POLAROGRAPHIC STUDY OF COMPLEXES
OF DIACETYL OXIME THIOSEMICARBAZONE WITH MANGANESE

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Dedicated to honour the memory of Professor J. Hanuš on the occasion of the centenary of his birthday.

The complex of diacetyl oxime thiosemicarbazone with manganese was studied polarographically in 8 wt. % ethanol–water medium both in inert atmosphere and in the presence of air. From the results supported by potentiometric and spectrophotometric measurements it follows that the colourless Mn(II) complex, $MnHL_2^-$, which is formed in the absence of air, is oxidized by air at pH > 9 to a red-violet Mn(III) complex, MnL_2^-, the stability constant of which was determined as log $\beta_2 = 26.5$.

Complexes of manganese, *e.g.* with tartaric[1] and oxalic[2] acids and with mannit[3] were already studied polarographically. The oxidation state of manganese was determined as $+3$ in the presence of these acids and air, $+3$ and $+4$ in the presence of mannit. The complex of manganese with diacetyl oxime thiosemicarbazone was studied first by Hovorka and Holzbecher[4,5]. Evidence was obtained from logarithmic analysis of the photometric curves and from paper electrophoresis[5] that the red-violet complex is a univalent anion in which two molecules of the complexing agent are bound with one manganese atom, assumed to be trivalent.

In this work the polarographic behaviour of diacetyl oxime thiosemicarbazone in the presence of manganese was studied to verify the assumed oxidation state of manganese in the complex, to check its composition and to determine its stability constant.

EXPERIMENTAL

Apparatus. Polarographic measurements were made both with a type LP 60 polarograph equipped with an EZ 2 type pen-recorder, and with a type LP 55 photorecording polarograph (both from Laboratorní Přístroje, Prague). The capillary constants were $m = 1.48$ mg/s and $t_1 = 3.16$ s at a height of mercury column 50 cm. The potential of the dropping electrode was measured against a normal calomel electrode separated from the measured solution by a salt bridge filled with 1M-KCl. The polarographic cell was provided with a thermostated (at 20 $\pm$ $\pm$ 0.1°C) mantle piece. A type P 576 Polaroscope (Závody Průmyslové automatizace, Prague) was used in oscillopolarographic measurements, and a type OP—205 precision pH meter (Radelkis, Budapest) in the measurements of pH; the glass electrode was calibrated with the use of standard

buffer solutions[6,7] except where otherwise indicated. A type SF 4 spectrophotometer of Soviet origin with a 1 cm quartz glass cuvette was used in spectrophotometric measurements.

Chemicals. Diacetyl oxime thiosemicarbazone (H_2L) was prepared by condensation of stoichiometric amounts of diacetylmonoxime and thiosemicarbazide in the medium of an acetate buffer at elevated temperature[8]. All chemicals were of reagent grade (Lachema or Merck).

Solutions. Stock solution of exactly $0.04M$-H_2L in 96 wt. % ethanol was freshly prepared every day. Stock solution of $0.02M$-$MnSO_4$ was standardized by the bismuthate method[9]. The buffer solution was $0.125M$-$NH_4Cl + NH_4OH$. Purified nitrogen was freed from traces of oxygen by bubbling through Cr(II) chloride solution containing zinc amalgam.

Polarographic measurements. Diacetyl oxime thiosemicarbazone was studied polarographically in its $0.001M$ solution (in 8 wt. % ethanol) in the presence of ammonium buffer (pH 4·5—10·9) in nitrogen atmosphere with a dropping mercury or rotating platinum electrode in the range from $+0.6$ to -0.6 V. For polarography of the complex, mixtures containing the complexing agent and manganese in various ratios were prepared both in the presence and absence of air. The components were mixed in the following order: first the alcoholic solution of the complexing agent was added to the buffer solution and then during stirring the solution of manganese sulphate. All mixtures contained 8 ml of the buffer mentioned above and 1 ml of ethanol in 10 ml (Figs 4, 5). In polarography of the Mn(III) complex, the mixtures were allowed to stand for 15 min open to the air, then bubbled with nitrogen for 5 min and analyzed polarographically. From the limiting diffusion current of the complexing agent and its mixtures with manganese ions in the range from 0 to -0.6 V at pH 9·5—10·6, the apparent stability constants of the Mn(III) complex were calculated (Table V).

