Thermochimica Acta, 86 (1985) 273–280
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

IONIC STRENGTH DEPENDENCE OF FORMATION CONSTANTS. PART 7. PROTONATION CONSTANTS OF LOW MOLECULAR WEIGHT CARBOXYLIC ACIDS AT 10, 25 AND 45°C

SANTI CAPONE, ALESSANDRO DE ROBERTIS, CONCETTA DE STEFANO, SILVIO SAMMARTANO and ROSARIO SCARCELLA
Istituto di Chimica Analitica dell'Università, via dei Verdi, 98100 Messina (Italy)

CARMELO RIGANO
Seminario Matematico dell'Università, viale A. Doria 6, 95125 Catania (Italy)

(Received 18 October 1984)

ABSTRACT

The protonation of ten carboxylic acids (formic, propionic, malonic, succinic, phthalic, itaconic, malic, oxydiacetic, thiodiacetic and thiodipropionic) has been studied potentiometrically at 10 (except succinic acid), 25 and 45°C (except succinic, malonic and oxydiacetic acids) at eight ionic strengths, $0.04 \leqslant I \leqslant 0.8$ mol l^{-1}, using tetraethylammonium iodide as background salt. As in previous works of this series, the dependence of protonation constants on ionic strength has been studied using the simple and general equation $\log \beta = f(I, z^*, p^*, c_0, c_1, d)$ (z^* and p^* are parameters depending on the stoichiometry of reactions under study; c_0, c_1 and d are general empirical parameters valid for all reactions). Furthermore, from the temperature coefficients of c_0, c_1 and d, the dependence of ΔH on ionic strength has been obtained. The results have been compared with previous findings.

INTRODUCTION

In some previous works of this series [1–6], we studied the dependence on ionic strength of formation constants of several M^{z+}-low molecular weight ligand systems (also considering mixed metal [4] and mixed ligand systems [2]) in the range $0.01 \leqslant I \leqslant 1$ mol l^{-1}. In some other works—regarding the hydrolysis of Na^+ and Ca^{2+} [7], the formation of alkali metal and alkaline earth metal–acetate complexes [8] and the formation of alkaline earth–succinate complexes [9]—the dependence of formation constants on ionic strength was also studied.

Here we report a systematic investigation on the protonation of ten carboxylic acids (formic, propionic, malonic, succinic, phthalic, itaconic, malic, oxydiacetic, thiodiacetic and thiodipropionic) at 10, 25 and 45°C and

0040-6031/85/$03.30

at eight ionic strengths (0.043, 0.09, 0.155, 0.24, 0.35, 0.46, 0.61, 0.76 mol l^{-1}). Since alkali metal ions form weak, but not negligible, complexes with carboxylic acids, we used tetraethylammonium iodide as background salt.

The aims of this work are: (i) to confirm previous findings about the possibility of using a general equation in computing the dependence of formation constants on ionic strength; (ii) to find the temperature dependence of parameters defining the function $\log \beta = f(I)$.

EXPERIMENTAL

Materials

Carboxylic acids (Fluka, purum or puriss.) were used without further purification; tetraethylammonium iodide (Fluka, puriss.) was recrystallized from methanol. The purity of the organic acids was checked by alkalimetric titrations and was always found to be $\geqslant 99\%$. Sodium hydroxide and hydrochloric acid solutions were prepared by diluting Carlo Erba ampoules. Grade A glassware and twice-distilled water were employed for all solutions.

Apparatus

Free hydrogen ion concentration, c_H, was measured by means of a model E 600 Metrohm potentiometer and a couple of glass/saturated calomel electrodes supplied by the same firm. The standard hydroxide solution (carbonate free) was added with a model 232 Amel dispenser, having a minimum reading of 1 μl. The electrode couple was calibrated in $-\log c_H$ units (pH) by titrating HCl (4–6 mmol l^{-1}) with standard NaOH in the same experimental conditions as the solution under study.

Procedure

The solution under examination (20 ml) containing 6 mmol l^{-1} of monocarboxylic acid or 3 mmol l^{-1} of dicarboxylic acid was titrated with a standard solution of NaOH (0.1 mol l^{-1}) up to neutralization (about 40 experimental points). An excess of HCl (4 mmol l^{-1}) was added to all solutions in order to complete the protonation of carboxylic acids and to calculate internal E^0 (E^0_{int}) directly. This value was compared with that calculated by separate calibration titrations, E^0_{ext}. If $|E^0_{\text{int}} - E^0_{\text{ext}}| \geqslant 1.5$ mV the titration was rejected. All the titrations were carried out by passing a stream of purified and presaturated nitrogen through the solution, in order to exclude the presence of CO_2 and O_2.

