Saccharose Complexes of Manganese in Different Oxidation States

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Abstract

The interaction between saccharose and manganese in different oxidation states was studied in alkaline media by polarographic, potentiometric, ESR spectroscopic and UV–Vis spectrophotometric methods. The results showed that stable manganese(II) and manganese(III) complexes and a complex of manganese(II,III) in a mixed oxidation state were formed with the composition $[Mn^{II}L(OH)_2]$, $[Mn_2^{III}L_2(OH)_8]^{2-}$ and $[Mn^{II}Mn^{III}L_2(OH)_6]^-$, respectively. The manganese(II)–saccharose complex was shown to dimerize in alkaline media. The stability constants of the Mn(II,III) and Mn(III) complexes were determined. The oxidation of the manganese(II)–saccharose complex by a stoichiometric amount of $K_3[FeCN]_6$ resulted in the formation of the manganese(III) and manganese(IV) complexes. However, oxidation by molecular oxygen only yielded the manganese(III) complex which reduced spontaneously in inert atmosphere to the mixed valence Mn(II,III) complex. The latter was able to be oxidized again by oxygen to the Mn(III) complex. This process proved to be reversible and could be repeated several times.

Introduction

Manganese plays a significant role in biological systems of vital importance (in photosystem II [1, 2], pyruvate carboxylase [3], superoxide dismutase [4], diamine oxidase [5], etc.). The biocatalytic behaviour of such macromolecules is mainly attributed to the presence of manganese in different oxidation states (+2, +3, +4) and its participation in the electron transfer processes.

To arrive at a better insight into the biological behaviour of such systems, manganese model complexes of low molecular weight simulating the bioactive molecule were synthetised and thoroughly investigated [6–13].

Recently Sawyer *et al.* [14] reported that the manganese(III) catechol system reversibly binds molecular oxygen in non-aqueous media. His system would appear to imitate the thermal step of the oxygen evolution model suggested by Kok *et al.* [15], for photosystem II. Our aim was to find a model of similar behaviour in aqueous solutions. Therefore, we began with the systematic study of manganese complex formation equilibria of sugar type ligands [16]. The present paper reports the results of our studies on saccharose complexes formed with manganese in different oxidation states.

Experimental

The polarographic, controlled-potential electrolysis, potentiometric and spectrophotometric measurements were performed as described in our previous paper [16]. The ESR spectra were recorded with a JEOL-JES-PE spectrometer in a standard quartz cuvette at room temperature. When working with solutions sensitive to oxygen, the cuvette was sealed.

Results and Discussion

Polarographic Studies

The polarographic characteristics of the manganese–saccharose system together with the results of controlled-potential electrolysis data performed to assist the assignment of the polarographic waves to the corresponding electron transfer processes, are presented in Table I. Some characteristic polarograms are shown in Fig. 1.

The polarogram of manganese(II) in the presence of excess saccharose in alkaline media and in inert atmosphere exhibits one anodic and one cathodic wave (Fig. 1, a). The cathodic wave is twice as high as the anodic one. According to the controlled potential electrolysis data, the cathodic wave can be assigned to the reduction of manganese(II) to

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TABLE I. Polarographic Characteristics of the Manganese–Saccharose System and the Corresponding Controlled Potential Electrolysis Data

Electrode process	$E_{1/2}$ (V *vs.* SCE)	α^c	$\bar{i}_d$ (μA)	Controlled potential electrolysis (V *vs.* SCE)	n
Mn(II) ⟶ Mn(III)[a]	−0.447	0.938	1.62	−0.30	1.02
Mn(II) ⟶ Mn(0)[a]	−1.732	0.832	3.50	−1.75	2.10
Mn(III) ⟶ Mn(II)[a]	−0.474	0.980	2.29	−0.600	0.99
Mn(II) ⟶ Mn(III)[b]	−0.542	1.004	1.89	–	–
Mn(II)–Mn(III) ⟷ Mn(III)–Mn(III)[b]	−0.493	1.019	1.8	–	–

Composition of the solutions: [saccharose] = 0.65 mol dm^{-3}; [manganese] = 2.5 × 10^{-3} mol dm^{-3}. [a][NaOH] = 1 mol dm^{-3}; [b][NaOH] = 3 mol dm^{-3}; [c]α = transition coefficient expressing the degree of reversibility; n = electron number changes obtained by controlled potential electrolysis.