Other measurements. In the study of protonation of the complex, the pH change due to the complex-forming reaction in the presence or absence of air was measured, the ratio $c_{Mn} : c_L$ being 1 : 3 to 1 : 5. The vessel used was provided with inlets of nitrogen (free from oxygen and carbon dioxide) and air (free from CO_2) and with a glass and normal calomel electrodes. It was

TABLE I

pK_1 Values for Diacetyl Oxime Thiosemicarbazone Determined Potentiometrically

pH	$c_L \cdot 10^3$	$(c_{BOH} - c_{HA}) \cdot 10^3$	$[OH] \cdot 10^4$	$[H_2L] \cdot 10^3$	$[HL] \cdot 10^3$	$\bar{n}_H$	pK_1
10·48	8·11	2·11	3·01	8·11	1·80	1·75	11·29
10·68	8·06	2·72	4·78	8·06	2·24	1·72	11·23
10·82	7·99	3·48	6·58	7·99	2·82	1·64	11·37
10·92	7·92	4·21	8·26	7·92	3·38	1·56	11·38
11·04	7·86	4·62	1·09	7·86	4·51	1·51	11·28
11·15	7·80	5·61	1·41	7·80	5·46	1·44	11·30
11·24	7·74	6·21	1·73	7·74	6·03	1·39	11·34
11·34	7·68	7·20	2·18	7·68	6·98	1·37	11·38
						mean	11·29 ±
							± 0·06

filled with 44·5 ml of $3 . 10^{-4}$M NaOH (free from CO_2) and the $pH_{(1)}$ value was measured. After adding 3, 4 or 5 ml of $4 . 10^{-3}$M-H_2L and 2, 1 or 0 ml of water, bubbling with nitrogen for 15 min and adding 0·5 ml of $8 . 10^{-3}$M-$MnSO_4$ (free from O_2) the $pH_{(2)}$ value was measured. Afterwards the solution was bubbled with air for 15 min and the $pH_{(3)}$ value was determined (Table II). To determine potentiometrically the dissociation constants of the complexing agent, a solution of 50 ml of 0·01M-H_2L + 5 ml of 0·1M-$HClO_4$ was titrated with 0·1M-NaOH in nitrogen atmosphere at 20°C; the ionic strength was kept at 0·1 by addition of sodium perchlorate. The glass electrode was calibrated[10] after every measurement so that the measured pH values correspond to the concentration of hydrogen ions. The results and other necessary data are summarized in Table I. To determine potentiometrically the stability constant of the Mn(II) complex (Table III), 50, 40 or 30 ml of 0·1M-H_2L + 10·2 ml of $9·8 . 10^{-3}$M-Mn^{2+} + 4 ml of 0·1M-$HClO_4$ + 10 ml of 1M-$NaClO_4$ were added into a 100 ml volumetric flask and made up to the mark with redistilled water. 50 ml of this mixture was titrated with 0·1M-NaOH; the glass electrode was calibrated as before[10]. The extinction curve of the Mn(III) complex was measured in the range 400—700 nm in $2 . 10^{-3}$M-$MnSO_4$ + $4 . 10^{-3}$M-H_2L + ammonium buffer of pH 10·4 in the medium of 8 wt.% ethanol (Fig. 3). (The Mn(II) complex exhibits no absorption in this range of wave lengths.)

RESULTS AND DISCUSSION

Polarography of Diacetyl Oxime Thiosemicarbazone

This agent gives two polarographic diffusion-controlled waves, the form and $E_{1/2}$ values of which depend on pH (Fig. 1). Their height at pH 5·3 is directly proportional to the concentration of the depolarizer in the range $5 . 10^{-4}$—$4 . 10^{-3}$M and to the square root of the height of the mercury column in the range 35—80 cm; their half-wave potentials are independent of the drop time in the range 3·16—4·6 s at pH 5·3. The anodic wave *I* at potentials from 0 to −0·4 V appears at pH 5·3 and corresponds to dissolution of mercury. This is evidenced by the fact that no anodic wave of diacetyl oxime thiosemicarbazone was obtained on a rotating platinum electrode. A similar behaviour was observed also with other compounds containing an SH group, *e.g.* dithiocarbaminoacetate[11], 2,3-dimercaptopropanol[12] or cysteine[13]). The cathodic wave *II* at potentials from −0·8 to −1·6 V is due to reduction of the oxime group[14]; at pH 5 it becomes separated into two waves (II_1 and II_2), the first of which disappears at pH 9·65. The oscillopolarographic curve $dE/dt = f(E)$ at pH 8·3 of $1 . 10^{-4}$M complexing agent (in 8 wt. % methanol) shows that the electrode processes on the dropping electrode are irreversible.

