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THERMOMETRIC BEHAVIOUR OF (METHYLTHIO)ACETIC, THIODIACETIC AND 3,3′-THIODIPROPANOIC ACIDS

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ABSTRACT

The thermometric behaviour of three thioether acids [(methylthio)acetic, thiodiacetic and 3,3′-thiodipropanoic] is studied in order to establish the best conditions for their enthalpimetric titrations with NaOH and calculate the corresponding enthalpies of neutralization. From the value of pK_a and of the neutralization enthalpies, the thermodynamic parameters of dissociation, $\Delta G°$, $\Delta H°$ and $\Delta S°$, at 25°C, of the three substances are estimated.

INTRODUCTION

There are several different organic reagents of chemico-analytical importance containing atoms of bivalent sulfur in which the capacity of coordination with metallic ions comes into play [1]. Although less studied than the chelate formation with the intervention of atoms of carbon and nitrogen, carbon and oxygen, or carbon, nitrogen and oxygen, the formation of complexes by acids with bivalent sulfur-containing functional groups also turns out to be of practical importance (e.g. dithizone, dithioxamide, etc.). The comparative study of all of this type of compound shows that the most important reagents containing sulfur also contain nitrogen in their molecules in an appropriate position for chelation. Some reagents which only contain sulfur as a coordinating atom (xantogenates, dithiol, etc.) are also important. On the other hand, the reagents that contain sulfur and oxygen as active atoms in the coordination are less well-known or applied, although some mercapto acids have found analytical application.

In the course of a research program designated to fill some of the gaps in this field, several different potentiometric and spectrophotometric studies have been made on several carboxylic acids which contain the thioether function and on the formation of metal complexes by these compounds, from which the weak bonding behaviour of these substances is deduced [2].

In the present paper the thermometric study of some of them [(methylthio)acetic,

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thiodiacetic and 3,3′-thiodipropanoic acids] is initiated from an analytical point of view and in order to estimate their thermodynamic dissociation parameters, $\Delta G°$, $\Delta H°$ and $\Delta S°$.

EXPERIMENTAL

Calorimetric equipment

A thermometric titrator was built according to the design of Lumbiarres et al. [3], consisting of an automatic 2.5 ml Radiometer ABU 12 burette, a temperature measuring bridge with thermistor, an adiabatic titration cell, an electric calibration system and a Yokogawa 4701 register with an imput impedance of 5 MΩ.

To measure temperature, a miniature thermistor of the thermometer type, with a nominal value of 10 kΩ at 25°C, has been selected. Its experimental calibration indicates that it follows this equation: $\ln R_T(\mathrm{k}\Omega) = -10.3993 + 3792.4/T(\mathrm{K})$ ($r = 0.9999$). From the values determined during this calibration, a temperature-measuring bridge, with a sensitivity of 20 mV K^{-1}, has been built. The temperature scale of the enthalpigrams is modified by varying the attenuation of the register, and its maximum sensitivity is 2.5×10^{-3}°C cm^{-1}.

The behaviour of the apparatus has been determined by the titration of 80.0 ml of several NaOH solutions of increasing their concentration with HCl 0.9933 N. The mean error of these titrations is of the order of 0.1%, acceptable for this technique.

Heat capacity of the cell

The titration cell proposed by Christensen et al. has been used [4].

In all the titrations 80.0 ml of the sample have been used and the heat capacity of the system has been determined under the same experimental conditions, by introducing a known quantity of heat by means of the electric calibration system or through a chemical reaction of well-known enthalpy (the neutralization of NaOH with HCl, $\Delta H = -55.814$ kJ mole^{-1} at 25°C [5]). The two methods have given concordant results, whose mean value is 0.3736 kJ $°\mathrm{C}^{-1}$.

Procedure

Three independent samples of each of the three thioether acids [at concentrations sufficiently high (see Table 1) that the calculated titration error would not be influenced by an excessive dilution of the sample] were titrated at 20°C with NaOH 0.9020 N.

