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ANALYTICAL PROPERTIES OF THE AMIDOXIME GROUP: SPECTROPHOTOMETRIC AND THERMOMETRIC BEHAVIOUR OF ETHANEDIAMIDOXIME AND ITS Cu(II) AND U(VI) COMPLEXES

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ABSTRACT

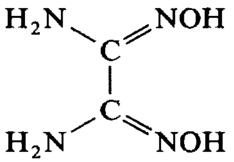
The spectrophotometric behaviour of ethanediamidoxime (EDA) and its Cu(II) and U(VI) complexes has been studied.

EDA pK values were first calculated and then refined using the MINISPEF (p$K_1 = 2.84$ and p$K_2 = 11.23$) and SQUAD programs (p$K_1 = 2.84$ and p$K_2 = 11.25$). The optimum formation conditions for the EDA complexes with Cu(II) and U(VI) have been established, as well as the precision for the spectrophotometric determination of these elements. Stoichiometries for the EDA-Cu(II) complexes are found to be 1:1 and 1:2. The behaviour of the Cu(II)-EDA complexes has also been studied thermometrically. A green 1:2 complex is formed in an acetic acid medium ($\Delta H = -35.6$ kJ mol^{-1}) and a brown precipitate in a sodium acetate medium with 1:1 stoichiometry ($\Delta H = -23.01$ kJ mol^{-1}).

INTRODUCTION

Ethanediamidoxime (EDA) is an analytical reagent which was proposed by Kuras [1] as a substitute for dimethylglyoxime in Ni(II) determination due to its greater solubility in water. Protonation and dissociation pK values of EDA have been determined by means of potentiometric techniques by Wenger et al. [2].

In the present paper a spectrophotometric study of EDA and its Cu(II) and U(VI) complexes is carried out with the aim of achieving a better knowledge of this reagent.



Ethanediamidoxime
Oxamidoxime
Diaminoglyoxime
1,2-diamino-1,2-dihydroxyimineethane (IUPAC)

0040-6031/91/$03.50

EXPERIMENTAL

Reagents

EDA was obtained by the Fischer method [3], modified by Wenger [2].

Photometric titration of EDA

Solutions of EDA (1.34×10^{-4} M), HCl (8.00×10^{-3} M) and KOH (1.79×10^{-2} M) were prepared in distilled water. An ionic strength of 0.1 M was maintained with KCl.

Spectrophotometric study of EDA complexes

The following stock solutions were used: EDA, 5.000 g l^{-1}; Cu(II) and U(VI), 1.00 g l^{-1}.

For the Cu(II) complex study phosphate buffer ($I = 0.1$ M) pH range 2.2–3.9, and acetic–acetate buffer ($I = 0.1$ M), pH range 4.4–4.8 were employed.

For the U(VI) complex study the following buffer solutions were used: pyridine-HCl pH range 4.7–6.4, tris-HCl pH range 7.2–8.5 and *N*-butylamine-HCl pH range 9.5–11.3.

Thermometric study of EDA–Cu(II) complexes

Concentrations of the reagents were, EDA 0.025 M, Cu(II) 0.500 M, acetic acid 0.5 M and sodium acetate 0.5 M.

Apparatus

Spectrophotometry

A Beckman ACTA III spectrophotometer, provided with a fixed (reference) and a quartz flow cell (sample), both of 1.000 cm thickness was employed with a Crison potentiometer (Digilab 517) provided with RS232C and a combined Ingold glass electrode, a Buchler peristaltic pump and a Crison 20 ml automatic burette provided with an RS232C interface. The thermostatic bath was set to $25.0 \pm 0.1°$C.

For the photometric titration of Cu(II) with EDA, an automatic system was built up by connecting the Crison automatic burette and potentiometer to a VIC-20 microcomputer via an RS232C serial interface.

All titrations were performed whilst bubbling pure nitrogen through the solutions in order to keep them under inert atmosphere.

Thermometry

The thermometric system used in the calorimetric experiments has been described elsewhere [4].

Procedures

Photometric titrations of EDA

These were carried out performing a simultaneous calibration of the electrodes using Gran's method, according to the technique of Albelda et al.