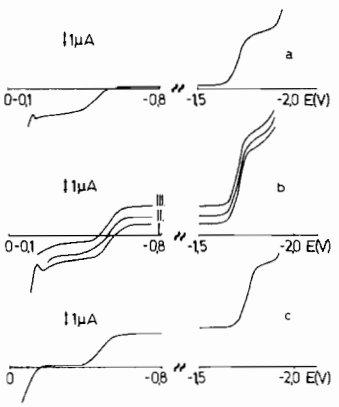

Fig. 1. Polarograms of the manganese–saccharose system: (a) [saccharose] = 0.65 mol dm^{-3}; [NaOH] = 1 mol dm^{-3}; [manganese] = 2.87 × 10^{-3} mol dm^{-3}. (b) [saccharose] = 0.65 mol dm^{-3}; [NaOH] = 3 mol dm^{-3}; [manganese] = 2.87 × 10^{-3} mol dm^{-3}. Recorded after storage of the solution in air for I. 5 min; II. 10 min; III. 30 min. (c) as (a) but with manganese(III) in the solution.

manganese(0), and the anodic wave to the oxidation of manganese(II) to manganese(III). The oxidation of manganese(III) to manganese(IV) does not appear on the polarogram. Because of the low redox potential of the latter process (see below), it is covered by the anodic dissolution of the mercury electrode.

The logarithmic analysis of the polarograms indicated that the anodic wave is reversible, while the cathodic wave is quasi-reversible.

On the basis of the dependence of the limiting current on the height of the mercury column, only the oxidation wave was found to be diffusion-controlled; the reduction wave was not. This may be explained by the formation of a non-conducting film on the surface of the mercury drop in the latter system [7].

The colour of the alkaline solution of manganese(II), in the presence of excess saccharose stored in an open beaker in air for 30 min, showed a gradual change from pale yellow through violet to brown. The violet colour appeared quickly and its intensity gradually increased. Recording the polarogram of the solution several times during the latter colour change, the originally anodic Mn(II) → Mn(III) wave was gradually transformed to a redoxi wave (Fig. 1, b). The intensity of the violet colour (the absorbancy at 490 nm wavelength) was found to attain the highest value when the intensities of the anodic and cathodic parts of the redoxi wave equalized. On the basis of these investigations, we suggest that the chromophore in the violet coloured solution is a binuclear manganese complex with one manganese(II) and one manganese(III) central atom. This violet complex was also formed during the controlled potential electrochemical oxidation taking place at −0.30 V *vs.* SCE.

If oxygen was bubbled through the alkaline solution of manganese(II) containing excess saccharose for 60 min, a brown chromophore was formed. The polarogram of this brown solution exhibited two cathodic waves (Fig. 1, c). On the basis of controlled potential electrolysis data the reduction of Mn(III) to Mn(II) could be assigned to the first cathodic wave ($E_{1/2}$ = −0.474 V *vs.* SCE), and that of Mn(II) to Mn(0) to the second one ($E_{1/2}$ = −1.732 V *vs.* SCE).

For the determination of the composition of the complexes (metal:saccharose:hydroxide ratio), formed in the solutions, the shift of the half-wave potential of the manganese(II) reduction was measured as a function of the hydroxide ion and saccharose concentrations, respectively. From measurements in a concentration range in which only complexes of the maximum coordination number were formed, aware of the change in electron number (n) during the electrode process, the following relationship

$$\Delta E_{1/2} = -p \frac{0.0591}{n} \log \Delta C_x \qquad [17]$$

led to the determination of the number of ligands (p), bound in the complex. ($\Delta E_{1/2}$ represents the

TABLE II. Changes due to the Electrode Process in the Number of Ligands Bound by one Metal

