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The Electrochemical Investigation of the Manganese Complexes of Lactobionic Acid

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Abstract

Interaction of manganese in different oxidation states with lactobionate ions in alkaline media was studied by polarographic, pH-metric and spectrophotometric methods. The results demonstrated that the lactobionate ligand forms stable parent and hydroxo mixed complexes with manganese(II) and manganese(IV), even in alkaline media. The composition of the complexes, and in the case of the manganese(II) system the corresponding conditional stability constants, were determined. The central atom of the manganese(III) complex is reduced to manganese(II) by the coordinated ligand. For comparison some analogous gluconate complexes were also studied.

Introduction

In spite of the great biological importance of carbohydrates and their derivatives, relatively few works [1, 2] have been published about their complex-forming characteristics, especially about their transition-metal complexes [3, 4, 5]. It is known that manganese plays a significant role in some biological redox systems of vital importance, *e.g.* photosystem II in green-plant photosynthesis [6, 7], mitochondrial superoxide dismutase [8], *etc.* The oxidation states +2, +3 and +4 of manganese seem to be involved in the redox systems, although their role has not been cleared completely until now.

Sawyer *et al.* studied the complex formation equilibria of manganese ions with D-gluconate and the kinetics [9, 10, 11] of the redox reactions of this complex in the presence and in the absence of oxygen. According to these authors the manganese–gluconate complexes can serve as a model of the photosynthetic oxygen evolution. Searching also for the model of the photosynthetic water-oxidation, the binuclear manganese(III)–β-cyclodextrene complex [12] has been synthesised.

Doležal *et al.* [13–16] investigated the interaction of some polyhydroxy ligands with manganese of different oxidation states in alkaline media by polarographic and potentiometric methods. Later Sawyer *et al.* studied the redox equilibria [17] of the manganese(II)–sorbit system, considered the most stable among these types of complexes (conditional stability constant 1.94×10^{16} mol^{-1}).

According to biochemical considerations the complexes of lactobionic acid, having greater molecular weights, can better simulate *in vivo* processes than can simpler complexes of monosaccharides and their derivatives. This initiated our investigations on the manganese complexes of lactobionic acid. The results of our equilibrium studies are presented below.

Experimental

The polarograms were recorded on a Radiometer PO4 Type polarograph. A saturated calomel electrode served as reference, the mercury height was usually 55 cm, the capillary constants: m = 2.04 mgs^{-1}, t = 3.4 s.

For controlled-potential electrolysis a Radelkis Model OH-404 Universal coulometric analyser was used. A mercury-pool electrode served as working electrode, and a platinum coil as counter electrode. The reference electrode was a saturated calomel one. The inert-atmosphere was secured by bubbling oxygen-free nitrogen through the solution.

For pH measurement a Radelkis Model OP 208/1 precision digital pH-meter was used. The spectrophotometric measurements were performed on a UNICAM SP 800 recording spectrophotometer using quartz cells of proper thickness.

The thermoanalytical curves of the manganese(IV)–lactobionate complex were recorded on a MOM-Q derivatograph. The heating rate was 10 °C/min, between 25–850 °C.

The electroanalytical and spectrophotometric measurements were carried out in solutions thermostatted to 20 ± 0.5 °C.

All reagents used were of analytical purity.

The manganese(II) stock solution was prepared from $MnSO_4 \cdot nH_2O$ (Reanal) and standardized with EDTA complexometrically. Lactobionic acid and Na-gluconate were Merck products. The 1 mol dm^{-3} stock solution of lactobionic acid was neutralized with sodium hydroxide.

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TABLE I. Polarographic Characteristics of Manganese–Lactobionate Complexes and the Results of the Corresponding Controlled Potential Electrolysis Studies (composition of the solutions: 4.5×10^{-3} mol dm^{-3} manganese; 4.5×10^{-2} mol dm^{-3} lactobionic acid; 1.77 mol dm^{-3} NaOH).