TABLE 1

Titration errors of thioethercarboxylic acids

Expt.	(Methylthio)acetic		Thiodiacetic		3,3′-Thiodipropanoic	
	Concn. (M)	E^a(%)	Concn. (M)	E^b(%)	Concn. (M)	E^b(%)
1	1.0277×10^{-2}	0.12	5.1948×10^{-3}	0.7	6.0115×10^{-3}	0.30
2	1.0585×10^{-2}	0.07	5.1945×10^{-3}	0.5	6.1167×10^{-3}	0.48
3	8.2168×10^{-3}	0.73	6.9369×10^{-3}	0.4	6.8252×10^{-3}	0.12
	$\bar{E}=$	0.31	$\bar{E}=$	0.53	$\bar{E}=$	0.30

[a] Neutralization of one proton.

[b] Neutralization of two protons.

RESULTS AND DISCUSSION

Titration errors

The errors in the thermometric titrations of these compounds (Table 1) are acceptable and in accordance with those to be expected according to the low pK_a values of the three thioether acids. These values explain the well-defined shape of the enthalpigrams, both in the case of (methylthio)acetic acid ($pK_a = 3.55$) as well as of thiodiacetic ($pK_{a1} = 3.14$ and $pK_{a2} = 4.01$) and 3,3′-thiodipropanoic ($pK_{a1} = 3.87$ and $pK_{a2} = 4.68$) acids, in which the two dissociable protons are simultaneously neutralized with a well-defined end point.

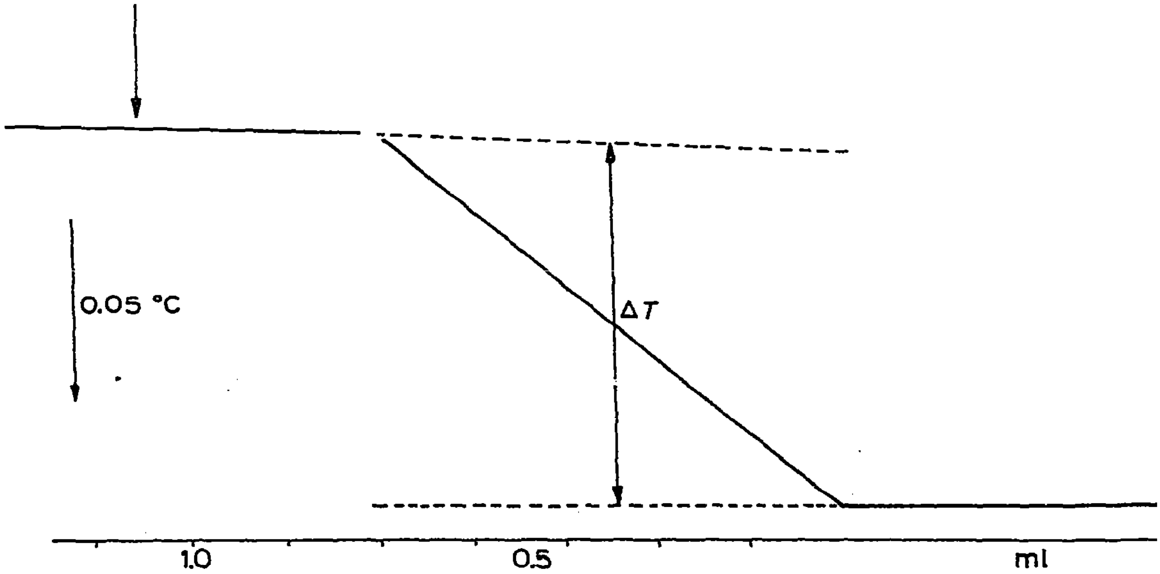

Fig. 1 Calculation of the neutralisation enthalpy of (methylthio)acetic acid with NaOH, $C_a = 8.2168\times10^{-3}$M; $C_b = 0.9020\times10^{-3}$M.

TABLE 2

Neutralization enthalpy of (methylthio)acetic acid. Overall heat capacity method.

