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FORMATION AND STABILITY OF MAGNESIUM–OXYDIACETATE COMPLEXES AT DIFFERENT TEMPERATURES AND IONIC STRENGTHS IN AQUEOUS SOLUTION

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ABSTRACT

The formation constants of the $[Mg(oda)]^0$ and $[Mg(oda)H]^+$ (oda = oxydiacetate) species were determined potentiometrically, by using the (H^+)-glass electrode, at different temperatures, 12.5, 25, 37 and 48 °C, and ionic strengths, $0 < I < 1$ mol l^{-1}. From the dependence on temperature of formation constants ΔH^0, ΔS^0 and ΔC_p^0 values were obtained. The dependence on ionic strength of formation parameters was also considered.

INTRODUCTION

Several investigations from this laboratory have been devoted to the study of weak complex formation between low molecular weight ligands and alkali and alkaline earth metal ions in aqueous solution at different temperatures and ionic strengths [1–7]. Oxydiacetate forms very weak alkali metal complexes (with a stability comparable to that of other dicarboxylate ligands [1]) and calcium complexes, abnormally strong when compared with other Ca^{2+}–dicarboxylate complexes [1].

In this paper we report an investigation on the stability of Mg^{2+}–oxydiacetate complexes, as a further contribution to the knowledge of the complexing ability of low molecular weight ligands towards alkaline earth metal ions, and, in particular, to verify whether the abnormal stability of Ca^{2+} is peculiar to this cation or is a characteristic of alkaline earth metal ions.

EXPERIMENTAL

Oxydiacetate (Fluka puriss) was used without further purification; its purity was always > 99.7% (checked by alkalimetric titrations). Magnesium nitrate stock solutions were prepared from Fluka purum reagents and

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TABLE 1

Experimental details of potentiometric titrations

t (°C)	C^0_{oda} [a]	C^0_{Mg} [a]	$C^0_{\text{HNO}_3}$ [a,b]	$\bar{I}$ [c]	log K_1^{H} [d]	log K_2^{H} [d]
12.5	4.76	19.3	5.07	0.06	3.686(2) [e]	2.802(8)
	4.93	50.3	4.56	0.15	3.527(5)	2.746(13)
	4.85	170.1	4.89	0.49	3.361(5)	2.719(12)
	5.22	320.9	4.17	0.92	3.165(6)	2.614(15)
25	5.03	18.9	5.28	0.06	3.681(2)	2.787(5)
	5.10	49.7	5.19	0.15	3.522(2)	2.754(7)
	5.10	168.0	5.47	0.48	3.274(3)	2.627(3)
	4.79	319.4	6.61	0.90	3.128(5)	2.577(7)
37	5.41	18.9	4.48	0.06	3.696(5)	2.845(7)
	5.16	49.5	5.03	0.15	3.474(3)	2.742(5)
	4.89	167.4	5.83	0.47	3.213(5)	2.623(7)
	5.23	318.3	5.99	0.91	3.127(3)	2.564(8)
48	5.09	18.8	4.86	0.06	3.680(3)	2.829(7)
	5.09	49.3	5.06	0.15	3.463(2)	2.775(3)
	4.71	166.8	6.54	0.47	3.180(5)	2.627(10)
	4.33	317.1	7.52	0.89	3.056(10)	2.545(15)

[a] Initial analytical concentrations in mmol l^{-1}; initial volume 50 cm^3; titrant NaOH 0.25 mol l^{-1}.

[b] The excess of strong acid was added in order to complete the protonation of the ligand and to calculate internal E^0 values (see refs. 1 and 4).

[c] Mean value of ionic strength in mol l^{-1}.

[d] Conditional protonation constants. These quantities are used for subsequent calculations (see refs. 1 and 4).

[e] The uncertainties, reported in parentheses, are three times the standard deviation in the last significant figure(s).

standardized by ethylenediaminetetraacetate titrations [8]. Other reagents and apparatus were as already reported [1]. Some experimental details of the titrations performed are reported in Table 1. All calculations were performed by nonlinear least squares programs, as already described [1,9,10]. In the calculations we used the protonation constants and the formation constants for Na^+–oxydiacetate complexes * previously determined [1], as reported in Table 2. The formation constants were expressed as (oda = oxydiacetate)

$$\beta_{pqr} = \left[\text{M}_p(\text{oda})_q\text{H}_r\right][\text{M}]^{-p}[\text{oda}]^{-q}[\text{H}]^{-r} \tag{1}$$

according to the general reaction

$$p\text{M} + q(\text{oda}) + r\text{H} \rightleftarrows \left[\text{M}_p(\text{oda})_q\text{H}_r\right] \tag{2}$$

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* We also took into account these complexes (Na^+ comes from the titrant NaOH) in the calculations.