Calculations

The protonation constants, the purity of ligands and the calibration constant, E^0, for the electrode systems were calculated using the nonlinear least-squares computer program ESAB [10]. The protonation constants are expressed as

$$\beta_j^{\mathrm{H}} = c_{\mathrm{H}_j\mathrm{L}} c_{\mathrm{L}}^{-1} c_{\mathrm{H}}^{-j}$$

where c = free concentration. The complexation of Na^+ (introduced into solutions as titrant NaOH) was taken into account as previously described [1].

Throughout this paper the errors are reported as three times the standard deviation.

RESULTS AND DISCUSSION

In Table 1 we report the protonation constants for the carboxylic acids studied at single temperatures and ionic strengths. The dependence of log β_j^{H} on I values was studied using the equation [1–9]

$$\log \beta_j^{\mathrm{H}}(I) = \log \beta_j^{\mathrm{H}}(I') - z_j^* \left[\frac{\sqrt{I}}{2 + 3\sqrt{I}} - \frac{\sqrt{I'}}{2 + 3\sqrt{I'}} \right] + C_j(I - I') + D_j(I^{3/2} - I'^{3/2}) \qquad (1)$$

where $z_j^* = j(1 - j - 2z)$ (z is the charge of the anion); I' is the reference ionic strength, internal to the studied range ($I' = 0.25$ mol l^{-1} in this work); C_j and D_j values are empirical parameters. Table 2 reports log $\beta_j^{\mathrm{H}}(I' = 0.25)$, C_j and D_j values. As can be seen, C_j and D_j values are practically constant for different acids when considering the same protonation reaction. These parameters can be expressed as a function of the reaction stoichiometry by the equations [1–9]

$$C = c_0 p^* + c_1 z^* \qquad (2)$$

$$D = dz^* \qquad (3)$$

where $p^* = j$ (in general, p^* is the difference between the number of reactants and products).

From the C_j and D_j values listed in Table 2 we were able to calculate c_0, c_1 and d at 10, 25 and 45°C; these values are reported in Table 3. From the temperature dependence of protonation constants, ΔH_j values were obtained. In Table 4 we report the thermodynamic parameters at 25°C and $I = 0$, together with some literature data. The knowledge of the temperature coefficients c_0, c_1 and d (see Table 3) allows us to calculate ΔH values at

TABLE 1

Protonation constants of the carboxylic acids under study

Acid	t (°C)	j	$\log \beta_j^H$							
			$I^a = 0.043$	0.09	0.155	0.24	0.35	0.46	0.61	0.76
Formic	10	1	3.53(2)[b]	3.52(1)	3.52(2)	3.52(1)	3.52(2)	3.55(1)	3.57(1)	3.61(1)
	25	1	3.57(1)	3.55(1)	3.54(2)	3.54(1)	3.55(1)	3.56(1)	3.59(1)	3.62(1)
	45	1	3.62(2)	3.59(1)	3.58(1)	3.57(1)	3.58(1)	3.59(1)	3.60(2)	3.65(2)
Propionic	10	1	4.68(2)	4.67(2)	4.67(2)	4.68(2)	4.72(3)	4.76(2)	4.79(1)	4.84(1)
	25	1	4.73(2)	4.71(2)	4.70(2)	4.70(1)	4.72(2)	4.74(2)	4.80(2)	4.84(2)
	45	1	4.75(2)	4.73(2)	4.73(2)	4.74(2)	4.75(2)	4.79(2)	4.84(1)	4.89(2)
Malonic	10	1	5.36(2)	5.32(2)	5.30(2)	5.30(2)	5.32(1)	5.33(2)	5.40(1)	5.47(2)
	25	1	5.47(2)	5.42(2)	5.39(1)	5.38(2)	5.41(1)	5.44(2)	5.50(1)	5.54(2)
	10	2	8.02(3)	7.95(2)	7.93(3)	7.92(3)	7.97(2)	7.99(3)	8.10(2)	8.24(3)
	25	2	8.16(4)	8.09(3)	8.05(2)	8.04(4)	8.10(2)	8.15(4)	8.25(3)	8.30(3)
Succinic	25	1	5.37(2)	5.33(1)	5.32(2)	5.28(1)	5.29(1)	5.30(2)	5.33(2)	5.39(2)
	25	2	9.41(4)	9.37(4)	9.35(3)	9.33(2)	9.35(2)	9.39(2)	9.47(3)	9.56(3)
Itaconic	10	1	5.27(2)	5.23(1)	5.21(2)	5.20(1)	5.22(1)	5.25(2)	5.28(1)	5.33(2)
	25	1	5.30(1)	5.25(1)	5.23(1)	5.23(1)	5.24(1)	5.27(1)	5.30(1)	5.36(1)
	45	1	5.31(3)	5.27(1)	5.24(1)	5.24(1)	5.25(1)	5.29(1)	5.33(1)	5.38(2)
	10	2	9.05(3)	8.97(2)	8.94(3)	8.94(2)	8.97(2)	9.04(2)	9.11(2)	9.21(3)
	25	2	9.02(2)	8.95(2)	8.92(2)	8.92(2)	8.97(3)	9.00(2)	9.07(3)	9.18(3)
	45	2	9.02(3)	8.95(3)	8.91(2)	8.90(2)	8.94(2)	8.99(2)	9.06(2)	9.15(3)
Malic	10	1	4.79(2)	4.76(2)	4.73(2)	4.70(2)	4.72(1)	4.73(1)	4.76(2)	4.81(2)
	25	1	4.82(1)	4.78(1)	4.74(2)	4.73(1)	4.74(1)	4.77(2)	4.78(3)	4.83(2)
	45	1	4.86(2)	4.78(2)	4.76(1)	4.76(2)	4.76(2)	4.77(3)	4.81(4)	4.85(3)
	10	2	8.17(3)	8.12(3)	8.09(4)	8.06(2)	8.08(2)	8.12(2)	8.16(4)	8.24(3)