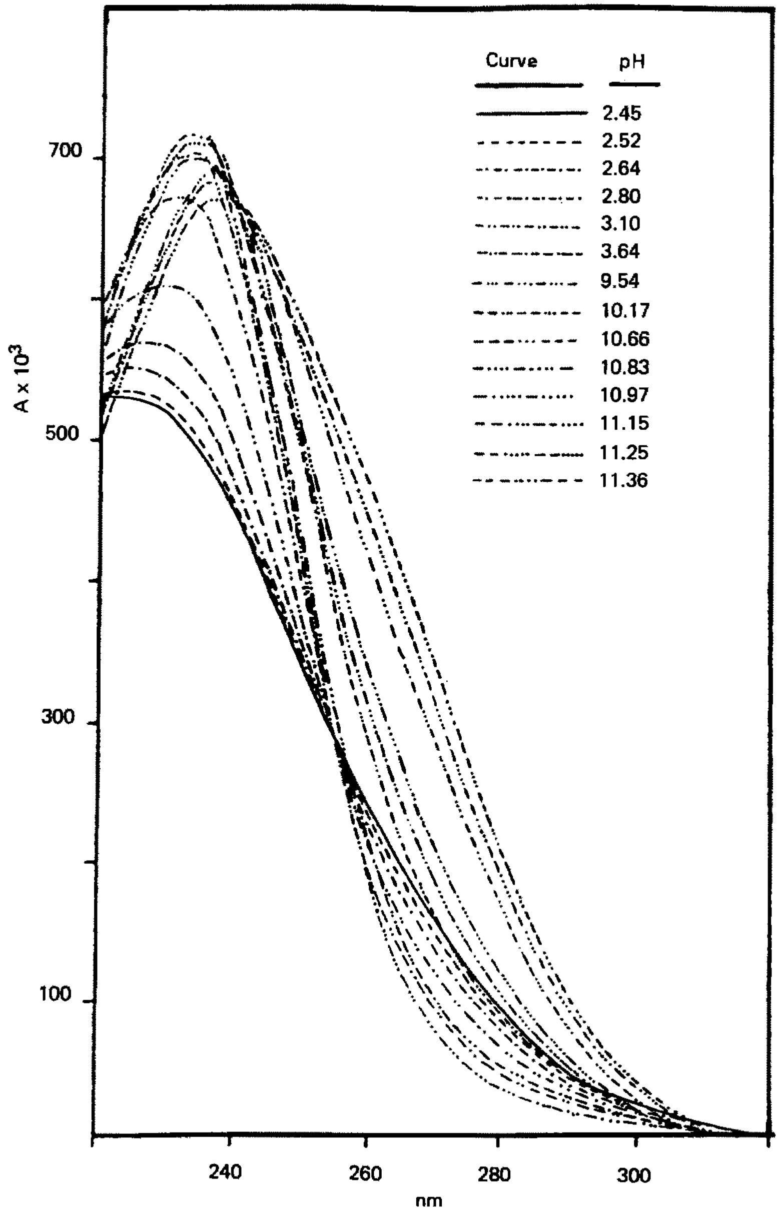


Fig. 1. pH dependence of the EDA spectra.

[4]: 25 ml of 1.34×10^{-4} M EDA ($I = 0.1$ M) and 25 ml of 8.00×10^{-3} M HCl ($I = 0.1$ M) were placed in the titration cell. Nitrogen was bubbled through this solution, which was titrated with 1.79×10^{-2} M KOH ($I = 0.1$ M). Potentials and absorbances were simultaneously read at different analytical wavelengths, which had previously been deduced from the UV spectrum of EDA (Fig. 1).

Spectrophotometric study of the complexes of EDA with Cu(II) and U(VI)

For the study of the influence of the different variables on EDA–Cu(II) complex formation, 1 ml of 1.00 g l^{-1} Cu(II), 10 ml of 5.000 g l^{-1} EDA and the appropriate quantities of buffer were placed in a volumetric flask. Water was added to bring the volume to 25 ml.

The same procedure was used for EDA–U(VI) complex formation, using 1 ml of 1.00 g l^{-1} U(VI) and 3 ml of 5.000 g l^{-1} EDA.