Electrode process	$E_{1/2}$ (V) *vs.* SCE	α [a]	Controlled pot. electrolysis (V) *vs.* SCE	n[b]
Mn(II) → Mn(III)	−0.615	0.865	–	–
Mn(II) → Mn(IV)	–	–	−0.22	2.04
Mn(II) → Mn(0)	−1.670	0.794	−1.70	2.03
Mn(III) → Mn(IV)	−0.315	0.954	–	–
Mn(III) → Mn(II)	−0.630	0.991	–	–
Mn(IV) → Mn(III)	−0.320	1.089	−0.45	0.98
Mn(IV) → Mn(II)	–	–	−1.30	1.97

[a] α is the transfer coefficient derived from the log plot analysis of the polarograms, expressing the degree of irreversibility of the electrode process. [b] n the change in the number of electrons determined by controlled potential electrolysis.

Manganese(III) acetate was prepared according to [18]. Its manganese(III) content was determined iodometrically. The 10 mol dm^{-3} sodium hydroxide (Reanal) solution was purified according to D'Ans and Mattner [19].

Preparation of the Manganese(IV)–Lactobionate Complex

2 cm^3 1 mol dm^{-3} manganese(II) sulphate solution, 20 cm^3 1 mol dm^{-3} neutral sodium lactobionate solution and 2.4 cm^3 10 mol dm^{-3} sodium hydroxide solution were mixed. Oxygen was bubbled through the solution for 20 min, while manganese(II) was oxidized to manganese(IV). The manganese(IV)–lactobionate complex was precipitated by addition of acetone and isolated by centrifugation. The precipitate was dissolved in a small amount (approx. 2.5 cm^3) of water and re-precipitated by acetone, and the centrifugation was repeated. The complex was washed with acetone and ether and was dried over phosphorpentoxide. The manganese(IV)–lactobionate complex is a light brown powder. Its composition was determined by standard microanalytical methods, the sodium content by flame photometry and that of manganese by atomic absorption.

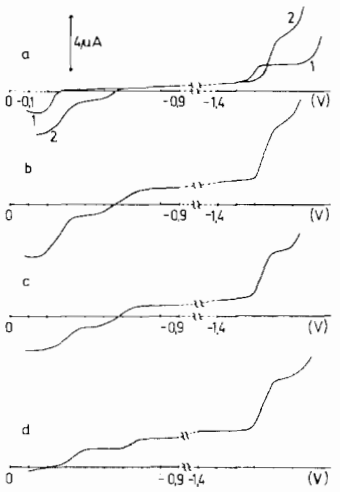


Fig. 1. Polarograms of the manganese–lactobionate system: (a1) 4.54×10^{-3} mol dm^{-3} Mn(II); 4.54×10^{-2} mol dm^{-3} lactobionic acid; 9.09×10^{-2} mol dm^{-3} NaOH; (a2) The same as in Fig. a1 except 1.77 mol dm^{-3} NaOH; (b) 4.16×10^{-3} mol dm^{-3} Mn(II); 19.2×10^{-2} mol dm^{-3} lactobionic acid; 1.66 mol dm^{-3} NaOH kept in the air for 10 min; (c) The same as Fig. a2 + 5.0×10^{-3} mol dm^{-3} Mn(III)–acetate; (d) 4.54×10^{-3} mol dm^{-3} Mn(IV); 4.54×10^{-2} mol dm^{-3} lactobionic acid; 1.77 mol dm^{-3} NaOH.

Results and Discussion

Polarographic Studies

The polarographic characteristics of the manganese lactobionate system, together with the results of the controlled potential electrolysis data performed to help the assignment of the corresponding polarographic waves, are presented in Table I. Some characteristic polarograms are shown in Fig. 1.

The analysis of the polarograms was performed by plotting lg $i/(i_d - i)$ against E (where E and i are the corresponding potential and current values and i_d the diffusion current) to determine the value of the half-wave potential ($E_{1/2}$) and—in the knowledge (from the controlled potential measurements) of the number of electrons (n) participating in the electrode reaction—the degree of reversibility of the process characterized by α in the equation:

$$\log \frac{i}{i_d - i} = \frac{\alpha n}{0.059} (E_{1/2} - E)$$

The dependence of the limiting current (i_d) on the height of the mercury column was determined for each polarogram to check the diffusion-controlled character of the waves.

In some cases chemical reactions were also used to get independent information on the character of the electrode reaction reflected by a polarographic wave.