Experiment	ΔT (°C)	n (mmoles)	ΔH_N (kJ mole^{-1})
1	0.1294	0.8180	−59.83
2	0.1362	0.8426	−60.38
3	0.1063	0.6540	−60.71
			$\overline{\Delta H_N} = -60.31 \pm 0.44$

Neutralization enthalpies of the thioether acids

In the determination of the neutralization enthalpies of thioether acids, two different situations have to be taken into consideration: that of a monoprotic acid, and that of a diprotic acid with similar dissociation constants. In both cases the calculations were done by two different methods, which we have designated as the overall heat capacity method and as the point-by-point heat capacity method.

(Methylthio)acetic acid

Overall heat capacity method. This method derives from the classic calorimetric method and consists of measuring the overall temperature variation (determined from the enthalpigram according to Fig. 1) produced during the titration of n moles of the compounds, supposing their reaction to be completed, and of applying the equation $\Delta H = -Q/n = -c\,\Delta T/n$.

In the case of very weak acids or bases, this condition of completed reaction is reached only if a sufficient excess of the titrant is added, which requires a graphic extrapolation, with the subsequent loss of accuracy and precision.

The results obtained by applying this method to calculate the neutralization enthalpy of (methylthio)acetic acid are set out in Table 2.

Point-by-point heat capacity method. This method allows us to make use of all the points of the experimental enthalpigram for the calculation of ΔH_N. For each point of the titration curve which is considered, defined by its coordinates ΔV_i and ΔT_i, it is necessary to know the fraction of compound actually neutralized, which is determined from the value of the acid dissociation constant or from the proton concentration in the solution.

In the case of a monoprotic acid, taking into consideration the matter, charge and heat balances as well as the expression of the dissociation constant, the general equation

$$\frac{1}{h} = -\frac{1}{K_a} - \Delta H \frac{C_a V_G^2}{c\,\Delta T_i V_T h}$$

is deduced which corresponds to that of a straight line in which

$$Y_i = \frac{1}{h}; \qquad X_i = \frac{C_a V_0^2}{c \, \Delta T_i \, V_T \, h}$$

where C_a = analytical concentration of the titrand; C_b = analytical concentration of the titrant; c = heat capacity of the cell and its contents; ΔT_i = temperature variation after having added $(V_T - V_0)$ ml of the titrant; V_T = total volume of the solution contained in the cell at all times during the titration; V_0 = initial volume of the solution to be titrated.

The straight line equation can be adjusted from the experimental data by applying the Gauss–Newton method and thus the value K_a is obtained from the intercept and that of ΔH from the slope.

The only difficulty in calculating the values X_i and Y_i lies in finding the values of the proton concentration h. This may be easily found, e.g. by doing a potentiometric titration in parallel with the thermometric titration. Nevertheless, it is possible to calculate it by solving the Brønsted equation for a monoprotic acid

$$h^3 + \left(K_a + \frac{C_b(V_T - V_o)}{V_T} \right) h^2 + \left(\frac{C_b(V_T - V_o) - C_a V_o}{V_T} K_a - K_w \right) h - K_a K_w = 0$$

which may be solved by applying the Newton–Raphson iterative method, as has been done in the present paper.

In Table 3, the results obtained by titrating a sample of (methylthio)acetic acid are shown. The values of h have been calculated taking a value of pK_a = 3.50 [13].

In applying the equations derived at each point on the titration curve, the effect produced by dilution has been taken into account, not only in connection with the analytical concentrations C_a and C_b of the titrand and of the titrant, but also in connection with the value of the heat capacity of the system.

TABLE 3

Determination of the neutralization enthalpy of (methylthio)acetic acid
Experiment 2: $C_a = 1.0532 \times 10^{-2}$; $C_b = 0.9092$; $V_o = 80$ ml; p$K_a = 3.50$; heat cap. = 0.3736 kJ °C^{-1}.

