

Thermometry — enthalpimetry

ANALYTICAL PROPERTIES OF THE AMIDOXIME GROUP. XII.

Potentiometric and thermometric behaviour of succinediamidoxime

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The acid-base equilibria of succinediamidoxime (SIDA) were studied by means of potentiometric and thermometric techniques. Refined pK values ($pK_1 = 4.19$; $pK_2 = 5.82$; $pK_3 = 10.70$; $pK_4 = 10.82$) and neutralization enthalpies were obtained using several computer programs (GRAN, MINQUAD and MINITERM).

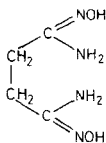
Titration errors and thermodynamic parameters of SIDA are compared with the corresponding values obtained previously for other amidoximes.

The amidoximes are a group of analytical reagents with several interesting applications [1]. Study of the analytical behaviour of this group began in the 1950s, mainly by Kuras et al. [2, 3]. The selected compounds studied by these researchers included succinediamidoxime (SIDA), which showed interesting reactions [4].

In a research project directed towards a better knowledge of this group of compounds, in a previous paper we performed a detailed study of SIDA, determining several of its physicochemical properties, e.g. its solubility in several solvents, R_f values, IR, UV-Vis., proton and NMR spectra, etc. The behaviour of SIDA as an analytical reagent for 37 metallic ions was studied as well [5].

In the present paper we report the acid-base properties of SIDA, determining the titration errors, dissociation constants and neutralization enthalpies. Results are

compared with those obtained for other aliphatic amidoximes previously studied [6].



SIDA

Experimental

Reagents

Succinylidenediamidoxime was obtained from succinylidenedinitrile by the Tieman method [4, 8]: yield 84%, m.p. = 176°.

All the other reagents were of analytical grade and their solutions were prepared with deionized and then bidistilled water.

Apparatus and experimental conditions

Potentiometer: PW 9414 Ion Activity Meter (Philips), with glass AG 9100 and calomel K401 Metrohm electrodes. All solutions were adjusted to 0.5 *M* ionic strength with KCl in the potentiometric experiments. Hydrochloric acid was added to perform the calibration of the electrodes in situ. All titrations were carried out at 25.0 ± 0.1° and a stream of nitrogen was bubbled through the sample in order to homogenize it and to achieve an inert atmosphere.

The apparatus and experimental conditions for the thermometric measurements were the same as described previously [9]. In all cases, 50 ml of a solution of the sample was titrated at 25°. It was not necessary to take into account the effect of the ionic strength, as it was verified that this does not significantly influence the value of ΔH . For calculations, an experimental value of 0.05 Kcal deg⁻¹ was used for the initial heat capacity of the system, which was corrected for the effect of dilution during the titrations.

Calculations

Except for MINQUAD, all calculations were performed on a HP-85 Hewlett Packard microcomputer with 32 Kbytes of RAM memory. Refinements with MINQUAD were carried out with a VAX/VMS 11 of Digital.

Results

The data resulting from the electrode calibrations were treated by the GRAN program [10–11], which yielded several parameters under the current experimental conditions: the standard potential of the glass electrode, the ionic product of water, etc. The resulting values were used as starting parameters for the MINIPOT refinement program [12], which also gave us the junction potentials of the electrodes.

On the other hand, the potentiometric curves corresponding to the titration of SIDA in the presence of HCl were used to calculate the values of \bar{j} [13], which were represented vs. pH for an approximate determination of the dissociation constants. These constants were first refined simultaneously with the standard potential by means of the MINIPOT program, and then with MINIQUAD [14–15], which does not refine E^0 .

The results show that succinediamidoxime has four dissociation constants (Table 1), two for the protonation of the $-\text{NH}_2$ groups and the other two for the deprotonation of the oxime groups. In both cases the constants overlap:

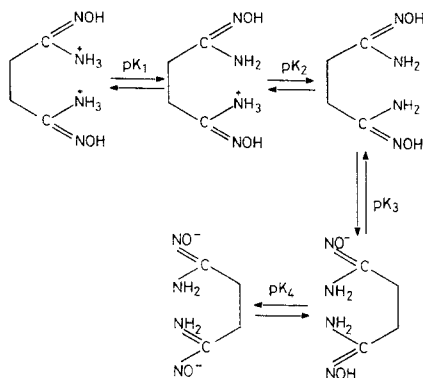


Table 1 pK values of succinediamidoxime obtained by several methods.