Our main aim was to get information on the composition and stability of the manganese complexes participating in the electrode reactions. The ligand concentration dependence of the half-wave potential and the competition reaction using EDTA as auxiliary ligand was used for this purpose. The results are summarized in the following.

The polarogram of manganese(II) (Fig. 1) in a solution containing lactobionate ions (in a metal: ligand ratio of 1:10) in strongly alkaline media (NaOH $>$ 0.2 mol dm^{-3}) and in inert-atmosphere exhibits two oxidation waves (with half-wave potentials of -0.615 and -0.315 V *vs.* SCE) and one reduction wave (-1.670 V *vs.* SCE). The ligand cannot be reduced or oxidized on the dropping mercury electrode.

The first oxidation wave ($E_{1/2} = -0.615$ V) is considerably lower than the second one ($E_{1/2} = -0.315$). The reduction wave is almost twice as high as the first oxidation wave. The manganese(II)–lactobionate complex could easily be oxidized by the oxygen content of air in alkaline media. This results in the increase of the height of the first oxidation wave, which shows a small shift in the cathodic direction and takes up a redox character (Fig. 1, curve b).

Similar results are obtained when Mn(III)–lactobionate complex prepared from Mn(III) acetate is added to the solution containing the manganese(II) complex (Fig. 1, curve c). This indicates that the first oxidation wave can be assigned to the oxidation step of Mn(II) to Mn(III), henceforward the second oxidation wave belongs to the oxidation of Mn(III) to Mn(IV). The polarogram of manganese(III)–lactobionate when completely free of manganese(II) could not be recorded, because manganese(III) was partly reduced by the ligand during the measurements and manganese(II) appeared in the solution.

The reduction wave appearing with a half-wave potential of -1.670 V *vs.* SCE can be assigned to the reduction of manganese(II)–manganese(0) in accordance with the controlled potential electrolysis measurements.

The analysis of the polarographic waves proved that both oxidation waves are reversible, while the reduction of manganese(II) to manganese(0) is quasi-reversible.

If the sodium hydroxide concentration was lower than 0.2 mol dm^{-3}, the polarogram of the manganese(II)–lactobionate complex displayed only one oxidation and one reduction wave with half-wave potential of -0.22 and -1.58 V *vs.* SCE, respectively. Both waves correspond to two-electron processes, and the transition of manganese(II) to manganese(III) does not appear in an independent wave.

In alkaline media manganese(II)–lactobionate is water-soluble and can be oxidized by oxygen to a manganese(IV)–lactobionate complex. The oxidation state of manganese was controlled iodometrically. The polarogram of the manganese(IV) complex (Fig. 1, curve d) exhibits three well-defined reduction waves, all diffusion-controlled.

The half-wave potential of the different polarographic waves do not differ considerably from the data obtained by Sawyer *et al.* [10] for the manganese–gluconate complexes. This indicates that the gluconate moiety of lactobionic acid plays a significant role in the complex formation.

The reduction wave of Mn(IV) to Mn(III) was higher than the transition of Mn(III) to Mn(II). This indicates that the electrochemical reduction of manganese(III) is accompanied by its chemical reduction, the reducing agent being presumably galactose, the monosaccharide component of lactobionic acid. This suggestion is supported by the following results:

(a) The oxidation capacity of the manganese(III)–lactobionate complex prepared from manganese(III) acetate decreased in solution almost to zero during its storage in inert-atmosphere for two days.

(b) The change in the number of electrons observed during the coulometric oxidation of the manganese(II)–lactobionate complex at -0.35 V *vs.* SCE is not reproducible and shows a surprisingly high value (3–5). This indicates that manganese(III) formed in the course of oxidation is reduced to manganese(II), which is oxidized again, etc. Examples for the reducing effect of the galactose moiety in lactobionic acid can also be found elsewhere [20].

In the case of reversible electrode processes polarographic data can be used to determine the composition (metal:ligand ratio) of the complexes.

Accordingly, the shift of the half-wave potential of the reduction of manganese(II) was measured as a function of the hydroxide and the organic ligand (lactobionate) concentrations, respectively. Assuming that in the concentration range studied only the complex of maximum coordination number is formed, in the knowledge of the change in the number of electrons and by use of the following relationship [21]:

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

the maximum coordination number (p) can be calculated, where C_x is the ligand concentration, and n the change in the number of electrons during the electrode process. The results are presented in Table II. Two hydroxide ions and one lactobionate ligand are coordinated in the manganese(II)–lactobionate complex.