	25	2	8.16(2)	8.08(2)	8.03(3)	8.02(2)	8.04(2)	8.12(3)	8.14(3)	8.23(4)
	45	2	8.19(2)	8.06(4)	8.04(2)	8.04(4)	8.06(3)	8.07(3)	8.15(4)	8.23(4)
Oxydiacetic	10	1	3.98(2)	3.93(1)	3.91(2)	3.89(1)	3.89(3)	3.92(1)	3.94(2)	4.00(2)
	25	1	4.08(3)	4.02(2)	4.01(1)	3.99(1)	3.99(2)	4.00(2)	4.05(3)	4.10(3)
	10	2	6.96(4)	6.85(5)	6.84(5)	6.83(4)	6.85(3)	6.86(3)	6.95(3)	7.00(4)
	25	2	7.00(3)	6.95(4)	6.90(4)	6.85(4)	6.90(4)	6.91(4)	6.94(4)	6.99(5)
Thiodiacetic	10	1	4.26(4)	4.10(4)	4.08(4)	4.07(3)	4.08(4)	4.11(3)	4.13(3)	4.18(3)
	25	1	4.30(3)	4.22(3)	4.17(2)	4.16(2)	4.17(1)	4.18(2)	4.20(3)	4.22(3)
	45	1	4.31(4)	4.24(4)	4.18(2)	4.16(3)	4.19(2)	4.21(3)	4.23(4)	4.31(4)
	10	2	7.39(5)	7.31(5)	7.27(4)	7.26(4)	7.26(4)	7.33(4)	7.39(4)	7.47(4)
	25	2	7.44(4)	7.40(4)	7.31(3)	7.30(4)	7.36(2)	7.38(3)	7.42(4)	7.48(3)
	45	2	7.51(4)	7.45(4)	7.37(3)	7.36(4)	7.38(3)	7.44(3)	7.49(4)	7.60(5)
Thiodipropionic	10	1	4.70(3)	4.66(2)	4.65(2)	4.65(2)	4.65(2)	4.68(1)	4.71(2)	4.76(3)
	25	1	4.81(5)	4.75(2)	4.71(2)	4.70(2)	4.72(2)	4.73(2)	4.78(4)	4.86(5)
	45	1	4.80(3)	4.75(3)	4.72(3)	4.71(2)	4.71(3)	4.78(3)	4.79(3)	4.86(4)
	10	2	8.66(4)	8.61(2)	8.60(3)	8.60(2)	8.63(2)	8.70(2)	8.77(3)	8.88(2)
	25	2	8.79(5)	8.70(3)	8.66(3)	8.63(3)	8.69(4)	8.72(4)	8.82(5)	8.98(6)
	45	2	8.80(3)	8.72(4)	8.69(4)	8.67(3)	8.72(5)	8.81(5)	8.84(5)	9.01(6)
Phthalic	10	1	5.03(4)	5.04(3)	5.04(3)	5.07(2)	5.08(3)	5.11(2)	5.20(3)	5.25(3)
	25	1	5.14(2)	5.09(2)	5.09(2)	5.10(1)	5.12(2)	5.16(2)	5.25(3)	5.30(3)
	45	1	5.18(3)	5.14(3)	5.13(2)	5.15(3)	5.20(2)	5.25(3)	5.32(3)	5.39(3)
	10	2	7.81(4)	7.75(4)	7.74(3)	7.78(3)	7.83(4)	7.90(4)	8.08(4)	8.16(4)
	25	2	7.91(3)	7.85(3)	7.83(3)	7.86(2)	7.90(3)	7.96(3)	8.11(4)	8.21(4)
	45	2	8.00(3)	7.90(3)	7.89(3)	7.93(3)	8.01(3)	8.07(3)	8.19(4)	8.29(5)

---

[a] Ionic strength in mol l^{-1}.

