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ANALYTICAL PROPERTIES OF THE AMIDOXIME GROUP. POTENTIOMETRIC AND THERMOMETRIC BEHAVIOUR OF ETHANEDIAMIDOXIME

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ABSTRACT

Dissociation equilibria of ethanediamidoxime were studied by means of potentiometric and thermometric techniques in a water medium.

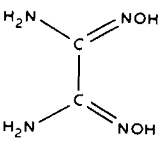
Refined pK values (p$K_1 = 2.97$; p$K_2 = 11.22$) and protonation and dissociation enthalpies ($\Delta H_1 = -5.78$ kcal mol^{-1}; $\Delta H_2 = -6.13$ kcal mol^{-1}) were obtained using different computer programs (GRAN, MINIPOT, MINIQUAD and MINITERM).

INTRODUCTION

Ethanediamidoxime (EDA) is an analytical reagent which has been proposed as a substitute for dimethylglyoxime because of its greater solubility in water [1].

Protonation and dissociation pK values of EDA were determined by means of potentiometric and spectrophotometric techniques [2]. Only two dissociation constants were found, one corresponding to one of the $-NH_2$ groups, and another corresponding to one of the =NOH groups.

In the present paper a thermometric study of EDA is carried out with the aim of gaining a better knowledge of this reagent.



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

EXPERIMENTAL

Reagents

EDA was prepared using Fischer's method [3], as modified by Wenger [2].

Apparatus

For potentiometric measurements, a Corning digital 112 potentiometer, provided with a combined Ingold glass electrode and Metrohm Herisau Dosimat E535 burette, was applied.

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

Procedures

In the potentiometric experiments, all solutions were adjusted to 0.1 M ionic strength with KCl. Calibration of the electrodes was performed in situ by adding hydrochloric acid. All titrations were carried out at $25.0 \pm 0.1^\circ C$ and a stream of nitrogen was bubbled through the samples in order to homogenize the solutions and maintain an inert atmosphere.

Experimental conditions for thermometric measurements were the same as those described in previous papers [4]. In all cases, 50 ml of solution of the sample were titrated at 25°C. An experimental value of 0.0524 kcal $^\circ C^{-1}$ 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 GRAN, MINIPOT and MINITERM. A Digital VAX 750 computer was used for MINIQUAD.

RESULTS

Potentiometric study

Experimental data obtained for the calibration of the electrodes were treated with the GRAN program [5], which gave the standard potentials and the ionic product of water at the chosen experimental conditions. These values were later used in the MINIPOT program [6] for the refinement of the electrode parameters. This program also yielded the junction potentials of the electrodes.

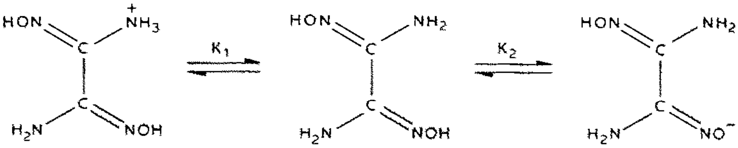
These parameters, with the titration data and approximate pK values of EDA were introduced into the MINIPOT program, whose results were refined by MINIQUAD [7], because better results are obtained when using the $E^\ominus$ values previously refined by the MINIPOT program, than when directly applying the $E^\ominus$ values calculated with the GRAN program [8].

TABLE 1

pK values of EDA refined using the MINIPOT and MINIQUAD programs. ($E^{\ominus}$ = 399.6 mV; pK_w = 13.86; t = 25.0 ± 0.1° C; and I = 0.1 M KCl)

	pK_1	pK_2	pK_w	U	s	X^2	R
MINIPOT	2.98	11.42	13.86	11.48	0.401	–	–
MINIQUAD	2.97	11.22	13.89	8.83×10^{-7}	1.41×10^{-5}	18.39	0.007

Potentiometric pK values of EDA provided by MINIQUAD were used for further work. The constants correspond to the following equilibria



Thermometry

In order to determine the thermodynamic parameters of EDA, it was titrated both with HCl and NaOH.

Tables 2 and 3 list the relative titration errors and molar enthalpies resulting from the overall heat capacity method ($\Delta H = -C\Delta T/n$, where n is the number of mols of the titrand, C is the heat capacity of the thermometric cell and its contents, and ΔT is the overall temperature increment of the thermometric curve).

In both HCl and NaOH titrations, a notable rounding of the titration curve is noticeable around the equivalent point, as is expected from the unfavourable pK values of EDA. Figure 1 represents a titration curve of this compound with HCl.

Different methods to calculate the reaction enthalpies corresponding to thermometric titrations of neutral weak bases with strong acids (protonation

TABLE 2

Titration of 50 ml of 0.0250 M EDA with 0.9873 M HCl

Experiment	V_{eq} (ml)	Error (%)	ΔT (K)	ΔH (kcal mol^{-1})
1	1.193	−5.8	0.132	−5.66
2	1.235	−2.4	0.141	−6.06
3	1.171	−7.5	0.120	−5.15
Average value	1.200	−5.2		−5.62

TABLE 3

Titration of 50 ml of 0.0250 M EDA with 1.1206 M NaOH

Experiment	V_{eq} (ml)	Error (%)	ΔT (K)	ΔH (kcal mol^{-1})
1	1.783	59.9	0.166	−7.21
2	1.584	42.1	0.138	−5.97
3	1.373	23.1	0.138	−5.94
Average values	1.580	41.7		−6.37

enthalpies) or of weak acids with strong bases (neutralization enthalpies) were applied.

The overall heat capacity method uses solely the overall change of temperature of the titration curve, whereas the different point-by-point heat capacity methods take advantage of a large number of points on the thermometric curve, thus yielding better results.