For the analysis of the oxidation waves of the manganese(II) complex the relation [22]:

TABLE II. The Composition of the Complexes before and after the Electrode Process.

Electrode process	Number of ligands		Change in the number of	
	Lactobionate	OH^-	lactobionate due to the electrode reaction	OH^-
Mn(II) → Mn(III)	–	–	0.75	1.18
Mn(III) → Mn(IV)	–	–	0.25	0.97
Mn(II) → Mn(0)	1.0	2.03	–	–
Mn(IV) → Mn(III)	–	–	0.99	1.98

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

was used, in which C_x is the ligand concentration, and p and q are the number of ligands per metal ion in the oxidized and reduced complexes, respectively. According to these data the oxidation of manganese(II) to manganese(IV) taking place in two steps requires two additional hydroxide and one additional lactobionate ligand, as shown in the following equation:

$$Mn^{II}L(OH)_2 + L + 2OH^- \longrightarrow Mn^{IV}L_2(OH)_4^{2-}$$

The stability constants of the manganese(II)–lactobionate complex could not be determined from the half-wave potential shift in solutions of different ligand concentrations, according to the DeFord-Hume method [23], because of the precipitation of metal hydroxide in alkaline media. Therefore the corresponding equilibrium constants were determined on the basis of the competition between lactobionate and EDTA ligands for manganese(II). The manganese(II)–EDTA complex is polarographically inactive, and the diffusion current of the reduction wave of manganese(II)–lactobionate increases linearly according to the Ilkovic equation in the manganese(II) concentration range of 0–0.005 mol dm^{-3}.

Due to the addition of EDTA to the solutions containing the manganese(II)–lactobionate complex, the height of the original Mn(II) → Mn(0) wave ($\bar{i}_{d1}$) decreases considerably (to $\bar{i}_{d2}$) (Fig. 2). On the basis

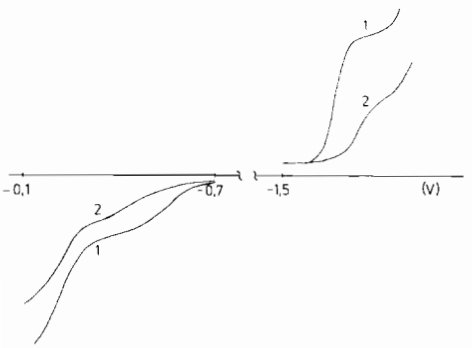


Fig. 2. The polarogram of the manganese(II)–lactobionate complex in the absence (Curve 1) and in the presence (Curve 2) of EDTA.

of the polarographic studies discussed above the composition of the manganese(II)–lactobionate complex is $MnL(OH)_2$.

Thus $\bar{i}_{d1} = k[MnL(OH)_2]$, $K_{MnL} = [MnL(OH)_2]/[Mn^{2+}][L][OH^-]^2$, $\bar{i}_{d2} = k([MnL(OH)_2] - [MnY])$, $K_{MnY} = [MnY]/[Mn^{2+}][Y]$ where k is the Ilkovic constant, K_{MnL} and K_{MnY} are the stability constants of lactobionate and EDTA complexes of manganese(II), respectively, $K_{MnY} = 7.41 \times 10^{13}$ according to [24]. The formulae in square brackets refer to concentrations in the constant ionic strength media.

From the above equations we get:

$$K_{MnL} = \frac{\bar{i}_{d1}}{\bar{i}_{d1} - \bar{i}_{d2}} K_{MnY} \frac{[Y]}{[L][OH^-]^2}$$

where [Y] denotes the EDTA concentration not bound by manganese and [L] the total lactobionate concentration, which is considered to be equal (within the experimental error) to the free L concentration.

