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THERMOMETRIC STUDY OF ETHANEDIAMIDOXIME COMPLEXES WITH METALLIC IONS

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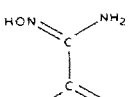
ABSTRACT

A thermometric study of the complexation reactions of ethanediamidoxime (EDA) with the metallic ions Ni(II), Cu(II), Co(II), Fe(III), Ag(I) and Hg(II) was performed. From the results of the study the stoichiometry and formation enthalpies of these complexes were determined. From the analytical point of view, good results were obtained in the case of Ni(II) (orange precipitate) and Cu(II) (brown precipitate) ions, which may be easily determined using thermometric techniques. The MINITERM program was applied to calculate and refine the formation enthalpies of the three blue complexes which form Ni(II) with EDA ($\Delta H_1 = -4.6$ kcal mol^{-1}, $\Delta H_2 = -10.2$ kcal mol^{-1}; $\Delta H_3 = -11.9$ kcal mol^{-1}).

INTRODUCTION

Ethanediamidoxime (EDA) is an analytical reagent which has been proposed as a substitute for dimethylglioxime, due to its similarity and greater solubility in water [1]. In a previous paper [2] we reported the thermodynamic parameters of the dissociation equilibria of EDA. In the present study, a thermometric study of the complexation reactions of EDA with a number of metallic ions has been carried out.

To perform this study, the most outstanding coloured reactions of EDA, i.e. those with Ni(II), Cu(II), Co(II), U(VI) and Fe(III), were chosen. Other uncoloured potential complexes were also considered, like those of Ag(I), Hg(II), Zn(II), Cd(II) and Pb(II).



ethanediamidoxime
oxamidoxime
diaminoglyoxime
1,2-diamino-1,2-dihydroxyimineethane (IUPAC)

0040-6031/89/$03.50

EXPERIMENTAL

Reagents

EDA was obtained by Fischer's method [3] as modified by Wenger [4]. The EDA solution was 0.0250 M and the solutions of metallic ions were 0.500 M.

Apparatus

The thermometric system used in the calorimetric experiments has been described previously [5].

Procedures

The experimental conditions used for thermometric measurements were the same as those described previously [2]. In all cases, 50 mL of EDA (0.0250 M) solution adjusted to the appropriate pH value were titrated at 25 °C. An experimental value of 0.0524 kcal $°C^{-1}$ for the initial heat capacity of the cell was applied, which was corrected throughout the calculation in order to take into account the dilution effect produced during the titrations.

Calculations

An IBM PC portable computer was used for MINITERM.

RESULTS

The thermometric titrations of Cd(II), Zn(II) and Pb(II) lead to null calorimetric curves. For the U(VI) the reaction heat was masked by the

TABLE 1

Enthalpies and stoichiometries of EDA complexes

Ion	Complex	ΔH (kcal mol^{-1})	Stoichiometry found	Stoichiometry assigned
Ni(II)	Blue	−11.4	1:3	1:3
Ni(II)	Orange precipitate	−8.2	1:2	1:2
Cu(II)	Green	−8.5	1:2.5	1:2
Cu(II)	Brown precipitate	−5.5	1:1	1:1
Co(II)	Brown precipitate	−4.8	1:2	1:2
Fe(III)	Brown precipitate	−3.9	1:1.2	1:1
Ag(I)	Colourless	−6.3	1:1.3	1:1
Hg(II)	Yellow precipitate	−20.3	1:3	1:3

dilution heat which was much higher. The stoichiometries and overall complexation enthalpies were determined for a range of inorganic ions as it is shown in Table 1.

The stoichiometry of some of these ions was already known from studies in which other techniques were used. The thermometric results obtained in this study agree with those published previously: Ni(II) orange precipitate [6], Ni(II) soluble blue complex [7] and Cu(II) brown precipitate [8].