V_T (lit)	ΔT (°C)	[H$^+$]	X	Y
8.02142×10^{-2}	0.03000	7.3422×10^{-4}	1.0211×10^2	1.3610×10^3
8.02856×10^{-2}	0.04000	5.5872×10^{-4}	1.0055×10^2	1.7898×10^3
8.03570×10^{-2}	0.05000	4.2628×10^{-4}	1.0534×10^2	2.3459×10^3
8.04284×10^{-2}	0.06125	3.2483×10^{-4}	1.1270×10^2	3.0785×10^3
8.04998×10^{-2}	0.07125	2.4566×10^{-4}	1.2805×10^2	4.0707×10^3
8.05712×10^{-2}	0.08250	1.8268×10^{-4}	1.1858×10^2	5.4742×10^3
8.06430×10^{-2}	0.09250	1.3141×10^{-4}	1.8405×10^2	7.6096×10^3
8.07140×10^{-2}	0.10250	8.9681×10^{-5}	2.4317×10^2	1.1151×10^4
8.07854×10^{-2}	0.11125	5.4604×10^{-5}	3.6765×10^2	1.8314×10^4
8.08570×10^{-2}	0.12250	2.4841×10^{-5}	7.3325×10^2	4.0255×10^4

$b = -3912.5 \pm 493.8$; $m = 60.46 \pm 1.70$; $r = 0.9994$; $\Delta H = -60.46 \pm 1.70$ kJ mole^{-1}; p$K_a = 3.59$.

TABLE 4

Neutralization enthalpy of (methylthio)acetic acid. Point-by-point heat capacity method

Expt.	Straight line	r	ΔH_N (kJ mole^{-1})	pK_a
1	$Y=-3991.7+60.29X$	0.9995	-60.29	3.60
2	$Y=-3912.5+60.46X$	0.9994	-60.46	3.59
3	$Y=-4360.4+60.84X$	0.9958	-60.84	3.64
			$\Delta H_N=-60.53\pm0.28$	p$K_a=3.61\pm0.03$

The application of several statistical criteria [4] has enabled us to calculate the value of the precision attained knowing the slope and the intercept to be accurate to within 95% of the confidence level. These values are also indicated at the bottom of Table 3.

Table 4 sets out the results of the application of the point-by-point heat capacity method to the experimental data obtained by titrating three independent samples of (methylthio)acetic acid.

From the comparison of the results expressed in Tables 2 and 4, it can be deduced that both methods lead to appreciably coincident results. It must be pointed out that if, in fact, the point-by-point heat capacity method offers a precision slightly more favorable than the overall heat capacity method, the latter method is much simpler and more direct to apply, as it does not require the knowledge of h or of the value of pK_a of the substance under study. On the other hand, the former method can in some cases be used for the simultaneous determination of the values of ΔH and pK_a. Thus, this method constitutes a variant of the entropic titrations suggested by Christensen et al. [7,8].

TABLE 5

Neutralization enthalpies of thioetherdicarboxylic acids. Overall heat capacity method.

Experiment	Acid	ΔH_T (kJ mole^{-1})
1	Thiodiacetic	-118.66
2	Thiodiacetic	-119.12
3	Thiodiacetic	-117.82
		$\Delta H_T=-118.53\pm0.66$
1	3,3′-Thiodipropanoic	-117.65
2	3,3′-Thiodipropanoic	-116.73
3	3,3′-Thiodipropanoic	-116.40
		$\Delta H_T=-116.93\pm0.65$

Thiodiacetic and 3,3'-thiodipropanoic acids

*Overall heat capacity method.*As in the case of (methylthio)acetic acid, the overall neutralization enthalpy is determined from the overall temperature variation of the system, $\Delta H_T = \Delta H_1 + \Delta H_2$, but it is not possible to determine separately the reaction enthalpies corresponding to the neutralization of each of the implicated protons. In Table 5, the results obtained for the thioetherdicarboxylic acids are given.