Electrode process	Changes in the number of ligands per metal in the electrode process	
	OH^-	saccharose
Mn(II) ⟶ Mn(0)	−1.04	−1.90
Mn(II) ⟶ Mn(III)	0	+1.82
Mn(III) ⟶ Mn(II)	0	−1.85
Mn(II) ⇄ Mn(III)	0	±2.0

half-wave potential change caused by ΔC_x ligand concentration change). The results are presented in Table II. It can be seen that the electrode reduction of Mn(II) to Mn(0) takes place according to the following equation

$$Mn^{II}L(OH)_2 + 2e \longrightarrow Mn^0 + L + 2OH^-$$

i.e. in the course of the reduction two hydroxide ligands and one saccharose ligand are liberated.

For analysis of the oxidation wave of Mn(II) → Mn(III) and the reduction wave of Mn(III) → Mn(II) in the alkaline solution with saccharose, the relationship

$$\Delta E_{1/2} = -(p - q)\ \frac{0.0591}{n} \log \Delta C_x \qquad [18]$$

was applied in which (beyond the symbols known) p and q represent the number of ligands bound to one metal ion in the oxidized and reduced complexes, respectively.

According to the results shown in Table II the number of saccharose ligands bound in the complex did not change during the oxidation of Mn(II) → Mn(III), but the complex retained two hydroxide ions per manganese atom. Analogously, in the course of the Mn(III) → Mn(II) transition, two hydroxide ions were released. The dependence of the half-wave potential of the redoxi wave on the hydroxide ion concentration also indicated that, during this process, two hydroxide ions were liberated and retained, respectively, without a change in the number of saccharose molecules in the complex.

Plotting the limiting current of the polarographic reduction of manganese(II) (in the presence of saccharose excess) as a function of the hydroxide ion concentration in the solution led to a maximum curve. On the basis of the results of the ESR spectroscopic studies of the manganese(II)–saccharose complex (see below) and literature analogies [7], we assume that the reason for this phenomenon was a hydroxide concentration dependent monomer–dimer equilibrium in the solution which shifted to dimer formation in strongly alkaline media (at 1–4 mol dm^{-3} sodium hydroxide). The dimer manganese(II) complex $[Mn_2L_2(OH)_4]$ participated in the electrode reactions according to the following equations (taking into consideration the results shown in Table II):

(a) oxidation of the manganese(II) complex to the violet mixed valence manganese complex

$$[Mn_2^{II}L_2(OH)_4] + 2OH^- \rightleftarrows [Mn^{II}L(OH)_2Mn^{III}L(OH)_4]^- + e$$

(b) oxidation of the violet complex to the brown manganese(III) complex:

$$[Mn^{II}L(OH)_2Mn^{III}L(OH)_4]^- + 2OH^- \rightleftarrows [Mn_2^{III}L_2(OH)_8]^{2-} + e$$

(c) oxidation of the dimer manganese(II) complex to the corresponding manganese(III) complex:

$$[Mn_2^{II}L_2(OH)_4] + 4OH^- \rightleftarrows [Mn_2^{III}L_2(OH)_8]^{2-} + 2e$$

The formation of manganese(IV) species was not observed in either system.

The equilibrium constants of the formation of the manganese saccharose complexes in alkaline media (the corresponding conditional stability constants) could not be determined by the conventional DeFord–Hume method [24] since, in the absence of saccharose, the hydrolysis products of manganese ions precipitated from the alkaline solution.

The competitive method (with EDTA as auxiliary ligand), used successfully in our previous studies [16] in the manganese lactiobionate system, also failed in the case of the manganese(II) saccharose complex because of the considerable difference between the stabilities of the saccharose and EDTA complexes of manganese(II). The latter method proved to be suitable, however, for the determination of the stability constants of the mixed valence Mn(II)–Mn(III) and of the Mn(III) saccharose complexes, respectively.

This method is based on the fact that all manganese EDTA complexes are polarographically inactive and the limiting current of the reduction wave of the manganese saccharose complexes increases linearly according to the Ilkovič equation with manganese concentration.