To calculate the protonation enthalpy of the amino group of EDA, two different point-by-point heat capacity methods were used, according to the following equations [9]

method (a) $B = -K_a B/h - \Delta H$

$$B = C_0 V_T \Delta T / C_b^0 \cdot V_0^2$$

method (b) $Y = \Delta H X + 1/\Delta H_a$

$$Y = \left(V_0^2\left(C_a^0 - C_b^0\right) - V_0 V_T\left(K_a + C_a^0\right)\right)/C_0 V_T \Delta T$$

$$X = \left(C_a^0 C_b^0 V_0^3\left(V_T - V_0\right)\right)/C_0^2 V_T^2 (\Delta T)^2$$

where K_a is the dissociation constant of the protonated amino group of EDA and $h = [H^+]$, C_0 is the initial heat capacity of the cell and its content, C_a^0 is the analytical concentration of the titrant acid, C_b^0 is the initial concentration of the base to be titrated and V_0 is the initial volume calculated by means of the Brönsted equation for a monoprotic acid. Results are listed in Table 4.

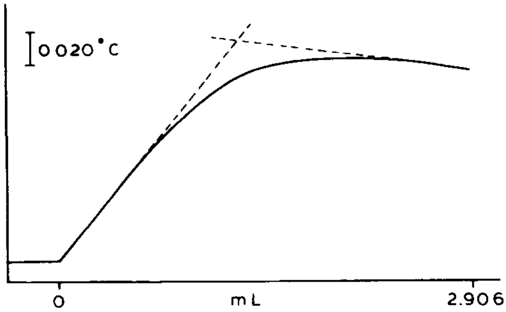


Fig. 1. Thermometric titration curve of 0.0250 M EDA with 0.9873 M HCl in aqueous medium.

TABLE 4

Protonation enthalpy and protonation constant of EDA obtained from the point-by-point heat capacity methods

Method	Experiment	ΔH (kcal mol^{-1})	pK	r
a	1	−5.63	3.014	−0.9996
a	2	−5.80	2.993	−0.9995
a	3	−5.86	2.970	−0.9994
b	1	−5.85	–	−0.9996
b	2	−5.96	–	−0.9999
b	3	−5.49	–	−0.9999
Average values		−5.76	2.992	

The neutralization enthalpy of EDA was determined by means of the point-by-point heat capacity method, using the following equations [10]:

$$Y = -\Delta H X - 1/K_a$$

$$Y = 1/h$$

$$X = C_a^0 V_0^2 / C_0 V_T h \Delta T$$

where K_a is the dissociation constant of one of the oxime groups of EDA. Results are shown in Table 5.

The values of the enthalpies and equilibrium constants were fed into the MINITERM program [4]. The refined parameters are shown in Table 6.

Because the neutralization process of an acid ($HA + OH^- \rightleftharpoons A^- + H_2O$; ΔH_N) may be considered as the sum of the acid dissociation reaction ($HA \rightleftharpoons H^+ + A^-$; ΔH) and the neutralization of the hydroxyl ion by a proton ($H^+ + OH^- \rightleftharpoons H_2O$; ΔH_w), the dissociation enthalpy is $\Delta H = \Delta H_N - \Delta H_w = 6.13$ kcal mol^{-1}.

$\Delta H_w = -13.34 \pm 0.01$ kcal mol^{-1}, considered the most probable value at 25 ° C, was taken from the literature [11–14]. The enthalpy and pK values of EDA obtained by thermometry were: for protonation of the $-NH_2$ group, $\Delta H = -5.78$ kcal $mol^{-1} = -24.2$ kJ mol^{-1} and p$K_1 = 2.99$; and for dissoci-

TABLE 5

Neutralization enthalpy and dissociation constant of EDA obtained from the point-by-point heat capacity method

Experiment	ΔH (kcal mol^{-1})	pK	r
1	−7.60	11.64	0.9995
2	−7.28	11.63	0.9992
3	−6.73	11.58	0.9995
Average values	−7.20	11.61	

TABLE 6

Refined ΔH and pK_a values of EDA using the MINITERM program

Experiment	ΔH (kcal mol^{-1})	pK_1	ΔH (kcal mol^{-1})	pK_2
1	−5.65	3.01	−7.64	11.65
2	−5.80	2.99	−7.25	11.63
3	−5.88	2.97	−6.75	11.59
Average values	−5.78	2.99	−7.21	11.62

TABLE 7

pK and dissociation thermodynamic parameters of EDA groups at 25 °C

Group	pK	ΔG^0 (kcal mol^{-1})	ΔH^0 (kcal mol^{-1})	ΔS^0 (cal K^{-1} mol^{-1})
$-NH_3^+$	2.97	4.06	5.78	6
$=NOH$	11.22	15.32	6.13	−31

ation of the −NOH group, $\Delta H = 6.13$ kcal mol^{-1} = 25.6 kJ mol^{-1} and p$K_2 = 11.62$.

Thermodynamic parameters of EDA

The free energies and entropies involved in the following dissociation equilibria of EDA at 25 °C

$$HL^+ = H^+ + L \quad \Delta H_1^0 = 5.78 \text{ kcal mol}^{-1} \tag{1}$$

$$L = H^+ + L^- \quad \Delta H_2^0 = 6.13 \text{ kcal mol}^{-1} \tag{2}$$

were calculated using the equations

$$\Delta G^0 = -RT \ln K_a \text{ and } \Delta S^0 = (\Delta H^0 - \Delta G^0)/T$$

The results are listed in Table 7, where the pK values considered were those determined by potentiometry.

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