*Point-by-point heat capacity method.*In the case of a diprotic acid the balances of matter, charge and heat (taking separately into consideration the reaction enthalpies, ΔH_1 and ΔH_2, corresponding to the neutralization of each of the implicated protons) together with the expressions of the successive dissociation constants, lead to the general relationship

$$\frac{cV_T \Delta T(h^2 + K_1 h + K_1 K_2)}{V_0^2 C_a K_1 h} = \Delta H_1 + \Delta H_T \frac{K_2}{h}$$

which can be put in the form of the equation of a straight line if we take

$$X_i = K_2/h; Y_i = \frac{-cV_T \Delta T_i(h^2 + K_1 h + K_1 K_2)}{V_0^2 C_a K_1 h}$$

This straight line is adjusted to the experimental points by means of the Gauss–

TABLE 6

Determination of the neutralization enthalpy of 3,3'-thiodipropanoic acid
Experiment 3: $C_a = 6.723 \times 10^{-3}$ M; $C_b = 0.9092$ M; $V_0 = 80$ ml; $pK_1 = 3.87$; $pK_2 = 4.68$.

V_T (lit)	ΔT (°C)	$[H^+]$	X	$-Y$
8.02856×10^{-2}	0.039375	1.7673×10^{-4}	0.118219	66.6541
8.03570×10^{-2}	0.050000	1.2971×10^{-4}	0.161072	74.0516
8.04284×10^{-2}	0.059375	9.7210×10^{-5}	0.214927	80.2568
8.04998×10^{-2}	0.069375	7.3770×10^{-5}	0.283217	88.7426
8.05710×10^{-2}	0.080000	5.6355×10^{-5}	0.370732	100.0974
8.07140×10^{-2}	0.100000	3.2614×10^{-5}	0.640621	131.9235
8.07854×10^{-2}	0.109375	2.4411×10^{-5}	0.855886	156.2691
8.08568×10^{-2}	0.119375	1.7838×10^{-5}	1.171286	193.0569
8.09280×10^{-2}	0.129370	1.2521×10^{-5}	1.668576	251.0298
8.09996×10^{-2}	0.140000	8.1402×10^{-6}	2.566654	357.1264
8.10710×10^{-2}	0.150000	4.5247×10^{-6}	4.617501	596.6906
8.11420×10^{-2}	0.160000	1.5192×10^{-6}	13.752286	1664.2564

$b = -55.73 \pm 0.88$; $m = -117.03 \pm 0.20$; $r = -0.999997$; $\Delta H_1 = -55.73$ kJ mole^{-1}; $\Delta H_2 = -61.30$ kJ mole^{-1}; $\Delta H_T = -117.03$ kJ mole^{-1}.

TABLE 7

Neutralization enthalpies of the thioetherdicarboxylic acids. Point-by-point heat capacity method

Acid	Expt.	Straight line	r	ΔH_1	ΔH_2
Thiodiacetic	1	$Y=-50.58-117.74\,X$	−0.99999	−50.58	−67.16
	2	$Y=-53.64-117.53\,X$	−0.99997	−53.64	−63.89
	3	$Y=-51.84-118.70\,X$	−0.9997	−51.84	−66.86
		−117.99±0.62		−50.02±1.54	−65.97±1.81
3,3′-Thiodipropanoic	1	$Y=-53.89-116.52\,X$	−0.9999	−53.89	−62.63
	2	$Y=-54.22-115.56\,X$	−0.99998	−54.22	−61.34
	3	$Y=-55.73-117.03\,X$	−0.99999	−55.74	−61.30
		−116.37±0.75		−54.61±0.98	−61.76±0.76

Newton method and the value of ΔH_1 is obtained from the intercept and that of ΔH_2 from the slope.

The values of h which are necessary to calculate X_i and Y_i may be obtained by applying the Newton–Raphson method to the equation

$$h^4+\left(\frac{C_b(V_T-V_0)}{V_T}+K_1\right)h^3+\left(\frac{C_b(V_T-V_0)-C_aV_0}{V_T}K_1+K_1K_2-K_w\right)h^2$$
$$+\left(\frac{C_b(V_T-V_0)-2C_aV_0}{V_T}K_1K_2-K_1K_w\right)h-K_1K_2K_w=0$$

In Table 6, the data which correspond to a titration of 3,3′-thiodipropanoic acid with NaOH 0.9092 N are given together with the results obtained by means of the Gauss–Newton method, from which ΔH_1 and ΔH_2 are obtained.