Knowing the total concentrations of manganese, saccharose, hydroxide ions and of EDTA used as auxiliary ligand as well as the composition (metal: ligand ratio) of the complexes formed, and the stability constants of the EDTA complexes, the corresponding conditional constants could be calculated from the decrease of the diffusion current in the manganese saccharose system due to the presence of EDTA. The detailed calculation mode is presented in our previous paper [16]. The results are shown in Table III. The extremely high values of the conditional complex products reflect the great stability of the saccharose complexes in alkaline media.

TABLE III. Overall Formation Equilibrium Constants (β Complex Products) of the Saccharose Complexes

Total concentrations (mol cm^{-3})			Composition of the complex	log β values
Mn	Saccharose	OH^-		
1.35×10^{-3}	0.65	3.0	$[Mn^{II}L(OH)_2Mn^{III}L(OH)_4]^-$	37.0
1.35×10^{-3}	0.55	1.0	$[Mn_2^{III}L_2(OH)_8]^{2-}$	51.9

Potentiometric Studies

To complement the polarographic study of the Mn(II) → Mn(III) transition in the saccharose complexes, the oxidation of manganese(II) by a 0.05 mol dm^{-3} hexacyanoferrate(III) standard solution was performed potentiometrically using platinum and saturated calomel electrodes in an oxygen-free nitrogen atmosphere in systems of analogous composition with those studied by polarography. A typical titration curve is shown in Fig. 2, curve 1. It can be seen that the oxidation takes place in two steps, each corresponding to one electron transfer. The Mn(II) → Mn(III) oxidation step occurs at ~−400 mV *vs.* SCE in agreement with the polarographic $E_{1/2}$ value. The Mn(III) → Mn(IV) oxidation takes place at ~0 mV on the same scale. For this reason, the latter step did not appear on the dropping mercury electrode. The formation of the manganese(IV) complex in the second step of the oxidation reaction was also reflected by the UV–Vis spectra of the system. The manganese(IV) complex thus formed could be reduced by an equivalent amount of manganese(II) to the manganese(III) complex which could be oxidized by an equivalent amount of the standard hexacyanoferrate(III) solution in one step to the manganese(IV) complex (Fig. 2, curve 2).

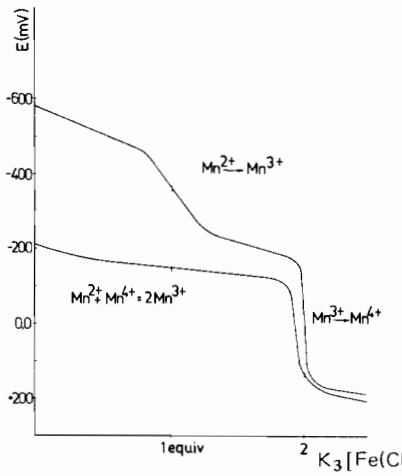

Fig. 2. Potentiometric titration curves of the manganese(II)–saccharose system by 0.05 mol dm^{-3} hexacyanoferrate in 2.5 mol dm^{-3} sodium hydroxide and 0.5 mol dm^{-3} saccharose solution in an inert atmosphere using Pt and SCE electrodes; T = 293 K; [manganese] = 1.80×10^{-3} mol dm^{-3}.

Spectroscopic Studies

ESR measurements

The ESR spectrum of the aqueous solution containing 2.85×10^{-3} mol dm^{-3} manganese(II) and 0.5 mol dm^{-3} saccharose (pH < 6) showed 6 lines of almost the same intensity which corresponds to the 5/2 nuclear spin of manganese (Fig. 3, curve 1). This spectrum is practically identical to that of any manganese(II) salt solution of similar concentration. The spectrum was 650 G broad with a g value of 2.017 ± 0.020.