The K_{MnL} conditional stability constants obtained in this way for solutions with 0.909 mol dm^{-3} NaOH, 4.54×10^{-3} mol dm^{-3} Mn^{2+} and $9.0–20.0 \times 10^{-2}$ mol dm^{-3} lactobionic acid concentrations were found to be:

$$\log K_{MnL} = 13.0$$

In a similar way and under identical conditions the conditional stability constant of manganese(II)–gluconate was determined, assuming according to [10] a complex composition of 1:2 metal:ligand ratio, and was found to be $\log \beta_2 = 14.7$.

Spectrophotometric Studies

The spectrophotometric characteristics of the manganese–lactobionate complexes are summarized in Table III and some typical absorption spectra are shown in Fig. 3. The manganese(II) complex has no characteristic absorption maximum, the absorbance increasing continuously in the UV spectrum.

The K_{MnL} conditional stability constant of the manganese(II)–lactobionate complex has also been determined by spectrophotometric methods, using the same EDTA competition as in the polarographic measurements. The result, $\log K_{MnL} = 12.9$ obtained

TABLE III. Spectrophotometric Characteristics of Manganese–Lactobionate Complexes.

Oxidation number of manganese	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	colour	NaOH (mol dm^{-3})
Mn(II)	–	at 250 nm 1299	light yellow	0.909
Mn(III)	235	1870	brown	0.1
Mn(IV)	288 shoulder 500	10880	red	1.0

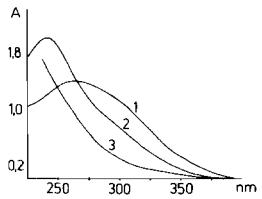


Fig. 3. Absorption spectra of manganese–lactobionate complexes: (1) manganese(IV) complex (5.88×10^{-4} mol dm^{-3} Mn(IV) + 5.88×10^{-2} mol dm^{-3} ligand +0.29 mol dm^{-3} NaOH); (2) manganese(III) complex (1.0×10^{-3} mol dm^{-3} Mn(III) + 5.0×10^{-3} mol dm^{-3} ligand +0.1 mol dm^{-3} NaOH); (3) manganese(II) complex (5.88×10^{-4} mol dm^{-3} Mn(II) + 5.88×10^{-2} mol dm^{-3} ligand +2.3 mol dm^{-3} NaOH).

in 0.77 mol dm^{-3} sodium hydroxide, is in very good agreement with the value obtained by the polarographic method.

The metal:lactobionate ratio in the manganese(IV) complex was determined from the ligand concentration dependence of the absorption spectrum.

Manganese(II) solutions containing manganese and lactobionate in different ratios were oxidized and the absorption spectra were recorded in the range of 250–550 nm. The absorbance was plotted against the ligand concentration. The resulting curves show sharp breaking points at metal:ligand ratios of 2:3. A lower ligand content resulted in the precipitation of black manganese(IV) dioxide. This indicates that in solutions of lower metal:ligand ratios a binuclear manganese(IV) complex is formed which contains three lactobionate ligands.

Potentiometric Studies

The number of OH^--ions consumed during the complex formation per metal ion ($\overline{OH}$) was determined by Calvin-type titrations in solutions with different ligand-to-metal ratios. In addition to the manganese–lactobionate system the manganese–gluconate system was also studied.

The results are shown in Fig. 4. Deprotonation starts in the course of the formation of the manganese(II)–lactobionate complex at about pH = 8.5, the $\overline{OH}$ number reaches 2.0 at pH 11, then gradually increases till 3. The manganese(II)–

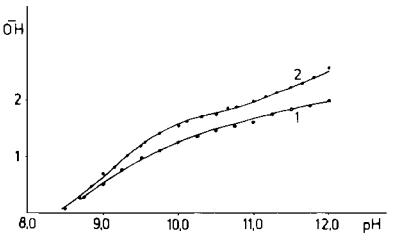


Fig. 4. The measured (●) and calculated (–) $\overline{OH}$-number-pH functions in the manganese(II)–gluconate (Curve 1) and –lactobionate (Curve 2) systems.

gluconate system behaves similarly, the only difference is that the $\overline{OH}$ number shows saturation at $\overline{OH} \sim 2$ near pH = 12.

Naturally this type of equilibrium study cannot distinguish between the different deprotonation processes e.g. hydrolysis of the central ion or the complex (formation of hydroxo mixed ligand complexes), or the deprotonation of the organic ligand. The carboxylic group of gluconic acid and lactobionic acid is completely dissociated at pH > 5 (pK = 3.56 and 3.37, respectively), thus it is available for the formation of the complex in the whole pH range studied.