The dependence of the $E_{1/2}$ value of the wave *I* on pH can be used in determining the dissociation constant of the complexing agent, since it consists of two linear portions (Fig. 2) which on extrapolation intersect to give the pK_1 value for dissociation of the SH group[15], namely 11·05. The dissociation constant K_2 cannot be found in this way since the $E_{1/2}$ values for waves II_1 and II_2 are too imprecise.

Assuming that dissociation to the second step is negligible at our experimental conditions, we can write[16]

$$[H_2L] = c_L - c_{OH} + c_H + [OH^-] - [H^+] , \qquad (1)$$

$$[HL] = c_{OH} - c_H - [OH^-] + [H^+] , \qquad (2)$$

$$\bar{n}_H = (2[H_2L] + [HL])/c_L , \qquad (3)$$

$$pK_1 = pH + \log([H_2L]/[HL]) , \qquad (4)$$

where c with an index denotes analytical concentration of the agent, of the added

TABLE II
Degree of Protonation of Complex ($c_{Mn} = 8 . 10^{-5}$M)

c_L	$pH_{(1)}$	$pH_{(2)}$	$pH_{(3)}$	$[HL^-] . 10^5$ $pH_{(2)}$	$[HL^-] . 10^5$ $pH_{(3)}$	x	y
$4 . 10^{-4}$	10·37	9·10	8·99	0·257	0·20	2·76	3·79
	10·47	9·75	9·75	2·04	1·29	2·70	3·72
$3,2 . 10^{-4}$	10·45	9·70	9·67	8·30	0·60	2·79	3·88
	10·38	9·15	9·00	2·88	0·16	2·80	3·86
$2,4 . 10^{-4}$	10·52	10·05	9·96	8·73	1·10	2·64	3·86
	10·48	9·85	9·83	8·70	0·83	2·80	3·94

TABLE III
Potentiometric Determination of Stability Constant of $Mn^{II}HL_2^-$

$\bar{z}$	$\log B$	pH^a	pH^b	pH^c
0·442	−0·762	7·98	8·01	7·99
0·637	−0·568	8·04	8·07	8·01
0·840	−0·424	8·07	8·11	8·03
1·03	−0·280	8·09	8·14	8·07
1·22	−0·164	8·14	8·16	8·12
1·415	−0·034	8·19	8·21	8·18
1·615	+0·072	8·25	8·24	8·20
1·82	+0·188	8·33	8·26	8·28

^{a} c_L 5 . 10^{-3}M; ^{b} c_L 4 . 10^{-3}M; ^{c} c_L 3 . 10^{-3}M.

strong acid or base in potentiometric measurements and $\bar{n}_H$ average number of bound protons. The results of calculation are shown in Table I. In view of the fact that even at pH 11·3 the $\bar{n}_H$ value was found rather high we can assume that the potentiometric determination of pK_2 would be subjected to a large error.

The dissociation constants of the complexing agent were determined spectrophotometrically[17] by analysis of the function $A = f(pH)$ as pK_1 11·34 and pK_2 13·13.
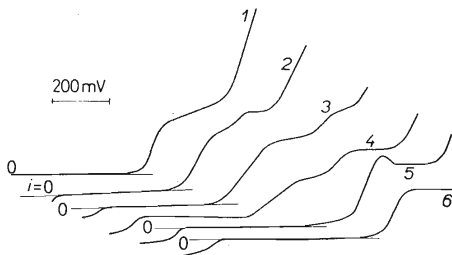

Fig. 1

Polarographic Curves of Diacetyl Oxime Thiosemicarbazone at Various pH

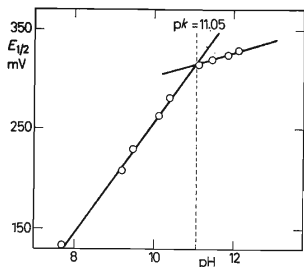c_L 1 . 10^{-3}M; sens. 1 : 200; 200 mV/absc.; all curves from 0 V. pH values: *1* 4·50; *2* 5·28; *3* 6·75; *4* 7·95; *5* 9·65; *6* 10·89.