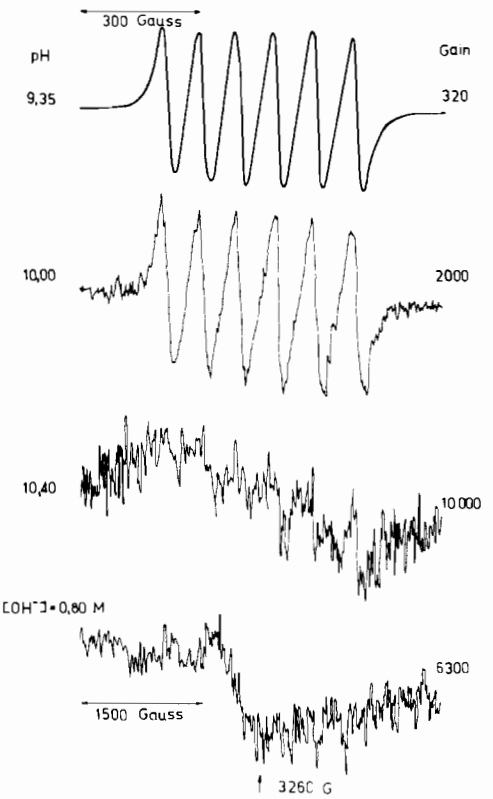

Fig. 3. The change of the ESR spectrum of the manganese(II)–saccharose complex with the pH of the solution [manganese(II)] = 2.85×10^{-3} mol dm^{-3}; [saccharose] = 0.50 mol dm^{-3}. Instrumental conditions: microwave frequency, 9.276 Hz; microwave power, 15 mV; modulation frequency, 100 kHz; modulation amplitude, 10 G; sample temperature, 300 K; response, 0.3 s; sweep time, 4 min. Relative scale factors on each spectrum were adjusted so that all signals should have equal intensity.

Increasing the pH of this solution by adding sodium hydroxide in an inert atmosphere did not cause any change in the pattern of the spectrum till pH ~10; only its intensity decreased (Fig. 3, curve 2). The further increase of pH resulted, however, in significant changes. At pH ~10.4 the intensity of the six-line pattern decreased further then started to be transformed into a broad curve (Fig. 3, curve 3). The latter increased in intensity with increasing pH of the solution, becoming dominant in strongly alkaline media where the six line pattern completely disappeared (Fig. 3, curve 4). The resulting broad line was 1500 G broad, showed a g value of 2.017 ± 0.020 and an intensity about twenty times smaller than that of the original manganese(II) spectrum.

This change in the ESR signal indicated that due to the increase of the pH in the aqueous, manganese(II) solution with excess saccharose, the manganese(II) complex dimerized, resulting in a decrease in the number of unpaired electrons. This behaviour is analogous with that observed for manganese(II) gluconate [7].

If oxygen was bubbled through the solution of the strongly alkaline manganese(II)–saccharose system, the intensity of the ESR signal gradually decreased, then disappeared, indicating the oxidation of the manganese(II) complex to the corresponding manganese(III) one.

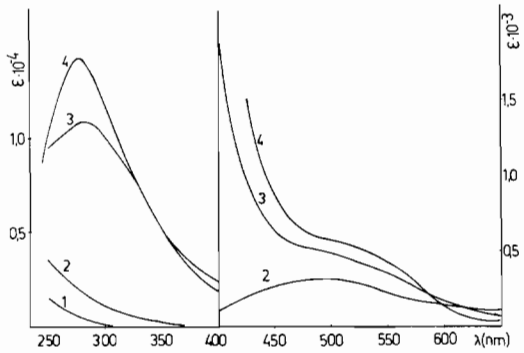

Fig. 4. Absorption spectra of the manganese–saccharose complexes in 3 mol dm^{-3} sodium hydroxide: (1) manganese(II); (2) manganese(II,III); (3) manganese(III); (4) manganese(IV).