Comparing the results of the polarographic investigations with those of the Calvin type titrations one may conclude that one of the three protons released during the latter investigation is due to the deprotonation of the lactobionate ligand, the other two coming from the formation of the dihydroxo mixed complex $MnL(OH)_2^{2-}$:

$$MnLH^+ \rightleftharpoons MnL + H^+ \qquad K_{dp}$$

$$MnL + OH^- \rightleftharpoons MnL(OH)^- \qquad K_1$$

$$MnL(OH)^- + OH^- \rightleftharpoons MnL(OH)_2^{2-} \qquad K_2$$

The $\overline{OH}$ number is:

$$\overline{OH} = \frac{C_{OH} - [OH^-]}{C_{Mn}}$$

(where C_{OH} and C_{Mn} are the corresponding total concentrations) which can be expressed with the help of the concentrations and equilibrium constants as:

$$\overline{OH} = \frac{K_{dp}[OH^-] + 2K_{dp}K_1[OH^-]^2 + 3K_{dp}K_1K_2[OH^-]^3}{K_w + K_{dp}[OH^-] + K_{dp}K_1[OH^-]^2 + K_{dp}K_1K_2[OH^-]^3}$$

where K_w is the ionic product of water.

On the basis of the above model a non-linear curve-fitting program has been constructed for the calculation of K_{dp} deprotonation, and K_1 and K_2 hydroxo complex formation constants, respectively. The results are presented in Table IV. By help of the equilibrium constants the computer simulated the experimental $\overline{OH}$-pH curves. The agreement within the experimental and calculated values in Fig. 4 supports the above interpretation.

TABLE IV. Deprotonation and Hydroxo Complex Formation Constants of the Manganese–Lactobionate and –Gluconate Complexes.[a]

Complex	log K_{dp}	log K_i	i
$[Mn^{II}L(OH)_2]^{2-}$	−9.84 ± 0.10	5.23 ± 0.20	1
		1.95 ± 0.15	2
$[Mn^{II}(GH)_2]^{2-}$	−9.95 ± 0.18	–	
	−11.5 ± 0.20		

[a] L denotes the deprotonated lactobionate ligand and GH the deprotonated gluconate.

In accordance with the statement of Sawyer *et al.* [10] we assumed that in the pH range examined manganese(II) forms with gluconate a parent complex of a 1:2 metal:ligand ratio, the deprotonation of which takes place according to the following eqns.:

$$Mn(G\dot{H})_2 \rightleftharpoons Mn(GH)(G)^- + H^+ \qquad K_{dp1}$$

$$Mn(GH)(G)^- \rightleftharpoons MnG_2^{2-} + H^+ \qquad K_{dp2}$$

The $\overline{OH}$ number can be expressed in the form:

$$\overline{OH} = \frac{K_{dp1}K_w[OH^-] + 2K_{dp1}K_{dp2}[OH^-]^2}{K_w^2 + K_{dp1}K_w[OH^-] + K_{dp1}K_{dp2}[OH^-]^2}$$

The calculated deprotonation constants are also presented in Table IV. The deprotonation of the alcoholic hydroxyl group from both ligands seems to start almost at the same pH in the presence of manganese(II).

Thermoanalytical Investigations

The manganese(IV)–lactobionate complex was prepared in the solid state, according to the procedure presented in the Experimental part of this paper. Its thermal decomposition was studied on a MOM-Q derivatograph. On the basis of the thermoanalytical curves (Fig. 5) the crystal water content and the molecular weight of the complex could be determined. The sodium ion content, determined by flame photometry, gave information on the number of charges on the complex anion.