TABLE 2

H^+- and Na^+-oxydiacetate species formation constants at different temperatures (reference ionic strength, $I' = 0.25$)

t (°C)	$\log \beta_{011}$, [a] C_{011}, $-D_{011}$	$\log \beta_{012}$, C_{012}, $-D_{012}$	$\log \beta_{110}$ (Na^+), C_{110}, $-D_{110}$	$\log \beta_{111}$ (Na^+), C_{111}, $-D_{111}$
12.5	3.88	6.75	0.33	3.6
	0.83	1.62	0.64	1.6
	0.30	0.75	0.12	0.6
25	3.97	6.79	0.34	3.5
	0.95	1.66	1.05	1.5
	0.41	0.75	0.50	0.5
37	4.02	6.85	0.51	3.8
	0.75	1.70	1.06	1.4
	0.20	0.75	0.50	0.4
48	4.11	6.96	0.66	4.0
	0.85	1.69	1.05	1.4
	0.29	0.75	0.50	0.3

[a] The indices refer to reactions (1) and (2); C and D are the empirical parameters of eqn. (3); First row $\log \beta$, second row C, third row $-D$.

Concentrations, and therefore thermodynamic formation parameters, were always expressed using molar concentrations. The dependence on ionic strength and on temperature was taken into account by the semiempirical equations [1,11]

$$\log \beta_I = \log \beta_{I'} - z^*[\sqrt{I}/(2+3\sqrt{I}) - \sqrt{I'}/(2+3\sqrt{I'})] + C(I-I') + D(I^{3/2} - I'^{3/2}) \qquad (3)$$

(where $z^* = pz^2_{\mathrm{M}} + qz^2_{(\mathrm{oda})} + r - z^2_{\mathrm{complex}}$, z = charge), and

$$\log \beta_t = \log \beta_\theta + a_1(t-\theta) + a_2(t-\theta)^2 \qquad (4)$$

In eqns. (3) and (4), I' and θ are the reference ionic strength and temperature, respectively, and C, D, a_1 and a_2 are empirical parameters, to be determined for each complex species. The uncertainties reported in the text are always expressed as three times the standard deviation.

RESULTS AND DISCUSSION

In the Mg^{2+}-oxydiacetate system the species $[Mg(oda)]^0$ and $[Mg(oda)H]^+$, as expected, are formed. In Table 3 we report the calculated formation constants for the complex species $[Mg(oda)]^0$, together with the parameters for the dependence on ionic strength. These parameters were

TABLE 3

Thermodynamic parameters for the formation of $[Mg(oda)]^0$ species at different temperatures and ionic strength

t(°C)	I (mol l^{-1})	log β_{110}	C_{110}	$-D_{110}$	ΔH^0 (kJ mol^{-1})	ΔS^0 (J K^{-1} mol^{-1})	ΔC_p^0 (J K^{-1} mol^{-1})
12.5	0	2.41(9)[a] [2.39][b]			17.8[d]	108[d]	-
	0.25	1.57(4)	1.51[1.59][c]	0.61[0.675][c]	16.9	89	178[d]
	1	1.71(5) [1.70]			17.6	94	-
25	0	2.51(7) [2.54]			20.2	116	-
	0.25	1.70(2)	1.73[1.53]	0.82[0.62]	19.2	97	194
	1	1.82(3) [1.85]			20.0	103	-
37	0	2.72(8) [2.68]			22.7	125	-
	0.25	1.85(3)	1.29[1.48]	0.39[0.57]	21.6	105	210
	1	2.02(4) [2.00]			22.5	111	-
48	0	2.82(8) [2.82]			25.2	132	-
	0.25	1.97(3)	1.48[1.43]	0.58[0.52]	24.0	113	225
	1	2.12(5) [2.13]			25.0	119	-

[a] The uncertainties, reported in parentheses, are three times the standard deviation in the last significant figure.

[b] In square brackets are reported the log β_{110} values calculated by using C_{110} and D_{110} values from eqns. (5) and (6).

[c] In square brackets are reported C_{110} and D_{110} values from eqns. (5) and (6).

[d] On average the uncertainties (three times the standard deviation) are: $\Delta H^0 \pm 0.5$–2 kJ mol^{-1}; $\Delta S^0 \pm 2$–8 J K^{-1} mol^{-1}; $\Delta C_p^0 \pm 15$–40 J K^{-1} mol^{-1}.