Automatic photometric titration of Cu(II) with EDA

50 ml of 1.260×10^{-3} M Cu(II) (pH 3.3) were placed in the titration cell, and increments of 0.2 ml of 4.234×10^{-2} M EDA solution were added. By means of a peristaltic pump, the solutions were continuously sent to the spectrophotometer and their absorbances measured at 630 nm. Data were stored in the computer memory.

Thermometric titrations of EDA with Cu(II)

The experimental conditions used for thermometric measurements were the same as those described previously [2]. In all cases, 50 ml EDA (0.0250 M) solution adjusted to the appropriate pH values were titrated at 25 °C. An experimental value of 0.2192 kJ $°C^{-1}$ 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 titration.

Data processing

An IBM PC portable computer was used for data processing and MINISPEF refining. SQUAD was run in a Digital VAX 750.

RESULTS

Spectrophotometric determination of EDA pK values

In observing the influence of pH on the UV spectra of EDA (Fig. 1), an isosbestic point may be observed in the acid zone (255 nm) and another in the basic zone (240 nm), which demonstrate the existence of two acid–base equilibria. The experimental data of the photometric curve are included in

TABLE 1

pK values refined by the MINISPEF program

Exp.	$\lambda = 241$ nm			$\lambda = 250$ nm		
	pK_1	$s_{\mathrm{p}K_1}$	$s(A)$	pK_2	$s_{\mathrm{p}K_2}$	$s(A)$
1	2.844	0.023	0.003	11.164	0.017	0.003
2	2.846	0.006	0.001	11.243	0.016	0.003
3	2.836	0.013	0.002	11.272	0.008	0.002

Table 1. Different calculation methods were applied to these data [5,6], which allowed determination of the molar absorptivities of the protonated and dissociated EDA and the approximative pK values of this reagent. These values were used in the program MINISPEF [7]. This program minimizes the function

$$U(\beta_j, \epsilon_j, \epsilon_{\mathrm{L}}, \epsilon_{\mathrm{M}}) = \sum_i \left(A_{\mathrm{exp},i} - A_{\mathrm{calc},i}\right)^2$$

where β_j are the stability constants of the complexes ($\mathrm{M_qL_pH_r}$), and ϵ_j are molar absorptivities of the complexes.

$$A_{\mathrm{calc}} = \epsilon_{\mathrm{m}}[\mathrm{M}] + \epsilon_{\mathrm{L}}[\mathrm{L}] + \sum \epsilon_j \beta_j [\mathrm{M}]_j^{\mathrm{q}} [\mathrm{L}]_j^{\mathrm{p}} [\mathrm{H}]_j^{\mathrm{r}}$$

Σ_i and Σ_j represent the sums for all experimental points and all the complexes, respectively.

Results obtained by applying MINISPEF to three independent experiments under the best analytical experimental conditions (pK_1 at $\lambda = 241$ nm and pK_2 at $\lambda = 250$ nm) are shown in Table 1. The averaged result for MINISPEF is p$K_1 = 2.84$ and p$K_2 = 11.23$. The same initial values used in MINISPEF, together with the titration experimental data, were introduced into the SQUAD program [8,9].

This program presents the following advantages over MINISPEF: it is more powerful; it computes the molar absorptivities; it permits simultaneous treatment of different wavelengths and experiments.

In the SQUAD program, the function for minimization is

$$U(\beta_j, \epsilon_{jk}) = \sum_{i=1}^{N_s} \sum_{k=1}^{N_l} \left(A_{ik}^{\mathrm{exp}} - A_{ik}^{\mathrm{calc}}\right)^2$$

where N_s is the number of solutions taken into account, N_l is the number of wavelengths, and A_{ik} is the absorbance value for solution i at wavelength k.

$$A_{ik}^{\mathrm{calc}} = \sum_{j=1}^{N_c} C_{ij} \epsilon_{jk}$$

Here N_c is the number of species which absorb in the visible or UV zone, C_{ij} is the molar concentration of the component j in solution i and ϵ_{jk} is the molar absorptivity of the component j in solution i.

TABLE 2

pK values refined by the SQUAD program

Exp.	$\lambda = 241$ nm			$\lambda = 250$ nm		
	pK_1	s_{pK_1}	$s(A)$	pK_2	s_{pK_2}	$s(A)$
1	2.845	0.023	0.003	11.206	0.031	0.003
2	2.850	0.006	0.001	11.260	0.020	0.004
3	2.829	0.013	0.002	11.284	0.011	0.002

pK values resulting from applying SQUAD to the same three independent experiments used in MINISPEF are shown in Table 2.