Some of the inorganic ions gave well-defined thermometric curves, with low titration errors. In other cases, in spite of their very well defined

TABLE 2

Titration errors of metallic ions with EDA

Ion	Found (mmol)	Stoichiometry (mmol)	E (%)	s	r.s.d.
Ni(II)	0.385	0.417	4.1	0.0267	6.4
(1 : 3)	0.426	0.417			
blue	0.435	0.417			
Ni(II)	0.620	0.625	1.6	0.0057	0.93
(1 : 2)	0.617	0.625			
orange					
precipitate	0.609	0.625			
Cu(II)	0.473	0.625	21.6	0.0147	3.0
(1 : 2)	0.501	0.625			
green	0.495	0.625			
Cu(II)	1.261	1.250	1.4	0.0137	1.1
(1 : 1)	1.283	1.250			
brown					
precipitate	1.258	1.250			
Co(II)	0.648	0.625	5.4	0.0393	6.2
(1 : 2)	0.679	0.625			
brown					
precipitate	0.601	0.625			
Fe(III)	1.014	1.250	17.9	0.0180	1.8
(1 : 1)	1.047	1.250			
brown					
precipitate	1.018	1.250			
Ag(I)	1.005	1.250	25.2	0.0862	9.2
(1 : 1)	0.839	1.250			
colourless	0.962	1.250			
Hg(II)	0.454	0.417	4.1	0.0254	6.0
(1 : 3)	0.410	0.417			
yellow					
precipitate	0.410	0.417			

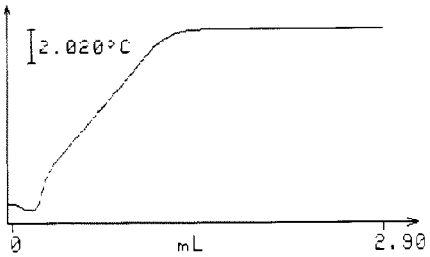


Fig. 1. Thermometric curve of the Ni(II)–EDA insoluble complex.

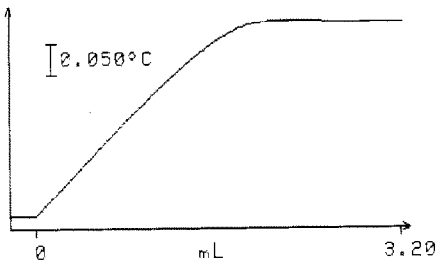


Fig. 2. Thermometric curve of the Hg(II)–EDA complex.

thermometric curves, the titration errors were inadmissible, probably due to hydrolysis processes, pH changes during the titration, side reactions, etc. The titration errors are summarized in Table 2. The results are particularly good for the Ni(II) thermometric titration (orange precipitate) and Cu(II) (brown precipitate) which permit thermometric determination with EDA. The thermometric curves of Ni(II) (orange precipitate) and Hg(II) (yellow precipitate) are given in Figs. 1 and 2, respectively. For Ni(II) a different soluble, blue complex was obtained, with a 1 : 3 stoichiometry (Ni : EDA), which agreed with that found previously [7].

The overall complex enthalpy was -11.4 kcal mol^{-1}. The thermometric curve of this complex is shown in Fig. 3. The MINITERM program [5] was

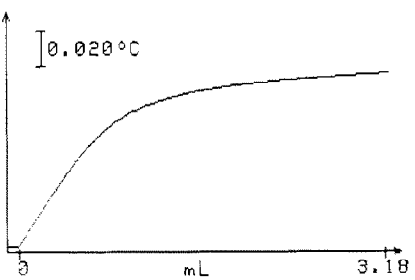


Fig. 3. Thermometric curve of the soluble Ni(II)–EDA complex.

TABLE 3

Refinement of the enthalpies and stability constants of the Ni(II)–EDA complexes by means of the MINITERM program

