Thermometry, enthalpimetry

THERMOMETRIC STUDY OF THE DISSOCIATION EQUILIBRIA OF THE MALEINIMIDODIOXIME

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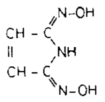
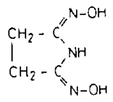
The values of the dissociation constants of the maleinimidodioxime are potentiometrically determined at various ionic strengths, and extrapolated to zero ionic strength ($pK_1^T = 10.41$; $pK_2^T = 11.60$). From these values and from the thermometric titration curves the enthalpies of neutralization ($\Delta H_{N1} = -21.76$, $\Delta H_{N2} = -23.77$ kJ/mol) and the thermodynamic parameters of dissociation of this substance at 25.0 °C are determined ($\Delta G_1^\theta = 59.41$, $\Delta G_2^\theta = 66.23$, $\Delta H_1^\theta = 34.06$, $\Delta H_2^\theta = 32.05$ kJ/mol; $\Delta S_1^\theta = -85.06$, $\Delta S_2^\theta = -114.64$ J/(K mol)).

The imidoximes constitute a group of organic reagents of great interest in inorganic analysis, because some of them give specific and/or sensitive qualitative and quantitative tests [1].

If the reactivity and sensitivity of imidoximes are compared, it is evident that the support of the functional group has a marked influence upon its behaviour, in the sense that the unsaturation increases the sensitivity of the reactions. So the unsaturated maleinimidodioxime (MIDO) [2] has greater sensitivity than the succinimidodioxime (SIDO) [3]:



MIDO



SIDO

This difference can be attributed to the double bond establishing a conjugation bridge between the two oxime groups.

Given the excellent analytical results obtained with the MIDO, we wanted to study this substance further to obtain information leading to the optimum experimental conditions for all its analytical applications.

For this reason in this work its thermodynamic dissociation constants have been determined (ΔG^θ, ΔH^θ, ΔS^θ). Although all these values can be determined applying only thermometric measures [4], we have thought it more opportune, as Barthel recommends [5], to determine the value of ΔG^θ from potentiometric measurement, which are considered more precise. The determination of the value of ΔG^θ has been taken from the value of pK^T, which has been calculated by extrapolation from the values obtained at ionic strengths of 0.05 and 0.10 *M*.

The opportunity has been taken also in this work to establish the variation of the values of the dissociation constants of the MIDO with the ionic strength.

From the determined values of *pK*, the necessary equations were established to determine the enthalpies of neutralization from the thermometric titration curves. With these values, the thermodynamic parameters of dissociation of MIDO have been determined.

Experimental part

Apparatus

For the determination of the values of *pK* a Crison Digilab 517 potentiometer with a resolution of 0.1 mV, a Radiometer G 202 B glass electrode and another of Ag/AgCl (Metrohm EA 441/5), a Metrohm Multidosimat E 415 automatic burette of 10 cm^3 and a thermostated titration cell at 25.0 ± 0.1° have been used. All the titrations have been undertaken in a nitrogen atmosphere.

For the thermometric titrations the apparatus designed by Lumbiarres *et al.* [6] equipped with a thermistor of 100 kΩ of nominal value has been used. As an adiabatic titration vessel a polystyrene cell placed in the inside of a block of porexpan [7] was used. The titrant was added with a Radiometer ABU 12 autoburette with a capacity of 2.5 cm^3.

Potentiometric determination of the dissociation constants

The dissociation constants at the values of ionic strength 0.05, 0.10, 0.25, 0.50 and 1.00 *M*, adjusted with KCl, have been determined. Using the method of Gran [8, 9], the calibration of the electrodes and the calculation of the values of the ionic product of water at each one of these ionic strengths has been carried out. This has allowed us to demonstrate that the liquid junction potential of the reference electrode remained constant during all the titrations.