The results obtained by titrating three independent samples of each of the thioetherdicarboxylic acids are given in Table 7.

Estimation of the dissociation parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ *of the thioethercarboxylic acids*

The ionization enthalpies, ΔH_i, of the three thioether acids have been calculated from the expression

$$\Delta H_i=\Delta H_N-\Delta H_w$$

where the values of ΔH_N are those determined at 20°C in this paper and the value of ΔH_w ($=-56.44$ kJ mole^{-1}) has been determined experimentally by means of the titration of a strong acid with a strong base under the same experimental conditions. To transform the values obtained for ΔH_i at 20°C to those corresponding to 25°C which are given in Table 8, we have employed an averaged molar heat capacity of $\Delta C_p=-0.130\pm0.017$ kJ K^{-1} mole^{-1} obtained from several papers concerning carboxylic acids [9–12].

TABLE 8

Estimated values of ΔG°, ΔH° and ΔS° of the thioethercarboxylic acids at 25°C and 0.10 M ionic strength

Acid	ΔG_1° (kJ mole^{-1})	ΔG_2° (kJ mole^{-1})	ΔH_1° (kJ mole^{-1})	ΔH_2° (kJ mole^{-1})	ΔS_1° (J K^{-1} mole^{-1})	ΔS_2° (J K^{-1} mole^{-1})
(Methylthio)acetic	20.25 ± 0.13		-3.33 ± 0.35		-79.09 ± 1.17	
Thiodiacetic	17.91 ± 0.13	22.89 ± 0.13	5.07 ± 1.54	-9.14 ± 0.65	-43.07 ± 5.17	-107.43 ± 2.18
3,3'-Thiodipropanoic	22.09 ± 0.13	26.69 ± 0.13	2.48 ± 0.98	-4.95 ± 70	-65.77 ± 3.29	-106.12 ± 2.35

The values of ΔG° at 25°C have been calculated from the known dissociation constants [2,13] by means of the expression

$$\Delta G^\circ = -RT\ln K.$$

From the values of ΔG° and ΔH°, those of ΔS° have been estimated from

$$\Delta S^\circ = \frac{(\Delta H^\circ - \Delta G^\circ)}{T}$$

In Table 8, the results obtained in the calculation of the values of ΔG°, ΔH° and ΔS° are given, together with their precision.

REFERENCES

1 E. Casassas, Institute of Catalen Studies, Archives of the Science Section XLV, Barcelona, 1971.
2 J.M. Vallés, Doctoral Thesis, University of Barcelona, 1980.
3 J. Lumbiarres, C. Mongay and V. Cerdá, Analusis, 8 (1980) 62.
4 J.J. Christensen, R.M. Izatt and L.D. Hansen, Rev. Sci. Instrum., 36 (1965) 779.
5 J. Barthel, F. Becker and N.C. Schmahl, Z. Phys. Chem. (Frankfurt am Main), 29 (1961) 58.
6 V.P. Spiridonov and A.A. Lopatkin, Mathematical Treatment of Physico-Chemical Data, MIR, Moscow, 1973.
7 L.D. Hansen, J.J. Christensen and R.M. Izatt, Chem. Commun., 3 (1965) 36.
8 R.M. Izatt, D. Eatough, R.L. Snow and J.J. Christensen, J. Phys. Chem., 72 (1968) 1208.
9 J.J. Christensen, J.L. Oscarson and R.M. Izatt, J. Am. Chem. Soc., 90 (1968) 5949.
10 K.J. Breslaner, J. Chem. Thermodyn., 11 (1979) 527.
11 J.J. Christensen, M.D. Slade, D.E. Smith, R.M. Izatt and J. Tsang, J. Am. Chem. Soc., 92 (1970) 4164.
12 D.L. Levi, W.S. McEvan and J.H. Wolfenden, J. Chem. Soc., (1949) 760.
13 A.E. Martell and R.M. Smith, Critical Stability Constants, Vol. 3 Plenum Press, New York, 1977.