$E^0 = 360.6 \text{ mV}$; $pK_w = 13.61$; $t = 25.0 \pm 0.1 \text{ }^\circ\text{C}$; $I = 0.5 \text{ M KCl}$

Method	pK_1	pK_2	pK_3	pK_4	pK_w
\bar{j} Plot	4.325	6.075	10.260	11.175	
MINIQUAD	4.190 ± 0.224	5.822 ± 0.153	10.695 ± 0.035	10.822 ± 0.081	13.609

$$\chi^2 = 18.35, R = 0.0441$$

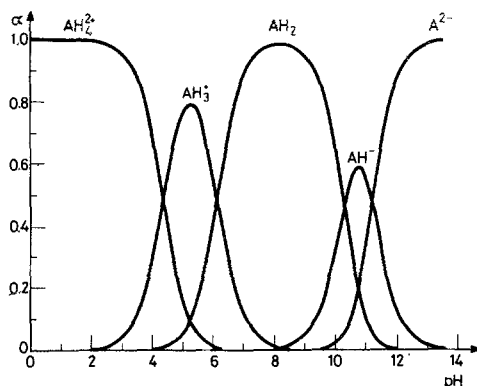


Fig. 1 Distribution diagram of succiniamidoxime

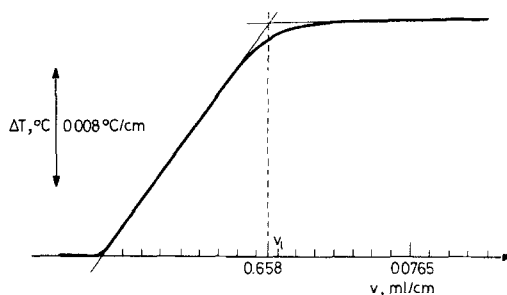


Fig. 2 Thermometric titration curve of succiniamidoxime 0.0130 *M* with HCl 0.9834 *M*

The distribution diagram for succiniamidoxime is given in Fig. 1.

A thermometric titration curve of SIDA, obtained in aqueous medium and using HCl 0.9834 *N* as titrant, is presented in Fig. 2.

Only and —NH_2 group is neutralized and, due to the high pK_b value of this group, a final rounding of the thermometric curve can be observed.

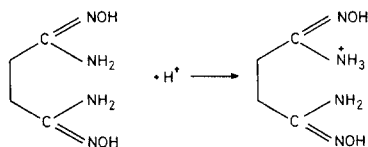
Three independent samples of SIDA were titrated thermometrically in order to obtain their corresponding errors:

Expt.	Concentration	% Error
1	0.01287	0.78
2	0.01290	0.56
3	0.01301	1.42

Since such results are usual in thermometry, we conclude that SIDA can be titrated successfully by calorimetric techniques. All pK values are unfavourable in SIDA titration by potentiometry (or other Gibbs titrations).

In the determination of the neutralization enthalpies of SIDA initially present in its electrically neutral form, two cases can be considered: (1) the nitrogen-containing groups are protonated with HCl, and (2) the oxime protons are neutralized with NaOH.

As shown previously [6], the high pK_a values of the oxime groups prevent the titration of amidoximes with NaOH, and render impossible the calculation of the neutralization enthalpies of these groups. Only a neutralization enthalpy corresponding to the second dissociation constant of SIDA could be calculated:



Several independent methods were used to calculate this neutralization enthalpy.