Table 1

Value of pK_w at various ionic strengths, at 25.0 °C

I	pK_W (found)	pK_W (ref. 10)
0.05	13.83 ± 0.01	
0.10	13.77 ± 0.02	13.78 ± 0.01
0.25	13.73 ± 0.01	
0.50	13.74 ± 0.01	13.74 ± 0.02
1.00	13.76 ± 0.01	13.79 ± 0.02

In Table 1, the average values of the pK_w determined for each one of the ionic strengths are shown, together with the ones found in the Critical Stability Constants [10]. These average values are the ones used in the subsequent calculations.

Titration of the reagent

The MIDO was titrated in the same experimental conditions as those used for the calibration of the electrodes, after adding an adequate quantity of HCl to standardize the electrode in each solution. The function of Grain in the acid zone has been applied, which together with the values of pK_w determined before, has supplied the necessary data for the calculation of $-\log[H^+]$ and for the degree of protonation $\bar{j}$.

To carry out the titrations, 20.0 cm^3 of MIDO of exactly known concentration and 25 cm^3 of HCl was transferred to the titration cell, both containing the KCl necessary to achieve the working ionic strength. The concentrations of the solutions obtained were of the order of 1.0×10^{-3} *M* both in MIDO and in HCl.

These solutions were titrated with KOH (0.035 *M*) containing the necessary KCl so as not to vary the ionic strength in the titration cell.

Once the HCl of the solution was neutralized, the titration of the MIDO was initiated, which was carried out to determine the potential value after each addition of KOH, so that the number of experimental points obtained has not been less than 40 in any of the titrations.

Calculation of the values of pK

Given that in the case of the MIDO two values of pK relatively close have been obtained, it has been necessary to apply methods of calculation that take into account simultaneously the two dissociation equilibria. We have applied the method of linear extrapolation of Speakman and that of elimination of Schwarzenbach.

a) *Method of linear extrapolation* [11]: For the MIDO, which we can represent by H_2A, a value of

$$\bar{j} = \frac{H_{\mathrm{tot}} - h + K_{\mathrm{w}}/h}{A_{\mathrm{tot}}}$$

can be defined, where

$$H_{\mathrm{tot}} = \frac{H_0 v_0 + 2A_0 v_0 - H_{\mathrm{T}} v_{\mathrm{T}}}{v_0 + v_{\mathrm{T}}}\,; \quad A_{\mathrm{tot}} = \frac{A_0 v_0}{v_0 + v_{\mathrm{T}}}$$

being:

h = concentration of the hydrogen ion
H_0 = initial concentration of the acid
A_0 = initial concentration of the reagent
v_0 = initial volume in the titration cell
H_{T} = concentration of the titrant
v_{T} = volume added of the titrant.

If one takes into account the expression of the dissociation constants of the MIDO, together with the anterior equations, the result is:

$$\frac{\bar{j}}{(1-\bar{j}) \cdot h} K_2 + \frac{(\bar{j}-2) \cdot h}{(1-\bar{j})} \cdot \frac{1}{K_1} = 1$$

Calling $y = \frac{\bar{j}}{(1-\bar{j})\cdot h}$ and $x = \frac{(\bar{j}-2)\cdot h}{(1-\bar{j})}$, and re-arranging:

$$y = \frac{1}{K_2} - \frac{1}{K_1 \cdot K_2}x$$

which gives a straight line of slope $-1/K_1K_2$ and of intercept $1/K_2$.

In Table 2, the results obtained by applying this method to the data of the titration of the MIDO to various ionic strengths are shown.