Fig. 2

pK_1 for Diacetyl Oxime Thiosemicarbazone from the Dependence $E_{1/2} = f(pH)$
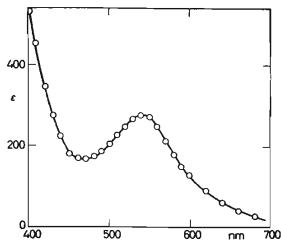

Fig. 3

Absorption Spectrum of $Mn^{III}L_2^-$

Complex of Manganese with Diacetyl Oxime Thiosemicarbazone

This red-violet complex is formed only in the presence of oxygen at pH $\geqq 9$ in an ammonium buffer. Its formation proceeds much more slowly in borate, phosphate or glycolate buffers; with increasing pH the reaction rate increases[18]. Its absorption maximum at 540 nm (ε 278) is an evidence for the presence of Mn(III) (Fig. 3) following by analogy with other octahedral Mn(III) complexes (bis-oxalate, bis-malonate and bis-acetylacetonate complexes), which exhibit an absorption band in the region $500-550$ nm ($\varepsilon = 130-370$)[19].

From polarography of reaction mixtures in the presence or absence of air and at various ratios $c_{Mn} : c_L$ (Figs 4, 5) it follows that the colourless Mn(II) complex exhibits the same polarographic behaviour in the region from 0 to -0.6 V as the complexing agent. The form of the wave as well as its $E_{1/2}$ value do not depend on concentration of Mn(II). With the red-violet complex, the anodic wave I is replaced by an anodic–cathodic wave which in logarithmic coordinates gives a straight line with a slope of 75 mV. The ratio of heights of the cathodic and anodic portions of the wave, $(\bar{i}_d)_k$ and $(\bar{i}_d)_a$, is proportional to the ratio $c_{Mn} : c_L$. With increasing concentration of Mn(III), at constant c_L, the total height $\bar{i}_d$ of the anodic–cathodic wave diminishes while the ratio $(\bar{i}_d)_k : (\bar{i}_d)_a$ increases. The $\bar{i}_d$ value is minimum for $c_{Mn} : c_L = 1 : 2$ (with further increase of c_{Mn} a precipitate forms, apparently MnO$_2$. x H$_2$O) and $(\bar{i}_d)_k : (\bar{i}_d)_a = 1$.

TABLE IV
Stability Constants of Mn^{II}HL$_2^-$

pH$_0$	log k	log β_2
8·22[a]	−18·62	16·82
8·20[b]	−19·16	16·28
8·17[c]	−19·41	16·03

[a] $c_L = 5 . 10^{-3}$ M, [b] $c_L = 4 . 10^{-3}$ M,
[c] $c_L = 3 . 10^{-3}$ M.

Fig. 4

Polarographic Curves for Reaction Mixture of Diacetyl Oxime Thiosemicarbazone with Mn^{2+} Ions

c_L 4 . 10^{-4} M, pH 10·25; sens. 1 : 100; 100 mV/abcs.; beginning from 0 V. I in absence of oxygen, c_{Mn} 0; 2 in absence of oxygen, c_{Mn} 2 . 10^{-4} M; 3 after 15 min contact with air, c_{Mn} 2 . 10^{-4} M.
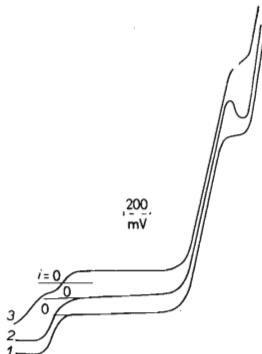
The cathodic wave *II* of the agent is not influenced by the presence of manganese regardless of the presence of oxygen. The wave of reduction $Mn(II) \rightarrow Mn(0)$ which should follow after the cathodic wave of the agent[20] is not distinct enough to enable measurement of changes of the $E_{1/2}$ value and of the concentration of Mn^{2+} ions caused by the formation of the complex.

Our results of the polarographic study of the red-violet complex prove that it contains one Mn atom bound to two molecules of the ligand which remains polarographically active, only its SH group is partially oxidized. The fraction of the oxidized form is proportional to the analytical concentration of manganese, added to the solution of the complexing agent. Assuming that the diffusion coefficients of the oxidized and reduced forms are equal (regardless of whether the ligand is free or in complex), we can express the height of the anodic–cathodic wave as

$$i_d = (i_d)_a + (i_d)_k = \varkappa([SH]_{ox} + [SH]) = \varkappa([SH]_{free} + [SH]_{bound}),$$

where $\varkappa$ is the Ilkovič constant and $[SH]$ or $[SH]_{ox}$ are concentrations of unchanged or oxidized reagent in the reaction mixture. In the absence of manganese is $[SH]_{free} = c_L$ and $[SH]_{bound} = 0$, whereas in a solution of the complex and free agent is $[SH]_{free} = c_L - 2c_{Mn}$ and $[SH]_{bound} = mc_{Mn}$. The coefficient m determines the polarographically active fraction of the agent bound in the complex. From the equations