The averaged values from SQUAD agree with those obtained with MINISPEF: p$K_1 = 2.84$ and p$K_2 = 11.25$. Averaged values of the molar absorptivities resulting from the refinement of the three independent experiments for all the selected wavelengths are shown in Table 3.

Spectrophotometric study of the EDA–Cu(II) complexes

Cu(II) reacts with EDA in acid media to give green-coloured solutions. The optimal conditions for absorbance measurements were at pH 3.3 and wavelength at 630 nm. The absorption spectrum in these conditions is represented in Fig. 2. Beer's law is followed within 20–240 ppm of Cu(II), according to the equation

$$A = 0.0065 + 0.0014\ C(\text{ppm}), \quad r = 0.9998$$

The minimum error interval (Ringbom), lies within 130–205 ppm, and the spectrophotometric precision, given by the r.s.d., is 2.8%. The relative error (95% confidence level) is 2.0%.

The complex stoichiometry has been calculated by means of the Yoe–Jones method [10], using a computer controlled automatic photometric system. If solutions of $q_L = L/M < 5$ are taken into consideration, then the extrapo-

TABLE 3

Molar absorptivities of the EDA species, calculated with SQUAD for fixed pK values (p$K_1 = 2.84$; p$K_2 = 11.25$)

λ (nm)	ϵ(L)	$s(\epsilon)$	$\epsilon(HL^+)$	$s(HL^+)$	$\epsilon(L^-)$	$s(L^-)$
280	534	6	1794	107	5569	353
270	1227	24	2913	144	8712	438
264	2152	59	3477	157	10206	400
250	6602	38	4279	164	11222	248
241	9820	27	4935	178	10468	143
234	10832	44	5800	189	9304	234

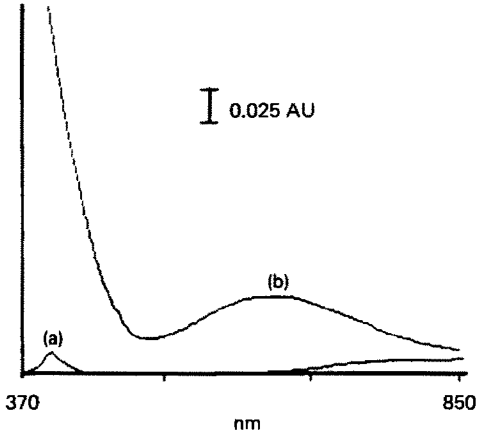


Fig. 2. Absorption spectra at pH 3.3: (a) Cu(II) solution; (b) Cu(II)–EDA complex.

lated point of intersection leads to ML complex. However, from the shape of the photometric curve, a mixture of both ML and ML_2 may be expected.

In order to confirm these stoichiometries and to determine the stability constants, the MINISPEF program was applied. As starting values for constants and molar absorptivities, approximate data deduced for other similar complexes of Cu(II) with different amidoximes were used.

Different stoichiometries were successively tested: (a) 1 : 1, (b) 1 : 1 and 1 : 2, and (c) 1 : 1, 1 : 2 and 1 : 3. A significant improvement in the residual and standard deviation values was observed in (b). On the other hand, no improvement was found when the potential 1 : 3 complexes were taken into account. Therefore, as is usual in these cases, the 1 : 1 and 1 : 2 stoichiometries were accepted.

When overall stability constants were refined by means of the MINISPEF program, different final values of log β_{11} and log β_{12} were obtained, depending on the estimated initial ones. Similar problems arose when SQUAD was used for refinement, since convergence was highly dependent upon the estimated initial values. This behaviour was attributed to the continuous slow change of the absorbance for each experimental point, which gave "noisy" experiments and prevented the achievement of reliable constants. Orientated values obtained by MINISPEF were log $\beta_{11} = 4.8$ and log $\beta_{12} = 7.8$.

