$\rightleftharpoons K_{n-1} SiW_{11}O_{39}Mn(IV)(OH)^{(6-n)-} + e^- + H^+$$

$$(E_{1/2} = 0.99 \text{ V at pH } 6.0) \quad (2)$$

In contrast with results in the phosphate buffer system, the pH dependence of $E_{1/2}$ of both the $SiW_{11}O_{39}Mn(IV/III)$ and $SiW_{11}O_{39}Mn(III/II)$ redox steps is non-linear in acetate buffer. The difference between $E_{1/2}$ in phosphate buffer and $E_{1/2}$ in acetate buffer increases with decreasing pH (see Fig. 1).

This phenomenon can be explained by considering a co-solvent effect of the acetic acid in the acetate buffer. The largest difference between the acetate buffer and the phosphate buffer is the acid concentration. Phosphoric acid is a strong acid, but acetic acid is a weak acid with a $pK_a$ value of 4.38. Thus, much more acid is required to adjust an acetate buffer to a given pH value (below its $pK_a$), than for the respective phoshate buffer. For example, a pH 4.1 acetate buffer contains ca. 12.5 vol% of acetic acid.

As shown in Fig. 2, the potential of the first redox step shifts to more negative values on increasing the acetic acid concentration in the acetate buffer. A linear relationship is obtained if the potentials are plotted against the acid concentration instead of plotting them against the pH value. This indicates that it is the acetic acid which affects the redox potential of the manganese incorporated into the heteropolyanion, presumably by acting as a ligand.

*Effects of co-solvents in phosphate buffer solution.* At first, the $SiW_{11}O_{39}Mn(III/II)(H_2O)$ redox couple was chosen as a means of exploring the co-solvent effect of organic solvents, because the potential of this redox pair is independent of the solution pH. DMSO, DMF, acetone, acetonitrile and acetic acid were selected as co-solvents. As presented in Fig. 3, all co-solvents affect the redox potential in the same way, shifting it linearly to more negative potentials on increasing co-solvent concentration.

The pH effects on both $E_{1/2}$ values of the $SiW_{11}O_{39}Mn(IV/III)$ and $SiW_{11}O_{39}Mn(III/II)$ redox steps were measured in the presence of 15 mol% (2.87 M) of acetonitrile in phosphate buffer and are summarized
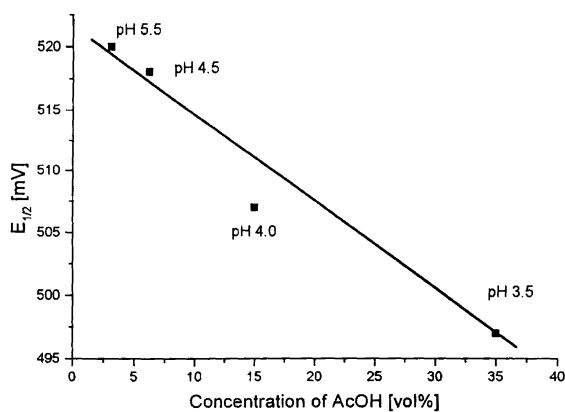


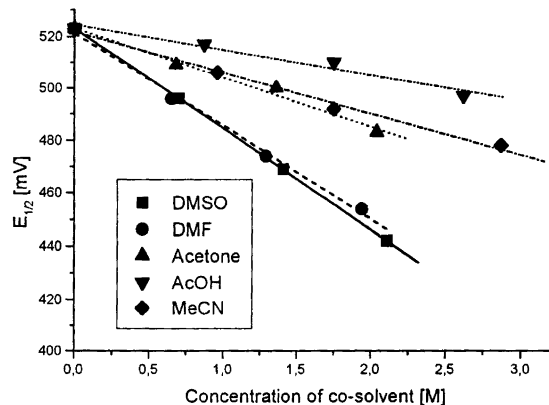*Fig. 3.* Potential shift of the $SiW_{11}O_{39}Mn(III/II)$ redox couple versus the co-solvent concentration.