$$(i_d)_0 = \varkappa c_L, \qquad i_d' = \varkappa[c_L + (m - 2)c_{Mn}] \qquad (6), (7)$$

and from the measured i_d values we obtain m values close to 1 ($m = 0.890 - 1.064$ by $c_{Mn} = 1.0 - 2.0 \cdot 10^{-3}M$; see Fig. 5). Hence, one of two molecules of the ligand is bound in the complex so that it does not react on the dropping electrode in the potential region of wave *I*. The proportionality between the height of the cathodic part of this wave and analytical concentration of manganese in the complex solution implies the possibility of a reaction of the SH group with $Mn(III)$ evidenced by its absorption spectrum. It cannot be excluded that the complex of $Mn(III)$ with diacetyloximethiosemicarbazone is reduced at more positive potentials than the potential of anodic dissolution of mercury, or that $Mn(III)$ is reduced in the potential range of the wave under discussion.

Composition and Thermodynamic Stability of Complexes in Solution

To calculate the stability constant of the complex of manganese with two molecules of the ligand, it is further necessary to determine its degree of protonation. The complex-forming reactions are
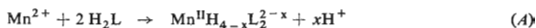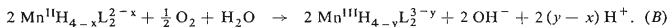
$$Mn^{2+} + 2 H_2L \rightarrow Mn^{II}H_{4-x}L_2^{2-x} + xH^+ \qquad (A)$$

TABLE V

Apparent and True Stability Constants of MnL_2^-

pH	$\log \alpha_{Mn(OH)}$	$\log \alpha_{L(H)}{}^a$	$\log \beta_2'$	$\log \beta_2$
9·49	9·43	5·44	6·54	26·95
9·82	9·76	4·79	7·42	26·76
9·89	9·83	4·65	7·07	26·20
10·19	10·13	3·99	7·23	25·34
10·65	10·59	3·14	8·06	24·93
			mean	*26·51*

a pK_1 11·29; pK_2 13·13.

$$2\,Mn^{II}H_{4-x}L_2^{2-x} + \tfrac{1}{2}O_2 + H_2O \;\rightarrow\; 2\,Mn^{III}H_{4-y}L_2^{3-y} + 2\,OH^- + 2\,(y-x)\,H^+. \quad (B)$$

Changes in the concentration of hydrogen ions in the studied system are obviously related to the state of equilibrium in both reactions and to the degree of protonation of both complexes. If the complexing agent is in excess it can be assumed that the concentration of the relatively stable complexes is equal to that of manganese. It is, however, necessary to consider the dissociation of the unreacted agent in the first step in which hydrogen ions are also set free, whereas the second dissociation step
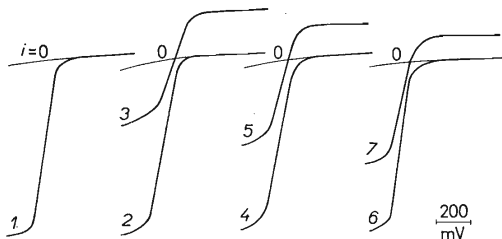

Fig. 5

Anodic–Cathodic Waves of Mn(II) and Mn(III) Complexes

c_L 4 . 10^{-3}M, pH 10·25; sens. 1 : 300; 100 mV/absc.; all curves from $-0·1$ V. c_{Mn}: *1* 0; *2, 3* 2 . 10^{-3}M; *4, 5* 1·5 . 10^{-3}M; *6, 7* 1 . 10^{-3}M. *2, 4, 6* in inert atmosphere, *1, 3, 5, 7* in presence of air.

is negligible at our experimental conditions:

$$[HL] = (c_L - 2c_{Mn})\left[1 + ([H^+]/K_1)\right]^{-1}. \qquad (8)$$

The number of hydrogen ions per 1 mol of the complex prior to oxidation, x, can be calculated as

$$x = ([OH^-]_{(1)} - [OH^-]_{(2)} - [HL]_{(2)})/c_{Mn}, \qquad (9)$$

and after oxidation as

$$y = 1 + ([OH^-]_{(1)} - [OH^-]_{(3)} - [HL]_{(3)})/c_{Mn}. \qquad (10)$$

Indexes in parentheses suggest to what experimental pH values belong the envisaged concentrations. From the results summarized in Table II ($x \approx 3$, $y \approx 4$) it can be concluded that the complex $Mn^{II}HL_2^-$ is formed in the absence of oxygen while three mol H^+ are set free per one mol Mn; after oxidation with air when in total four mol H^+ per one mol Mn are set free, the complex $Mn^{III}L_2^-$ is formed.