Overall heat capacity method: This consists in measuring the total temperature variation produced in the titration of n moles of the substance, assuming a complete reaction, and applying the equation

$$\Delta H = -Q/n = -c\Delta T/n$$

The following results were obtained:

Expt.	n (moles)	ΔT °C	ΔH (Kcal mol ⁻¹)
1	6.434 E-4	0.0912	-7.59
2	6.448 E-4	0.0936	-7.86
3	6.503 E-4	0.0936	-7.86

Point-by-point heat capacity methods: These methods consist in analyzing point by point the thermometric titration curve. For each point, from the expression for the equilibrium constant and the charge, matter and heat balances, we have

$$-K_a\Delta H = \frac{C_a C_b V_t}{Q_{T_i}} \Delta H^2 + (C_a + C_b)\Delta H + \frac{Q_{T_i}}{V_T} \quad (1)$$

Method A

This was used by Christensen et al. [16] to calculate the values of ΔH and pK_a of bisulphate. Equation (1) may be represented in the form:

$$-K_a\Delta H = A \cdot \Delta H^2 + B \cdot \Delta H + C$$

As the left side remains constant throughout the titration, for any two points of the

enthalprogram (i, j) the following is verified

$$(A_i - A_j)\Delta H^2 + (B_i - B_j)\Delta H + (C_i - C_j) = 0$$

which allows evaluation of ΔH , since A , B and C are calculable from the titration data.

The results obtained in three independent titrations of SIDA were:

Expt. 1: $\Delta H = -7.36$ Kcal/mol

Expt. 2: $\Delta H = -7.93$ Kcal/mol

Expt. 3: $\Delta H = -7.62$ Kcal/mol

Method B

Rearrangement of Eq. (1) gives

$$\frac{C_0 \Delta T V_T}{C_b^0 V_0^2} = -\Delta H - \frac{C_0 \Delta T V_T K_a}{C_b^0 V_0^2 h}$$

which may be expressed in a simplified form as

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

(A more detailed discussion can be found in Ref. [6].)

This expression is adjustable to the experimental values by means of the Gauss-Newton method. In order to apply this method, the value of the proton concentration h must be known at each point, either from a parallel potentiometric titration, or from calculus from the K_a value. In the present case the pK_a value of the amide group is available, and therefore the second alternative was chosen. The Brönsted equation was solved by means of the iterative method of Newton and Raphson. The results obtained by this method, with one of the thermometric titrations of the amidoxime, are presented in Table 2.

Method C

Expression (1) may be reordered to give the final equation

$$\begin{aligned} \frac{V_0^2(C_a^0 - C_b^0) - V_0 V_T (K_a + C_a^0)}{C_0 V_T \Delta T} &= \\ &= \frac{C_a^0 C_b^0 V_0^3 (V_T - V_0)}{C_0^2 V_T^2 \Delta T^2} \Delta H + \frac{1}{\Delta H} \end{aligned}$$

which, as in the previous cases, allows the experimental data to be adjusted by means of the Gauss-Newton method to obtain the value of ΔH from either the

Table 2 Determination of the neutralization enthalpy of $-\text{NH}_2$ group of SIDA (method B; experiment 2; $C_a^0 = 0.9834 \text{ N}$; $C_b^0 = 0.01289 \text{ M}$; $V_0 = 50 \text{ ml}$; $pK = 5.9$; $C_0 = 0.0524 \text{ Kcal/}^\circ\text{C}$)

V_T (ml)	ΔT $^\circ\text{C}$	h	X_i	Y_i	D
50.152	0.0224	3.233E-007	5.647E+006	1.826	-.450E-001
50.190	0.0280	4.371E-007	5.226E+006	2.284	-.191E-001
50.228	0.0328	5.711E-007	4.689E+006	2.677	-.175E-001
50.266	0.0388	7.312E-007	4.335E+006	3.170	-.457E-001
50.304	0.0444	9.258E-007	3.921E+006	3.630	-.101E-001
50.342	0.0504	1.168E-006	3.531E+006	4.123	8.485E-002
50.380	0.0556	1.476E-006	3.084E+006	4.552	5.550E-002
50.418	0.0616	1.883E-006	2.681E+006	5.047	1.372E-001
50.456	0.0672	2.444E-006	2.255E+006	5.510	1.636E-001
50.494	0.0720	3.268E-006	1.808E+006	5.908	1.039E-001
50.532	0.0768	4.596E-006	1.372E+006	6.307	5.627E-002
50.570	0.0816	7.089E-006	9.460E+005	6.706	1.880E-002
50.608	0.0856	1.344E-005	5.239E+005	7.040	-.795E-001
50.646	0.0884	5.487E-005	1.326E+005	7.276	-.244E-000

$$r = -0.9980; \Delta H = -7.657 \pm 0.136 \text{ Kcal mole}^{-1}; pK_a = 5.989$$