Spectrophotometric study of the U(VI)–EDA complex

Uranil reacts with EDA in weak acid, neutral and basic media giving orange–yellow solutions. Their absorption spectra present no maxima within the wide spectral range considered (pH 4.7–11.3). The best analytical conditions for absorbance measurements are pH 10 (Fig. 3) and 380 nm

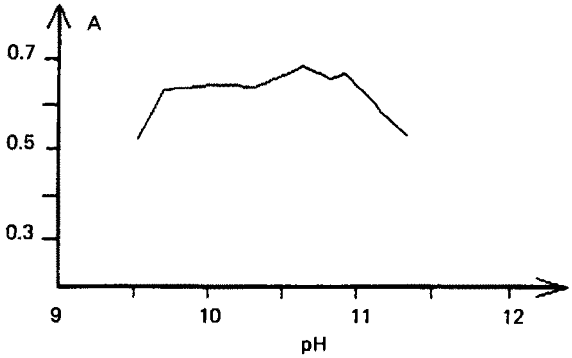


Fig. 3. pH influence on the absorbance of the U(VI)–EDA complex.

(Fig. 4). Under these conditions, Beer's law is followed within a 5–60 ppm range, with a linear equation

$A = -0.0525 + 0.0183\ C(\mathrm{ppm}), \quad r = 0.9999$

The minimum error zone lies between 18 and 35 ppm, the precision of the spectrophotometric method (relative standard deviation) is 1.8% and the relative error 1.3%.

The stoichiometry of the complex could not be determined, either by the Yoe–Jones [10] or by the Job methods. This agrees with the behaviour of uranil with other amidoximes [11].

Thermometric study of the Cu(II)–EDA complexes

EDA reacts with Cu(II) giving a green soluble complex in acetic acid medium and a brown–yellow precipitate in sodium acetate.

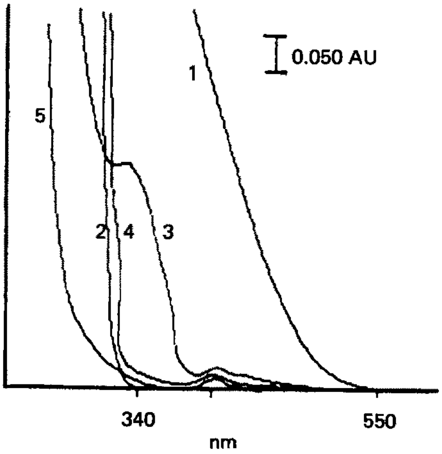


Fig. 4. Absorption spectra of: (1) 1.48×10^{-4} M UO_2^{2+}, 50.80×10^{-4} M EDA and pH 10 buffer; (2) 1.48×10^{-4} M UO_2^{2+}; (3) 1.48×10^{-4} M UO_2^{2+} and buffer; (4) 50.80×10^{-4} M EDA and buffer; (5) 50.80×10^{-4} M EDA.

To carry out the thermometric study of the soluble green complex in acetic acid media, 50 ml of 0.025 M EDA and 0.50 M acetic acid were titrated with 0.500 M Cu(II). The initial pH of the solution was 2.9, whereas the final pH was 2.3. This decrease of pH may be attributed to the protons coming from the protonated amino group of EDA, which are released during its complexation with Cu(II). The stoichiometry found with the thermometric technique was 1 : 2.5, which agrees with the stoichiometry 1 : 2 deduced from spectrophotometry. The overall complexation enthalpy for the 1 : 2 complex was -35.56 kJ mol^{-1}.

To perform the thermometric titration in a sodium acetate medium, 50 ml of 0.0250 M EDA and 0.50 M $NaCH_3COO$ were titrated with 0.500 M Cu(II). The initial pH was 8.2 and the final pH 5.4. This sudden pH decrease may be attributed to the release of protons, coming from the oxime groups of EDA during the complexing reaction.

The stoichiometry corresponded to a 1 : 1 complex, which agrees with the stoichiometry described for other amidoxime complexes in the literature [12]. The complexation enthalpy was -23.01 kJ mol^{-1}, which agrees [13] with the averaged value obtained for the Cu(II)–nitrogen bond (-23.85 kJ mol^{-1}).

Thermometric study of the U(VI)–EDA complexes

The thermometric study of the U(VI)–EDA complexes could not be carried out, since the U(VI) reaction heat was masked by the dilution heat, which was much higher.

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