ml	Total M	$\Delta T,m$	$\Delta T,c$	D
0.144	0.144E−02	0.01440	0.01463	−0.00023
0.165	0.164E−02	0.01720	0.01693	0.00027
0.185	0.185E−02	0.01920	0.01921	−0.00001
0.206	0.205E−02	0.02160	0.02147	0.00013
0.247	0.246E−02	0.02640	0.02593	0.00047
0.257	0.256E−02	0.02720	0.02706	0.00014
0.288	0.287E−02	0.03040	0.03029	0.00011
0.309	0.307E−02	0.03240	0.03246	−0.00006
0.361	0.358E−02	0.03760	0.03771	−0.00011
0.412	0.409E−02	0.04280	0.04278	0.00002
0.463	0.459E−02	0.04800	0.04755	0.00045
0.515	0.510E−02	0.05160	0.05205	−0.00045
0.567	0.560E−02	0.05600	0.05626	−0.00026
0.618	0.610E−02	0.06000	0.06012	−0.00012
0.669	0.661E−02	0.06360	0.06360	−0.00000
0.721	0.711E−02	0.06640	0.06671	−0.00031
0.772	0.761E−02	0.06920	0.06952	−0.00032
0.824	0.811E−02	0.07200	0.07198	0.00002
0.927	0.910E−02	0.07600	0.07613	−0.00013
1.030	0.101E−01	0.07960	0.07948	0.00012
1.133	0.111E−01	0.08240	0.08219	0.00021
1.236	0.121E−01	0.08480	0.08433	0.00047
1.339	0.130E−01	0.08640	0.08622	0.00018
1.442	0.140E−01	0.08800	0.08782	0.00018
1.545	0.150E−01	0.08920	0.08918	0.00002
1.648	0.160E−01	0.09040	0.09035	0.00005
1.751	0.169E−01	0.09120	0.09137	−0.00017
1.854	0.179E−01	0.09200	0.09227	−0.00027
1.957	0.188E−01	0.09280	0.09306	−0.00026
2.060	0.198E−01	0.09360	0.09376	−0.00016
2.163	0.207E−01	0.09440	0.09438	0.00002
2.266	0.217E−01	0.09480	0.09494	−0.00014
2.369	0.226E−01	0.09520	0.09543	−0.00023
2.472	0.236E−01	0.09600	0.09588	0.00012
2.575	0.245E−01	0.09600	0.09627	−0.00027
2.678	0.254E−01	0.09680	0.09663	0.00017
2.781	0.263E−01	0.09680	0.09694	−0.00014
2.884	0.273E−01	0.09720	0.09712	0.00008
2.987	0.282E−01	0.09760	0.09737	0.00023
3.090	0.291E−01	0.09760	0.09760	0.00000

Q	P	R	log β	ΔH (cal mol^{-1})
1	1	0	2.682	−4861
1	2	0	4.698	−10250
1	3	0	7.320	−12328

TABLE 3 (continued)

H metal = 8.4535
H ligand = 73.025
Square of the residuals = 1.929×10^{-6}
Standard deviation = 2.315×10^{-4}
Error in parameter 4 = 33.95361
Error in parameter 6 = 43.75287
Error in parameter 5 = 173.1018

$\Delta T,m$, measured temperature increment; $\Delta T,c$, calculated temperature increment.

applied to obtain and refine the overall enthalpies of formation of the 1 : 1, 1 : 2 and 1 : 3 complexes. The starting log β_i values, introduced in the input data file, were found in the bibliography [7] (log $\beta_1 = 2.69$, log $\beta_2 = 4.70$, log $\beta_3 = 7.33$). The overall complexation enthalpy $\Delta H = -11.4$ kcal mol^{-1} was arbitrarily divided by three and assigned to $\Delta H_1 = -4.0$ kcal mol^{-1}, $\Delta H_2 = -8.0$ kcal mol^{-1}, and $\Delta H_3 = -12.0$ kcal mol^{-1} to the complexes 1 : 1, 1 : 2 and 1 : 3, respectively which were taken as the starting ΔH values for MINITERM.

The experimental data of the thermometric experiment and the overall results are shown in Table 3. The averaged values resulting from MINITERM for the Ni(II)–EDA blue complexes formed in weak acid media are: log $\beta_1 = 2.69$, $\Delta H_1 = -4.6$ kcal mol^{-1}; log $\beta_2 = 4.69$, $\Delta H_2 = -10.2$ kcal mol^{-1}; log $\beta_3 = 7.32$, $\Delta H_3 = -11.9$ kcal mol^{-1}.

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