Table 3 Determination of the neutralization enthalpy of the $-\text{NH}_2$ group of SIDA (method C; experiment 2; $C_a^0 = 0.9834 \text{ N}$; $C_b^0 = 0.01289 \text{ M}$; $V_0 = 50 \text{ ml}$; $pK_a = 5.9$; $C_0 = 0.0524 \text{ Kcal/}^\circ\text{C}$)

V_i (ml)	ΔT ($^\circ\text{C}$)	X_i	Y_i	D
50.152	0.0224	6.958E-002	-0.674	-0.151E-002
50.190	0.0280	5.558E-002	-0.564	-0.142E-002
50.228	0.0328	4.853E-002	-0.503	4.600E-003
50.266	0.0388	4.040E-002	-0.443	6.703E-004
50.304	0.0444	3.521E-002	-0.403	1.642E-004
50.342	0.0504	3.069E-002	-0.369	-0.105E-002
50.380	0.0556	2.798E-002	-0.347	-0.309E-002
50.418	0.0616	2.504E-002	-0.324	-0.860E-003
50.456	0.0672	2.292E-002	-0.307	-0.764E-003
50.494	0.0720	2.159E-002	-0.296	-0.225E-003
50.532	0.0768	2.041E-002	-0.287	3.665E-005
50.570	0.0816	1.934E-002	-0.278	1.083E-004
50.608	0.0856	1.872E-002	-0.273	2.208E-004
50.646	0.0884	1.862E-002	-0.272	3.544E-004

$$r = -0.9999; \Delta H = -7.87 \pm 0.00 \text{ (intercept)}; \Delta H = -7.85 \pm 0.06 \text{ (Slope)}$$

intercept or the slope. To apply this method, it is first necessary to know the value of the acidity constant.

The results obtained by this method for the calculation of the neutralization enthalpy of SIDA in one of the experiments are given in Table 3. It may be observed that the values of ΔH obtained from the slope coincide reasonably with those obtained from the intercept.

Finally, we used MINITERM to refine the pK and ΔH values of SIDA [17]. In this program the overall enthalpies and the logarithms of the overall stability constants are treated as unknown parameters. The values which give the minimum of the non-weighted sum of the squares of the residuals of the measured and calculated temperature increments are calculated together with the probable errors:

$$U(\log \beta_i, \Delta H_i) = \sum_i (\Delta T_{meas,i} - \Delta T_{calc,i})^2 =$$

$$= \sum_i [\Delta T_{meas,i} + (\Delta H_M[M] + \Delta H_L[L] +$$

$$+ \sum \Delta H_j \beta_j [M]^{qj} [L]^{pj} [H^+]^{rj}) (V_0/C_0) 1000]^2$$

Table 4 Refinement of pK and ΔH values of SIDA with MINITERM: experiment 2; initial heat capacity 0.0524 Kcal/°C; $T_L = 0.01289 M$; $T_M = 0$

<i>ML</i>	<i>pH</i>	Tot. <i>M</i>	Tot. <i>L</i>	<i>T_{meas}</i>	<i>T_{calc}</i>	<i>D</i>
0.152	6.490	1.000E+000	1.286E-002	+0.02240	+0.02295	-0.00055
0.190	6.359	1.000E+000	1.285E-002	+0.02800	+0.02854	-0.00054
0.228	6.243	1.000E+000	1.284E-002	+0.03280	+0.03407	-0.00127
0.266	6.136	1.000E+000	1.283E-002	+0.03880	+0.03953	-0.00073
0.304	6.033	1.000E+000	1.282E-002	+0.04440	+0.04493	-0.00053
0.342	5.933	1.000E+000	1.281E-002	+0.05040	+0.05024	+0.00016
0.380	5.831	1.000E+000	1.280E-002	+0.05560	+0.05555	+0.00005
0.418	5.725	1.000E+000	1.279E-002	+0.06160	+0.06081	+0.00079
0.456	5.612	1.000E+000	1.278E-002	+0.06720	+0.06599	+0.00121
0.494	5.486	1.000E+000	1.277E-002	+0.07200	+0.07112	+0.00088
0.532	5.338	1.000E+000	1.276E-002	+0.07680	+0.07620	+0.00060
0.570	5.149	1.000E+000	1.275E-002	+0.08160	+0.08125	+0.00035
0.608	4.872	1.000E+000	1.274E-002	+0.08560	+0.08618	-0.00058
0.646	4.261	1.000E+000	1.273E-002	+0.08840	+0.09085	-0.00245
<i>q</i>	<i>p</i>	<i>r</i>	log β	ΔH (cal. mol ⁻¹)		
0.00	1.00	1.00	6.0040	-76.132E+002		