Table 2

Determination of the pK_1 and pK_2 values of MIDO

I	Experiment	Method of Speakman		Method of elimination	
		pK_1	pK_2	pK_1	pK_2
0.05	1	10.25	11.17	10.22	11.19
	2	10.25	11.35	10.22	11.36
	3	10.25	11.22	10.21	11.24
	4	10.25	11.30	10.20	11.33
		$pK_1 = 10.25 \pm 0.00$	$pK_2 = 11.26 \pm 0.08$	$pK_1 = 10.21 \pm 0.01$	$pK_2 = 11.28 \pm 0.08$
0.10	1	10.17	11.21	10.16	11.1
	2	10.17	11.13	10.20	11.06
	3	10.15	11.07	10.15	11.02
	4	10.13	11.00	10.13	10.99
	5	10.07	11.04	10.09	11.02
		$pK_1 = 10.14 \pm 0.04$	$pK_2 = 11.09 \pm 0.08$	$pK_1 = 10.15 \pm 0.04$	$pK_2 = 11.06 \pm 0.08$
0.25	1	10.09	11.04	10.08	11.03
	2	10.10	11.01	10.09	11.01
		$pK_1 = 10.10 \pm 0.01$	$pK_2 = 11.02 \pm 0.02$	$pK_1 = 10.08 \pm 0.01$	$pK_2 = 11.02 \pm 0.01$
0.50	1	10.08	10.98	10.08	10.98
	2	10.09	11.08	10.11	11.06
	3	10.08	11.03	10.08	11.02
		$pK_1 = 10.08 \pm 0.01$	$pK_2 = 11.03 \pm 0.05$	$pK_1 = 10.09 \pm 0.02$	$pK_2 = 11.02 \pm 0.04$
1.00	1	10.06	11.08	10.09	10.95
	2	10.08	11.00	10.13	11.10
	3	10.09	11.21	10.07	11.07
	4	10.13	11.13	10.09	11.20
		$pK_1 = 10.09 \pm 0.03$	$pK_2 = 11.10 \pm 0.09$	$pK_1 = 10.10 \pm 0.02$	$pK_2 = 11.08 \pm 0.10$

b) *Method of elimination* [12]: From the diverse linear equations used in this method [13], the best results have been obtained with the equation:

$$\frac{\bar{j}}{(2-\bar{j})\cdot h^2}K_1K_2 + \frac{\bar{j}-1}{(2-\bar{j})\cdot h}K_1 = 1$$

To calculate the values of K_1 and K_2, for each experimental pair $(\bar{j}, h)$ a pair of points $(y^{-1}, 0)$, $(0, x^{-1})$ is calculated, being $x = \bar{j}/(2-\bar{j})\cdot h^2$ and $y = (\bar{j}-1)/(2-\bar{j})\cdot h$, that define a straight line. *A* group of straight lines is obtained in this way whose intersection at the point (K_1, K_1K_2) permits the calculation of these constants (Fig. 1).

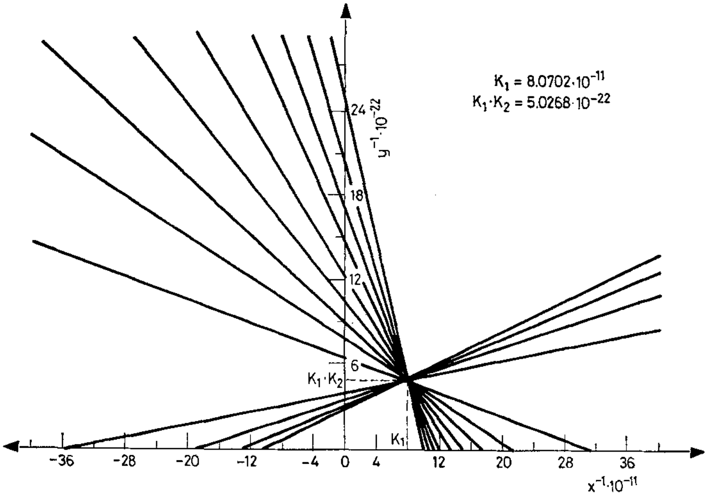


Fig. 1. Graphic representation of the method elimination $I = 1.00$ exp. 4

In Table 2, the results obtained by applying this method of calculation at the different ionic strengths are also shown.