in Fig. 4. In the presence of acetonitrile, the $E_{1/2}$ of the $SiW_{11}O_{39}Mn(IV/III)$ redox system decreases linearly with a slope of ca. 60 mV per pH unit on increasing the pH, which is identical with the situation in the absence of a co-solvent. This indicates that the $SiW_{11}O_{39}Mn(IV)(OH)$ complex can be produced also in the presence of acetnitrile. The $E_{1/2}$ of the
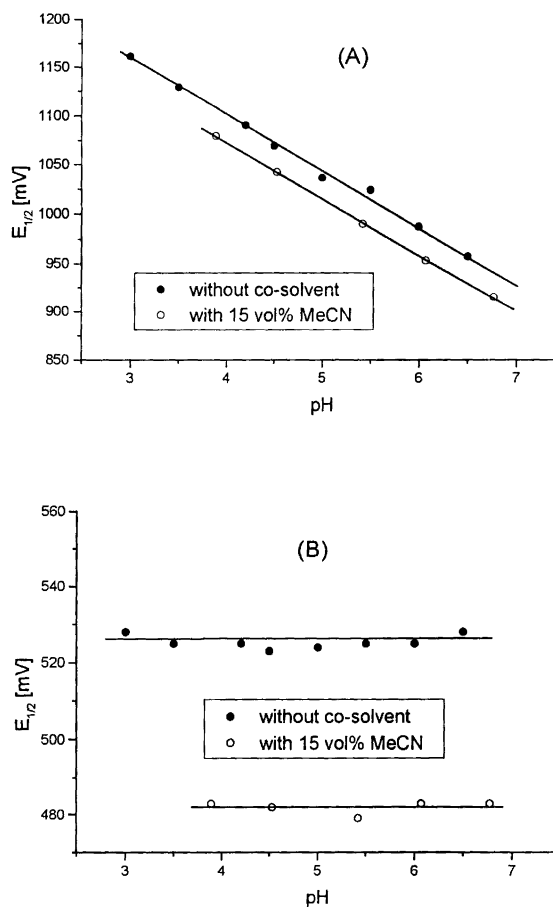




*Fig. 4.* pH effect on the $SiW_{11}O_{39}Mn(IV/III)$ (A) and $SiW_{11}O_{39}Mn(III/II)$ (B) redox couples with no co-solvent (●) and with 15 vol% of MeCN (○) in phosphate buffer solution ([K⁺] = 0.5 M).



*Fig. 2.* Relationship between the $E_{1/2}$ values for the $SiW_{11}O_{39}Mn(III/II)$ redox couple and acetic acid concentration.

$SiW_{11}O_{39}Mn(III/II)$ redox couple is also independent of pH in the presence of acetonitrile, indicating that the observed potential shift with increasing co-solvent concentrations is solely caused by the co-solvents. A similar result is observed with using acetone as the co-solvent.

The generation of the $SiW_{11}O_{39}Mn(IV)(OH)$ demonstrates that the water ligand coordinated to the manganese is not replaced by the co-solvent molecule. This strongly supports the assumption that co-solvents must interact through the anionic polyoxometallate ligand and not via the transition metal. The added solvents stabilize the higher-valent metal complex relative to the lower-valent metal complex, thus lowering the formal redox potential. It is known that the formal potentials of many redox-active compounds can be affected by solvents in a variety of ways and the potential shifts can be explained in terms of solvent parameters such as acceptor or donor numbers.[18] It has been already reported that the redox potential of the $\alpha$-Keggin-type silicon polyoxometallate $SiW_{12}O_{40}^{4-}$ is a function of the acceptor number of the solvents used.[19] Similar effects of solvents and especially of the counter-cations have been discussed for 12-tungstocobaltate (II/III).[20] In the system reported here, it was not possible to obtain a reasonable correlation between the potential shifts and only one solvent parameter. The explanation of the potential shift with only one solvent parameter seems to be insufficient because the manganese-substituted silicon polyoxotungstate has at least two sites which can interact with the solvents: the oxoanion and the counter cation. Detailed studies of the solvent effects with regard to the discrimination of the different sites of interaction are planned.