Stability of the Complex $Mn^{II}HL_2^-$

The stability of the Mn(II) complex was determined from potentiometric titration by the Bartušek method[21] which leads to the equations

$$\bar{z} = x[MnHL_2]/c_{Mn}, \quad B = \bar{z}/(x - \bar{z}), \qquad (11), (12)$$

where in our case

$$- \log B = x \log [H^+] + \text{const.} \qquad (13)$$

On plotting log B against pH we obtain a straight line with a slope equal to 2·8 whereby it is checked that three H^+ ions are set free in reaction (A). To calculate the equilibrium constant k and stability constant β_2 from the equations

$$- \log k = x\,pH_0 + 2 \log [L], \qquad (14)$$

$$[L] = c_L - 2c_{Mn}, \quad \beta_2 = k/(K_1^2 + K_2), \qquad (15), (16)$$

the pH_0 value was determined from the dependence (13) for log $B = 0$ (Table III). The calculated constants k and β_2 are in Table IV; the average value log $\beta_2 = 16·5$.

Stability of the Complex $Mn^{III}L_2^-$

The total diffusion current of the described anodic–cathodic wave is given by the sum of anodic and cathodic currents and is proportional to the concentrations of free ligand c'_L and complex c_K:

$$i_d = c'_L D_L + c_K D_K , \qquad (17)$$

where D_L and D_K are constants of proportionality. For $c_{Mn} : c_L = 1 : 2$ is $c'_L = c_L - 2c_K$ and Eq. (17) gives

$$c_K = (c_L D_L - i_d)/(2D_L - D_K) . \qquad (18)$$

The D_L value was obtained from the dependence $i_d = c_L D_L$ but the D_K value cannot be found in this way since it is not possible to prepare a solution of the complex without free complexing agent. On introducing the expressions

$$c_K = c_{Mn} - [Mn] , \quad c'_L = c_L - 2(c_{Mn} - [Mn]) \qquad (19), (20)$$

into Eq. (17) and rearranging, we obtain

$$i_d/c_{Mn} = (c_L/c_{Mn}) D_L + (D_K - 2D_L)(1 - [Mn]/c_{Mn}) . \qquad (21)$$

If the dissociation of the complex is negligible, then for $c_{Mn} \to c_L$ we obtain (since in this case $[Mn] \approx 0.5 c_{Mn}$)

$$\lim_{c_{Mn} \to c_L} (i_d/c_{Mn}) \approx 0.5 D_K . \qquad (22)$$

The D_K value was determined by graphical extrapolation of the dependence of i_0/c_{Mn} on $1/c_{Mn}$ as $2.7 \cdot 10^4$ at pH $9.5-10.6$.

The apparent stability constant of the Mn(III) complex MnL_2^- is calculated as

$$\beta'_2 = c_K/(c_L - 2c_K)^2 (c_{Mn} - c_K) . \qquad (23)$$

The c_K value is found from Eq. (18). Since the Mn(III) ions form hydroxo complexes in alkaline medium[22] and the free agent in equilibrium with the complex is protonated, β'_2 has to be corrected to obtain the true stability constant b_2 as

$$\beta_2 = \beta'_2 \alpha_{Mn(OH)} \alpha^2_{L(H)} , \qquad (24)$$

where $\alpha_{Mn(OH)}$ and $\alpha_{L(H)}$ are coefficients of side reactions of the metal ions and the ligand. The formation of Mn(III) hydroxo complexes is after Wells[22] characterized by $K_{hydr} = [MnOH^{2+}] [H_3O^+]/[Mn^{3+}(H_2O)] = 0.88$. The corresponding value of $\log \beta_1 = 13.94$ served in calculating $\alpha_{Mn(OH)} = 1 + \beta_1[OH^-]$. The coefficient of protonation of the ligand was calculated as

$$\alpha_{L(H)} = 1 + K_2^{-1}[H^+] + K_1^{-1} K_2^{-1}[H^+]^2 \qquad (25)$$

for various pH values; K_1 and K_2 are dissociation constants of the complexing agent.

The calculated apparent and true stability constants are summarized in Table V. The average β_2 value for the $Mn^{III}L_2^-$ complex is 26·5. Its variation with pH can be attributed to the existence of the hydroxo complex $Mn(OH)_2^+$ the stability of which is not known.

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