THERMODYNAMIC FUNCTIONS OF THE COORDINATED SYSTEM Pb(II)–OXALATE

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The coordinated Pb(II)–oxalate system has been polarographically studied in aqueous medium at 15, 20, 30 and 35 °C. The formation of the coordinated species $[Pb(ox)]$ and $[Pb(ox)_2]^{2-}$, their stability constants and the values of the ΔG^0, ΔH^0 and ΔS^0 have been determined.

For an accurate knowledge of coordination equilibria, it is fundamental to determine the values of their thermodynamic quantities, ΔG^0, ΔH^0 and ΔS^0, few reports on which are currently to be found in the literature. This is basically due to the great amount of experimental work required for their calculation, which has frequently given rise to the formulation of values on the basis of a study at only two temperatures, with the high probability of large errors that this practice may imply.

We have previously reported[1] the analysis of the coordinated system Cd(II)–oxalate and present in this work that of the system Pb(II)–oxalate, employing a similar systematic approach.

EXPERIMENTAL

Each of the *i–E* curves was plotted with a Metrohm E506 polarograph with an E505 polarographic stand. Two EA427 (Ag/AgCl/NaCl sat) Methrom electrodes were used as counter and reference electrodes, and the working one was a mercury drop electrode. The ionic strength was adjusted to I = 1.0 mol l^{-1} with $NaClO_4$. Measurements of pH were carried out with a pHM 84 Radiometer digital potentiometer with a GK 2401C Radiometer combined electrode. With the exception of the solution of Pb(II) in the absence of ligand which was polarographed at pH 4, all the rest were polarographed at pH 6.5 in order to ensure that the concentration of the oxalate ion was not below 99% of the total concentration of the salt[2]. The concentration of metal ion was 0.08 mmol l^{-1} in all recordings. Drop time was maintained at 3.0 s. The sodium perchlorate and sodium oxalate were Merck products of p.a. quality, the sodium hydroxide used for adjusting the pH was of p.a. quality from May and Baker and the lead perchlorate from Fluka of purum quality.

RESULTS AND DISCUSSIONS

Eight experimental studies were carried out at four temperatures: 15 (I and II), 20 (III and IV), 30 (VIII and IX) and 35 °C (X and XI). Previously, this system[3] was studied at 25 °C (V, VI, VII)

The plots of $\log [(\bar{i}_d - \bar{i})/\bar{i}]$ vs $-E$ show that the discharges occured by a reversible two-electron process. The values for the reversible half-wave potentials were directly obtained from these plots.

Determination of Stability Constants

The application of the DeFord and Hume method[4] to this coordinated system shows that the F_1 vs oxalate concentration dependence is a straight line, which implies the stability of the $[Pb(ox)]$ and $[Pb(ox)_2]^{2-}$ complexes.

The values of β_1 and β_2 obtained from eight measurements are given in Table I together with those corresponding to 25 °C.

The good agreement observed in general between two measurements at each temperature allows the mean value of both to be proposed as the best for β_1 and β_2, summarized in Table I.

Thermodynamic Values

The dependences of $\log \beta_i$ vs $1/T$ (Figs 1 and 2) show an acceptable continuity. By least squares, for the equilibria of formation of the complexes with one and two ligands, the following slopes are obtained:

$$-\Delta H_1^0 / 2.303 R = 465.2$$

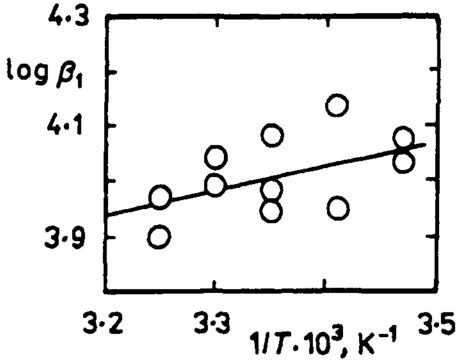

FIG. 1
Plot of log β_1 vs $1/T$

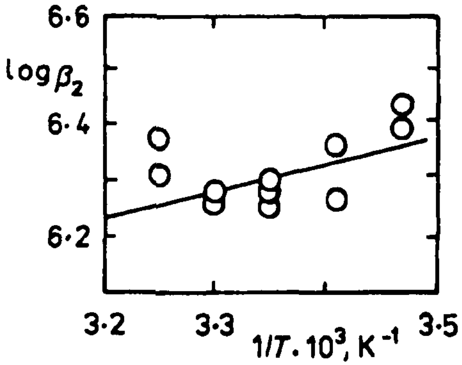

FIG. 2
Plot of log β_2 vs $1/T$

$$-\Delta H_2^0 / 2.303\, R = 513.6 .$$

From these expressions and following the approach indicated[1], the changes in standard enthalpy, free energy and entropy can be calculated for all the equilibria and all the temperatures, the values of which are given in Table I. The changes in free energy increase slightly with the temperature and the changes in enthalpy for the species [Pb(ox)] and $[Pb(ox)_2]^{2-}$ are similar. With respect to the entropic changes, it can be seen that they remain practically constant in the range of temperatures studied although the values for the complex $[Pb(ox)_2]^{2-}$ are almost twice those for [Pb(ox)].

TABLE I
The overall stoichiometric stability constants and thermodynamic quantities for the coordinated system Pb(II)–oxalate

Set	t, °C	$\beta_1 \cdot 10^{-4}$	$\beta_1 \cdot 10^{-4}$ average	$\beta_2 \cdot 10^{-6}$	$\beta_2 \cdot 10^{-6}$ average	ΔG^0 kJ mol^{-1}	ΔH^0 kJ mol^{-1}	ΔS^0 J mol^{-1}
I	15	1.19	1.14 ± 0.1			-22.4 ± 0.2	-8.91 ± 1	46.8 ± 4
II		1.08						
III	20	1.36	1.12 ± 0.25			-22.7 ± 0.6	-8.91 ± 1	47.0 ± 4
IV		0.885						
V[a]	25	1.20	1.00 ± 0.2			-22.8 ± 0.5	-8.91 ± 1	46.6 ± 4
VI[a]		0.88						
VII[a]		0.96						
VIII	30	1.10	1.04 ± 0.1			-23.3 ± 0.2	-8.91 ± 1	47.5 ± 4
IX		0.985						
X	35	0.933	0.86 ± 0.1			-23.2 ± 0.3	-8.91 ± 1	46.4± 4
XI		0.795						
I	15			2.48	2.61 ± 0.2	-35.4 ± 0.2	-9.83 ± 1	88.7 ± 8
II				2.73				
III	20			1.84	2.28 ± 0.4	-35.7 ± 0.5	-9.83 ± 1	88.2 ± 8
IV				2.72				
V[a]	25			2.00	1.90 ± 0.1	-35.8 ± 0.2	-9.83 ± 1	87.1 ± 8
VI[a]				1.90				
VII[a]				1.80				
VIII	30			1.84	1.88 ± 0.1	-36.4 ± 0.1	-9.83 ± 1	87.6 ± 8
IX				1.91				
X	35			2.05	1.97 ± 0.1	-37.1 ± 0.2	-9.83 ± 1	88.5 ± 8
XI				1.89				

[a] Taken from ref.[3].

The marked concordance between our values and those reported by Klatt[5] at 25 °C in the medium of 0.3M-KNO_3, namely $\Delta H^0 = -8.37$ kJ mol^{-1} and $\Delta S^0 = 45.6$ J mol^{-1} for β_1 and $\Delta H^0 = -5.86$ kJ mol^{-1} and $\Delta S^0 = 90.0$ J mol^{-1} for β_2 must be pointed out.

It is interesting to note the large errors that could be induced by an attempt to obtain the data of ΔH^0 by means of two studies only at different temperatures. For instance, experiments IV and VIII led for the complex [Pb(ox)] to the value $\Delta H_1^0 = 16.1$ kJ mol^{-1}, which implies an endothermic nature of its formation reaction, whereas this is really exothermic, with $\Delta H_1^0 = -8.91$ kJ mol^{-1}.

Likewise experiments III and X would also give place to considering an endothermic formation of the complex $[Pb(ox)_2]^{2-}$, $\Delta H_2^0 = 5.44$ kJ mol^{-1}. All the above suggests that it would be worthwhile to revise the existing literature on thermodynamics on the basis of a larger number of experimental studies.

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