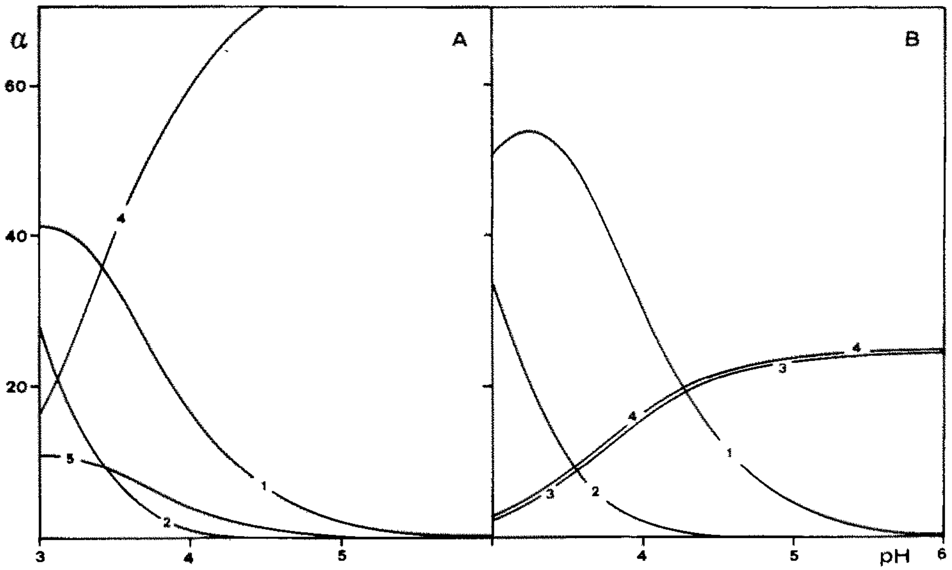

Fig. 1. Distribution of the species versus pH for the system $Na^+ - Mg^{2+}$-oxydiacetate (the percentages are calculated with respect to the ligand): curve 1, $[H(oda)]^-$; curve 2, $[H_2(oda)]^0$; curve 3, $[Na(oda)]^-$; curve 4, $[Mg(oda)]^0$; curve 5, $[Mg(oda)H]^+$ (the formation percentages for the species $[Na(oda)H]^0$ are < 4% and are not reported in the diagram). A: $C_{Na} = 0.001$, $C_{Mg} = 0.08$ and $C_{oda} = 0.02$ mol l^{-1}. B: $C_{Na} = 0.22$, $C_{Mg} = 0.01$ and $C_{oda} = 0.001$ mol l^{-1}.

calculated both for each temperature and for all temperatures by considering a linear dependence of C and D on t:

$$C_{110} = 1.53 - 0.0045(t - 25) \tag{5}$$

$$D_{110} = -0.62 + 0.0044(t - 25) \tag{6}$$

In Table 3, we report formation constants calculated with both methods and, as one can see, no significant difference is observed. In Fig. 1, the distribution of the species versus pH of the system under study is reported.

By using eqn. (4) it was possible to calculate ΔH^0, ΔS^0 and ΔC_p^0 values, as reported in Table 3.

As regards the species $[Mg(oda)H]^+$, we obtained, for the reaction

$$Mg^{2+} + [H(oda)]^- \rightleftarrows [Mg(oda)H]^+ \tag{7}$$

the formation constant

$$\log K = 0.62(\pm 0.09) - 4[\sqrt{I}/(2 + 3\sqrt{I}) - 0.143] + 0.55(I - 0.25) - 0.002(t - 25) \tag{8}$$

By combining values from eqn. (8) and the protonation constants of Table 2 one can obtain β_{111} values.

In the literature, only the value log $\beta_{110} = 1.7[I = 0.1$ (KCl), $t = 30\,°C]$ is reported [12], which is in good agreement with our results. No formation constants for the species $[Mg(oda)H]^+$ are reported, and no ΔH^0 and ΔS^0 values are reported for the complex formation in the Mg^{2+}–oxydiacetate system.

The values of log β_{110} obtained for the Mg^{2+} complex (Table 3) confirm the abnormal character of the stability of the $[Ca(oda)]^0$ complex. In fact, the ratio $\beta_{110}(Ca)/\beta_{110}(Mg)$ is 1.1, 0.3 and 0.95 for succinate [4], malonate [13] and glutarate [14], respectively (i.e. the stability of Ca^{2+} and Mg^{2+} dicarboxylate 1 : 1 complexes have the same order of magnitude), whilst the same ratio is 60 for oxydiacetate complexes. Furthermore, by comparing the absolute stability of Mg^{2+}–succinate and glutarate complexes (log $\beta_{110}[Mg(succ)]^0 = 1.4$, log $\beta_{110}[Mg(glutarate)]^0 = 1.1$; $t = 25\,°C$ and $I = 0.2$ mol l^{-1}), it seems reasonable to hypothesize the involvement of the ethereal oxygen in the coordination. On the contrary, for the species $[Mg(oda)H]^+$, by considering reaction (7), we may exclude the involvement of the ethereal oxygen in the complexation (or else this involvement is less important than in the $[Mg(oda)]^0$ species). In fact, the equilibrium constants relating to the reaction (7) are 4.3 ± 0.3 and 4.2 ± 0.3 mol^{-1}l ($t = 25\,°C$, $I = 0.25$ mol l^{-1}) for succinate and oxydiacetate, respectively; these values are comparable to the formation constant of $[Mg(acetate)]^+$ complex [5] (3.6 ± 0.2 mol^{-1} l, in the same experimental conditions).

As regards the dependence on ionic strength, the results obtained in this work are in good agreement with previous findings [1,11,15].

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