UV–Vis spectroscopic measurements

The UV–Vis spectra of the manganese(II), manganese(II,III) mixed valence, manganese(III) and manganese(IV) saccharose complexes were recorded in solutions which contained the components in suitable concentrations to assure the quantitative formation of the complexes (Fig. 4). The spectrum of the manganese(II) complex does not show any characteristic maxima, the absorbance increases towards the UV range similarly to that of the corresponding gluconate and lactobionate complexes

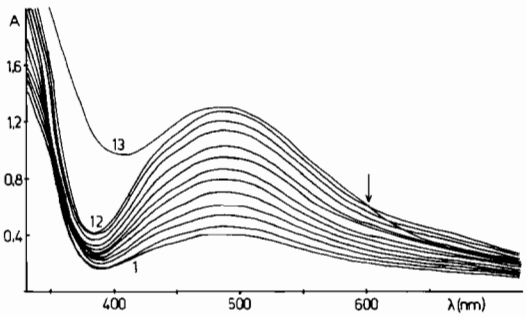

Fig. 5. Oxidation of the manganese(II) complex by molecular oxygen to the mixed valence Mn(II,III) complex. Curves 1–12: the time of oxygenization gradually increases. Curve 13 shows the start of oxidation of the manganese(II,III) complex to the manganese(III) one.

[7, 16]. The mixed valence manganese(II,III) complex yields a maximum at 490 nm (ϵ = 324 M^{-1} cm^{-1}) and a minimum at 380 nm (ϵ = 79 M^{-1} cm^{-1}). The spectrum of the manganese(III)–saccharose complex reveals a shoulder at about 500 nm (ϵ = 511) and a maximum of high intensity at 280 nm (ϵ = 10 810). Although the spectrum of the manganese(IV) complex is similar to that of the manganese(III) complex, the molar absorbancy values significantly differ. There is a shoulder at about 500 nm (ϵ = 580) and a maximum at 275 nm (α = 14 200).

In order to study the chemical oxidation of the manganese(II)–saccharose complex, oxygen was bubbled through its alkaline solution and the spectrum of this solution was periodically recorded. The series of the spectra indicated the appearance and an increase in concentration of the violet mixed valence manganese(II,III) complex as a function of the oxidation time (Fig. 5). The polarogram of the solution containing the maximum concentration of the violet complex, according to the spectrum, showed a redoxi wave. The mixed valence complex could be oxidized quantitatively to the corresponding manganese(IV) complex by 0.05 mol dm^{-3} standard hexacyanoferrate(III) solution. For the complete oxidation 1.5 equivalent of the standard solution per manganese was needed. Thus, this measurement also proved the +2 and +3 oxidation states of manganese central atoms in the violet complex.

The mixed valence (violet) complex could be oxidized gradually by the addition of oxygen to the manganese(III) complex. The series of spectra recorded periodically during this oxidation process displayed an isosbestic point at 608 nm indicating the equilibrium of the two saccharose complexes (Fig. 6). The polarogram recorded for the solution, after complete oxidation of the manganese content in the complex, reflected the cathodic reduction of Mn(III) → Mn(II). The +3 oxidation state of manganese in the complex was also proved by oxidizing it

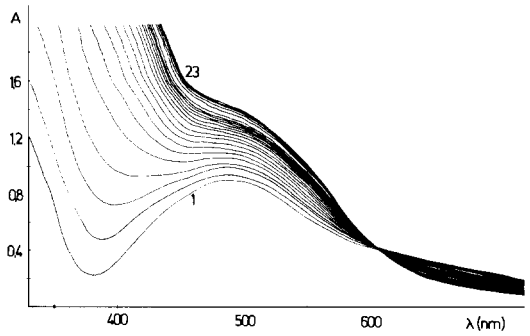

Fig. 6. Oxidation of the manganese(II,III) complex by molecular oxygen to the manganese(III) complex. Curves 1–23; the time of oxygenization gradually increases.

to manganese(IV) with the aid of the hexacyanoferrate(III) standard solution. For the complete oxidation, 1.0 equivalent of the oxidizing agent per manganese was required.

Storing the solution, containing the manganese(III) complex prepared by oxidation of the mixed valence manganese(II,III) complex by oxygen, in an oxygen-free nitrogen atmosphere for 24 h, the complex spontaneously reduced to the parent mixed valence (violet) complex. The whole procedure proved to be completely reversible and was repeated several times. The Mn(II,III) saccharose complex was again oxidized by bubbling oxygen through its alkaline solution to the corresponding Mn(III) complex which was reduced back to the Mn(II,III) complex in an inert atmosphere. Further investigations are planned to determine the mechanism of these processes.

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