Thermometric study of the MIDO

Titration of the reagent

In Fig. 2 one can observe the resultant curve of titrating 40.0 cm^3 of a solution 1.414×20^{-2} *M* of MIDO with NaOH (1.1207 *M*). As one can observe, from the initiation of the titration, the curve shows a continuous curvature corresponding to the neutralization of two protons. This curvature, together with the absence of a rapid change of the slope, prevents the establishment of a definite end point.

Calculation of the enthalpies of neutralization

The determination of the enthalpies of reaction can be carried out by comparison with a reaction of a known enthalpy [14, 15], or using a system of electric calibration, which has the advantage of being an absolute method [16].

The calculation based on an electric calibration can be carried out by the method of slopes [17], in which the slope of the titration curve is compared with the slope of an electric simulation of the same, or using the method of the entropy titration, suggested by Christensen *et al.* [18, 19], in which the heat capacity of the system electrically determined is used, and a general equation is established as a function of all the equilibria present and also of the mass and energy balances. This equation can be solved by adjusting the various parameters with an iterative method using a function of the type:

$$U(\beta_i, \Delta H_i^\theta) = \sum_{i=1}^{n} w_i(Q_{\exp i} - Q_{\text{calc}i})^2$$

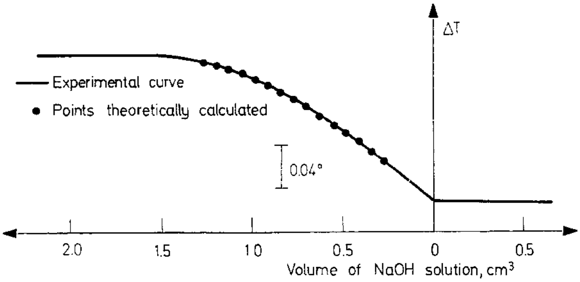


Fig. 2. Thermometric titrimetry of MiDO. — Experimental curve; • points theoretically calculated. Working conditions: concentration of MIDO: 1.414×10^{-2} *M*; concentration of NaOH: 1.1207 *M*; volume added 1.484 cm^3

In the present work we have been able to use a more simple method of calculation, because the values of the *pK* of the MIDO have been determined previously. To do that we have taken into account the corresponding equations of the dissociation equilibria of the MIDO and of the water, the mass balance and the heat balance of the neutralization reaction:

$$Q_T = c \cdot \Delta T = [\text{HA}^-] \cdot \Delta H_1 \cdot v + [\text{A}^{2-}](\Delta H_1 + \Delta H_2) \cdot v$$

Combining these equations, gives:

$$\frac{Q_T(h^2 + K_1 h + K_1 K_2)}{A_0 v_0 K_1 K_2} = (\Delta H_1 + \Delta H_2) + \frac{h}{K_2} \Delta H_1$$

in which, representing the first member as the ordinate Y, against the abscissa $X = h/K_2$, a straight line of slope ΔH_1 and of intercept $\Delta H_1 + \Delta H_2$, is obtained. To carry out this representation, the heat of the reaction, Q_T, is known as follows:

$$Q_T = c \cdot \Delta T = (c' + v_T \cdot c_e) \cdot \Delta T$$

where c is the heat capacity of the system at any point of the titration, ΔT the variation of the temperature from the initial point of the titration up to the point that is being considered, v_T the volume of the titrant added, c' the initial heat capacity of the system and c_e the specific heat of the titrant once diluted in the interior of the solution, that we can take approximately as equal to unity. The initial heat capacity c' has been determined dissipating a known quantity of heat by the Joule effect. The average value obtained was 188.27 J/degree.

The value of h at each point of the titration can be calculated from the values of pK_w, pK_1 and pK_2, and from the balance of the mass and of the charge in the solution, which gives the expression:

$$h^4 + h^3 \left(k_1 + \frac{H_T v_T}{v_0 + v_T}\right) + h^2 \left(K_1 K_2 - K_w + K_1 \frac{H_T v_T - A_0 v_0}{v_0 + v_T}\right) +$$

$$+ h \left(K_1 K_2 \frac{H_T v_T - 2A_0 v_0}{v_0 + v_T} - K_1 K_w\right) - K_1 K_2 K_w = 0$$

This expression can be resolved by the method of Newton–Raphson.