*Further oxidation of the $SiW_{11}O_{39}Mn(IV)(OH)$ complex.* As shown in Fig. 5, the $SiW_{11}O_{39}Mn(IV)(OH)$ complex can be stabilized in two ways, either by increasing the pH or the co-solvent concentration. Therefore, it seemed possible to use these effects to reach the pentavalent oxidation state of the manganese substituent by further oxidation of the tetravalent hydroxymanganese complex. This should take place even in aqueous media in the presence of a co-solvent at the appropriate pH value. Indeed, in a pH 6.8 phosphate buffer containing 15 vol% of acetonitrile, a strong further oxidation wave was observed (Fig. 5). The irreversibility of the oxidation step does not, however, lead to the irreversible destruction of the redox system because the reduction wave for the $Mn(IV)(OH)$ complex is unchanged. The new oxidation wave can thus be explained by the formation of the $Mn(V)$ oxo complex which is observed for the first time in an aqueous system This $Mn(V)$ oxo complex acts as an oxidizing agent and spontaneously oxidizes water regenerating the $Mn(IV)$ hydroxy complex which is reduced at the electrode. The high oxidation current for the formation of the $Mn(V)$ oxo complex is thus due to its catalytic activity towards the oxidation of water.
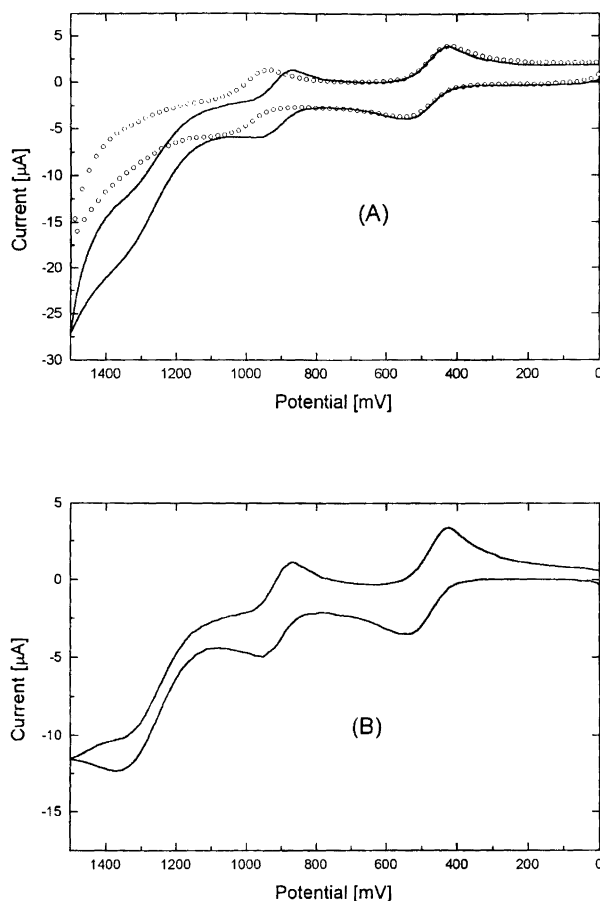


*Fig. 5.* Further oxidation of the $SiW_{11}O_{39}Mn(IV)(OH)$ complex (A) in a pH 5.4 (O) and a pH 6.8 (——) phosphate buffer containing 15 vol% of MeCN. (B) Voltammogram corrected for the background current.

Studies of the redox catalytic behavior of the $Mn(V)$ oxo complex towards organic compounds are currently under way.

## References

1. Meunier, B. *Chem. Rev. 92* (1992) 1411.
2. Hill, C. L., Ed., *Chem. Rev. 98* (1998), special edition on polyoxymetallates.
3. Hill, C. L. and Prosser-McCartha, C. M. *Coord. Chem. Rev. 143* (1995) 407.
4. Rong, C. and Pope, M. T. *J. Am. Chem. Soc. 114* (1992) 2932.
5. Bart, J. C. and Anson, F. C. *J. Electroanal. Chem. 390* (1995) 11.
6. Rong, C. and Anson, F. C. *Inorg. Chem. 33* (1994) 1064.
7. Toth, J. E. and Anson, F. C. *J. Electroanal. Chem. 256* (1988) 361.

8. Toth, J. E., Melton, J. D., Cabelli, D., Bielski, B. H. J. and Anson, F. C. *Inorg. Chem. 29* (1990) 1952.

9. Toth J. E. and Anson, F. C. *J. Am. Chem. Soc. 111* (1989) 2444.

10. Ortéga, F. and Pope, M. T. *Inorg. Chem. 23* (1984), 3292.

11. Sadakane, M. and Steckhan, E. In Ref. 2, p. 219.

12. Sadakane, M. and Steckhan, E. *J. Mol. Catal. A 114* (1996) 221.

13. Steckhan, E., Hilt, G., Kempf, R. and Sadakane, M. In: Helmchen, G., Ed., *Organic Synthesis via Organometallics (OSM5. Heidelberg)*, Vieweg, Braunschweig 1997, p. 253.

14. Zhang, X.-Y., Pope, M. T., Chance, M. R. and Jameson, G. B. *Polyhedron 14* (1995) 1381.

15. Zhang, X.-Y. and Pope, M. T. *J. Mol. Catal. A 114* (1996) 201.

16. Müller, A., Dloczik, L., Diemann, E. and Pope, M. T. *Inorg. Chim. Acta 257* (1997) 231.

17. Tourné, C. M., Tourné, G. F., Malik, S. A. and Weakley, T. J. R. *J. Inorg. Nucl. Chem. 32* (1970) 3875.

18. Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed., VCH, Weinheim 1998; Gurmann, V. *The Donor–Acceptor Approach to Molecular Interactions*, Plenum Press, New York 1978.

19. Keita, B., Bouaziz, D. and Nadjo, L. *J. Electrochem. Soc. 135* (1988) 88.

20. Carloni, P. and Eberson, L. *Acta Chem. Scand. 45* (1991) 373.