$$\Delta H_M = +00.000E-001 \text{ cal. mol}^{-1}$$

$$\Delta H_L = +00.000E-001 \text{ cal. mol}^{-1}$$

$$\text{Square of residuals} = 1.271E-005 \text{ } ^\circ\text{C}^2$$

$$\text{Standard deviation} = 0.00107 \text{ } ^\circ\text{C}$$

$$\text{Error of parameter no. 1} = 5.7648E-000$$

$$\text{Error of parameter no. 2} = 5.1163E+001$$

Table 4 shows the good agreement between the calculated and measured temperatures after refinement. In Table 5 it can be observed that the pK and ΔH values of the amidoxime groups of SIDA are similar to those obtained previously for other amidoximes.

Table 5 Values of pK and ΔH of the amidoxime groups of SIDA and other amidoximes

Compound	pK_1	pK_2	pK_3	pK_4	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_3$	Ref.
SIDA	4.19*	5.82*	10.70**	10.82**	—	7.39*	—	This work
ODPA	4.60*	6.06*	11.21**	—	6.09*	8.05*	—	[6]
TDPA	4.56*	5.80*	11.05**	—	6.71*	7.68*	—	[6]
IDPA	3.18*	4.79*	8.66	11.39**	6.38*	7.81*	8.81	[6]
DMIAA	4.05*	11.34**	—	—	?	—	—	[18]
DMIA	3.73*	11.66**	—	—	?	—	—	[19]
MPIA	2.34*	—	—	—	—	—	—	[19]
DPIA	2.96	4.83*	11.96**	—	—	—	—	[19]

* $-\text{NH}_2$ group

** NOH group

ODPA = 3,3'-oxydipropidamidoxime

TDPA = 3,3'-thiodipropidamidoxime

IDPA = 3,3'-iminodipropidamidoxime

DMIAA = 3,5-dimethyl-4-isoxazolylacetamidoxime

DMIA = 3,5-dimethylisoxazolylamidoxime

MPIA = 3-phenyl-5-methyl-4-isoxazolylamidoxime

DPIA = 3,5-diphenyl-4-isoxazolylamidoxime

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Zusammenfassung — Säure-Basen-Gleichgewichte von Succindiamidoxim (SIDA) wurden mittels potentiometrischer und thermometrischer Techniken untersucht. Verbesserte pK -Werte ($pK_1 = 4.19$; $pK_2 = 5.82$; $pK_3 = 10.70$; $pK_4 = 10.82$) und Neutralisationsenthalpien wurden unter Verwendung einiger Computerprogramme (GRAN, MINQUAD, MINITERM) erhalten. Titrationsfehler und thermodynamische Parameter von SIDA werden mit entsprechenden Werten verglichen, die in früheren Arbeiten für andere Amidoxime erhalten wurden.

Резюме — Потенциометрическим и термометрическим методами изучено кислотно-основное равновесие для сукциндиаминоксима. Используя несколько компьютерных программ (Гран, Миниквад и Минитерм) были получены улучшенные значения pK ($pK_1 = 4,19$; $pK_2 = 5,82$; $pK_3 = 10,70$ и $pK_4 = 10,82$) и энтальпии реакции нейтрализации. Ошибки титрования и термодинамические параметры для сукциндиаминоксима сопоставлены с таковыми для других амидоксимов.