In Table 3, the results obtained by applying the anterior equations to two independent titrations of MIDO with NaOH can be found. The Table includes

Table 3

Thermometric titration of MIDO

Experiment 1				Experiment 2			
$A = 1.414\ 10^{-2}$ M $v = 40.0$ cm^3 $H_T = 1.1207$ M				$A = 1.352\ 10^{-2}$ M $v = 40.0$ cm^3 $H_T = 1.1207$ M			
v_T, cm^3	pH	ΔT_{exp}, degree	ΔT_{calc}, degree	v_T, cm^3	pH	ΔT_{exp}, °C	ΔT_{calc}, °C
0.283	10.201	0.035	0.0355	0.285	10.152	0.036	0.0359
0.353	10.368	0.044	0.0442	0.356	10.314	0.045	0.0447
0.424	10.523	0.052	0.0527	0.427	10.462	0.054	0.0534
0.495	10.670	0.062	0.0611	0.498	10.603	0.062	0.0620
0.565	10.810	0.070	0.0692	0.570	10.737	0.070	0.0703
0.636	10.943	0.078	0.0769	0.641	10.866	0.079	0.0784
0.707	11.071	0.084	0.0842	0.712	10.990	0.086	0.0861
0.777	11.192	0.091	0.0908	0.784	11.109	0.094	0.0934
0.848	11.308	0.097	0.0969	0.855	11.223	0.100	0.1000
0.919	11.416	0.102	0.1021	0.926	11.332	0.105	0.1061
0.989	11.516	0.107	0.1065	0.997	11.435	0.111	0.1114
1.060	11.609	0.110	0.1103	1.068	11.531	0.115	0.1159
1.131	11.693	0.114	0.1133	1.140	11.620	0.118	0.1197
1.201	11.769	0.116	0.1157	1.211	11.701	0.121	0.1228
1.272	11.838	0.118	0.1176				
$Y = -46.27 - 21.38$ X (r = 0.99993) $\Delta H_1 = -21.38$ kJ/mol $\Delta H_2 = -24.89$ kJ/mol				$Y = -44.81 - 22.13$ X (r = 0.99999) $\Delta H_1 = -22.13$ kJ/mol $\Delta H_2 = -22.68$ kJ/mol			

the *pH* value of each point of the titration curve, and the corresponding values of *Y* and *X* necessary to adjust the straight line of regression. In this table 3 the results are also shown.

For the calculation of the *pH*, the average values of pK_w, pK_1 and pK_2 obtained at ionic strength 0.05 *M*, which is the most approximate to the working conditions, have been used.

Results and conclusions

Dissociation constants

We give in Table 4 the average values of pK_1 and pK_2 of the MIDO at various ionic strengths, found by applying the method of linear extrapolation of Speakman and of elimination.

Table 4

I	pK_1	pK_2
0.05	10.23 ± 0.02	11.27 ± 0.07
0.10	10.14 ± 0.04	11.08 ± 0.08
0.25	10.09 ± 0.01	11.02 ± 0.02
0.50	10.09 ± 0.01	11.02 ± 0.04
1.00	10.09 ± 0.02	11.09 ± 0.09

From the values of pK_w found at ionic strength 0.05 and 0.10 *M*, to which the equation of Guggenheim [20] can be applied, the thermodynamic value of the ionic product of water has been calculated, giving in both cases a value of 14.02, that coincides with that of 13.997 of the "Critical Stability Constants" [10], which supposes less than 0.2% deviation.

In the same way, the values of the thermodynamic dissociation constants of MIDO from these same ionic strengths have been calculated. These values are shown in Table 5.