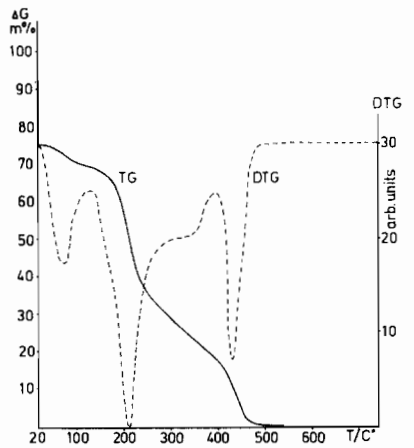
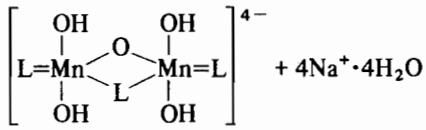


Fig. 5. Thermoanalytical curves of the manganese(IV)–lactobionate complex.

The ignition residue (Na_2MnO_4) was found to be 24.7 ± 0.7%. The molecular weight calculated from it, assuming on the basis of the spectrophotometric measurements two manganese(IV) central atoms in the complex ion, is 1336 ± 9.

The weight loss at ~100 °C was found to be 5.3%, corresponding to 4 water molecules.

On the basis of the spectrophotometric and thermoanalytical data, and taking into consideration the charge balance in the system, the composition of the manganese(IV) complex is:



The molecular weight calculated from this formula is 1326, in good agreement with that obtained from the thermoanalytical curve.

The carbon, hydrogen and sodium content of the sample shows a good agreement with the values calculated (in brackets) on the basis of this composition: C: 30.5% (31.1%); H: 4.8% (4.74%); Na^+: 7.2% (6.80%).

References

1 J. A. Rendleman, *Adv. Carbohydr. Chem.*, *21*, 209 (1966).
2 S. J. Angyal, *Chem. Soc. Rev.*, *9*, 415 (1980).
3 P. J. Charley, B. Sarkar, C. F. Stitt and P. Saltman, *Biochim. Biophys. Acta*, *69*, 3/3 (1963).
4 I. Zay, F. Gaizer and K. Burger, *Inorg. Chim. Acta*, *80*, L9 (1983).
5 J. Doležal, K. S. Klausen and F. J. Langmyhr, *Anal. Chim. Acta*, *63*, 71 (1973).

6 R. L. Heath, *Int. Rev. Cytol., 34,* 49 (1973).
7 G. M. Cheniae, *Annu. Rev. Plant Physiol., 21,* 467 (1970).
8 B. B. Keele, J. M. McCord and J. Fridovich, *J. Biol. Chem., 245,* 6176 (1970).
9 D. T. Sawyer and M. E. Bodini, *J. Am. Chem. Soc., 97,* 6588 (1975).
10 M. E. Bodini, L. A. Willis, T. L. Riechel and D. T. Sawyer, *Inorg. Chem., 15,* 1538 (1976).
11 M. E. Bodini and D. T. Sawyer, *J. Am. Chem. Soc., 98,* 8366 (1976).
12 B. U. Nair and G. C. Dismukes, *J. Am. Chem. Soc., 105,* 124 (1983).
13 G. Donoso, J. Doležal and J. Zyka, *J. Electroanal. Chem., 49,* 461 (1974).
14 J. Doležal, E. Julakova, M. Cerny and M. Kopanica, *J. Electroanal. Chem., 52,* 261 (1974).
15 J. Doležal and H. Kekulova, *J. Electroanal. Chem., 69,* 239 (1976).
16 B. L. Velikov and J. Doležal, *J. Electroanal. Chem., 71,* 91 (1976).
17 D. T. Richens, C. G. Smith and D. T. Sawyer, *Inorg. Chem., 18,* 706 (1979).
18 G. Brauer, 'Handbook of Preparative Inorganic Chemistry, Vol. 2', Academic Press, New York, 1965, p. 1469.
19 J. D'Ans and J. Mattner, *Angew. Chem., 64,* 488 (1952).
20 I. Zay, A. Vértes, G. Takácsi Nagy, M. Suba and K. Burger, *J. Radioanal. Chem., 88,* 343 (1985).
21 J. Heyrovsky and J. Kuta, 'Principles of Polarography', Academic Press, New York, 1966, p. 86.
22 I. M. Kolthoff and J. J. Lingane, 'Polarography, Vol. I', Interscience, New York, 1952, chap. 12.
23 D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc., 73,* 5321 (1951).
24 A. E. Martell and R. M. Smith, 'Critical Stability Constants, Vol. 1', Plenum Press, New York/London, 1977.