Table 5

I	pK_1^C	pK_1^T	pK_2^C	pK_2^T
0.05	10.23	10.42	11.27	11.64
0.10	10.14	10.40	11.08	11.57
		$pK_1^T = 10.41$		$pK_2^T = 11.60$

Enthalpies of neutralization

The results obtained in the two thermometric titrations of the MIDO are coincident. These results are more exact and have a higher precision than those obtained by the method of the slopes [21], which often occurs when the dissociation constants are very small [22]. In both titrations, the correlation coefficients obtained are close to unity, which shows the precision of the method of calculation used. The median values found of the enthalpies of neutralization are $\Delta H_1 = -21.76$ kJ/mol and $\Delta H_2 = -23.77$ kJ/mol.

From these medium values, some points of the theoretical curve have been calculated. These points are shown in Fig. 2, together with the experimental curve, showing that both coincide. In Table 3, these theoretical values of ΔT, calculated from these enthalpies, are included.

Thermodynamic parameters

Once the values of the neutralization enthalpies of the MIDO are known, it is possible to determine the value of its dissociation enthalpies, as the neutralization reaction of an acid corresponds to the sum of its process of dissociation with that of water formation.

In the beginning, one can accept that the neutralization enthalpies determined at ionic strength 0.05 *M*, have practically the same value as those at zero ionic strength [10]. Taking the value −55.81 kJ/mol for the formation enthalpy of water at zero ionic strength [10, 23], the results obtained for the dissociation enthalpies for the MIDO are shown in Table 6.

Table 6

Thermodynamic parameters of dissociation of the MIDO (25.0 °C; $I \rightarrow 0$)

	pK	ΔG^0, kJ mol^{-1}	ΔH^0, kJ mol^{-1}	ΔS^0, J K^{-1} mol^{-1}
1st dissociation	10.41	59.41	34.06	−85.06
2nd dissociation	11.60	66.23	32.05	−114.64

From the thermodynamic values of pK, it is possible to calculate the corresponding values of the variations of the free energy of dissociation, using the expression $\Delta G^0 = -RT \times \ln K^T$, and the variations of the dissociation entropies of the MIDO from $\Delta S^0 = (\Delta H^0 - \Delta G^0)/T$. In Table 6, the values of these thermodynamics parameters for the dissociation of the MIDO are shown. These values have been obtained at 25.0 °C extrapolated to zero ionic strength.

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Zusammenfassung — Die Werte der Dissoziationskonstanten von Maleinimidodioxim wurden potentiometrisch bei verschiedenen Ionenstärken bestimmt und auf die Ionenstärke Null extrapoliert ($pK_1^T = 10.41$; $pK_2^T = 11.60$). Aus diesen Werten und aus den thermometrischen Titrierungskurven wurden die Neutralisierungsenthalpien ($\Delta H_{N1} = -21.76$, $\Delta H_{N2} = -23.77$ kJ/mol) und die thermodynamischen Dissoziationsparameter dieser Substanz bei 25 °C bestimmt ($\Delta G_1^\theta = 59.41$, $\Delta G_2^\theta = 66.23$, $\Delta H_1^\theta = 34.06$ kJ/mol, $\Delta H_2^\theta = 32.05$ kJ/mol; $\Delta S_1^\theta = -85.06$, $\Delta S_2^\theta = -114.64$ J/Kmol.

Резюме — Потенциометрическим методом определены константы диссоциации ($p\mathrm{K}_1^T = 10.41$ и $\mathrm{p}K_2^T = 11.60$) малеинимидодиоксима при различных ионных силах и экстраполированных до нулевой ионной силы. На основе этих значений и кривых термометрического титрования определены энтальпии нейтрализации $\Delta H_{N1} = —21.76$ и $\Delta H_{N2} = —23.77$ кдж/моль и термодинамические параметры диссоциации этого вещества при 25.0°: $\Delta G_1^0 = 59.41$; $\Delta G_2^0 = 66.23$. $\Delta H_1^0 = 34.06_2$ $\Delta H_2^0 = 32.05$ кдж/моль, $\Delta S_1^0 = —85.06$; $\Delta S_2^0 = —114.64$ Дж/Кмоль.