[b] 3σ in parentheses.

TABLE 2

Protonation constants at $I' = 0.25$ mol l^{-1} and C and D parameters for the dependence on ionic strength

Acid	t (°C)	$\log \beta_1^H(I')$	C_1	$-D_1$	$\log \beta_2^H(I')$	C_2	$-D_2$
Formic	10	3.515(12) [a]	0.65	0.28			
	25	3.539(5)	0.56	0.21			
	45	3.570(8)	0.41	0.08			
Propionic	10	4.690(7)	0.88	0.39			
	25	4.702(5)	0.47	0.02			
	45	4.736(9)	0.60	0.11			
Malonic	10	5.294(16)	1.04	0.33	7.92(3)	1.45	0.29
	25	5.390(6)	1.05	0.37	8.061(12)	1.77	0.70
Succinic	25	5.281(13)	0.90	0.32	9.33(2)	1.64	0.63
Phthalic	10	5.05(3)	1.29	0.40	7.77(2)	2.07	0.72
	25	5.095(15)	1.29	0.49	7.851(16)	1.85	0.57
	45	5.16(2)	1.23	0.40	7.936(16)	2.10	0.81
Itaconic	10	5.203(8)	1.18	0.55	8.942(9)	1.61	0.52
	25	5.225(8)	1.12	0.48	8.922(13)	1.70	0.64
	45	5.239(8)	1.11	0.45	8.908(9)	1.59	0.55
Malic	10	4.706(16)	0.96	0.38	8.063(15)	1.63	0.72
	25	4.732(9)	1.02	0.45	8.025(15)	1.48	0.51
	45	4.749(9)	0.91	0.34	8.03(2)	1.34	0.38
Oxydiacetic	10	3.887(12)	0.93	0.35	6.83(2)	1.60	0.68
	25	3.981(13)	0.89	0.29	6.875(15)	1.62	0.82
Thiodiacetic	10	4.07(3)	1.18	0.54	7.26(3)	1.43	0.45
	25	4.165(13)	0.83	0.33	7.32(3)	1.69	0.79
	45	4.17(2)	0.95	0.40	7.36(2)	1.52	0.60
Thiodipropionic	10	4.639(13)	1.24	0.62	8.598(16)	1.90	0.78
	25	4.698(10)	1.08	0.40	8.638(15)	1.71	0.60
	45	4.711(16)	0.93	0.27	8.683(17)	1.37	0.20

[a] 3σ in parentheses.

$I \neq 0$ by the equation

$$\Delta H^0 = \Delta H^0(I = 0) - (0.73p^* + 0.57z^*)I + 0.69\, I^{3/2}(\text{kcal mol}^{-1}) \tag{4}$$

TABLE 3

Values of general parameters for the dependence of formation constants on ionic strength

t (°C)	c_0	c_1	$-d$
10	0.22	0.24	0.13
25	0.19	0.21	0.10_5
45	0.16	0.19_5	0.07

$c_0 = 0.19 - 1.8 \times 10^{-3}\,(t - 25)$

$c_1 = 0.21 - 1.4 \times 10^{-3}\,(t - 25)$

$d = -0.105 + 1.7 \times 10^{-3}\,(t - 25)$

In order to evaluate the significance of the present results, we should like to consider the following points: (a) taking into consideration all protonation constants studied in this work, the mean deviation for the difference $|\log \beta_j^{\mathrm{H}} - \log \beta_j^{\mathrm{H}}(\mathrm{calcd})|$ (β_j^{H}(calcd) is the value of β_j^{H} calculated by eqns. (1)–(3) using the general parameters of Table 3) is < 0.04 log units; (b) the differences $\log \beta(I = 0) - \log \beta(I = 0.25) = 0.37$ and $\log \beta(I = 0) - \log \beta(I = 1) = 0.19$ (for $p^* = 1$ and $z^* = 4$) obtained in this work are in very good agreement with previous findings [1–9], 0.36 ± 0.02 and 0.16 ± 0.04, respectively; (c) the difference $\Delta H(I = 0) - \Delta H(I = 0.25)$ (for $p^* = 1$ and $z^* = 4$)

TABLE 4

Thermodynamic parameters [a] for the protonation of carboxylic acids at 25°C and $I = 0$ mol l^{-1} (some literature data are also reported)

Acid	j	$\log \beta_j$	$-\Delta G_j^0$ (kcal mol^{-1})	ΔH_j^0 (kcal mol^{-1})	ΔS_j^0 (cal mol^{-1} K^{-1})	Ref.
Formic	1	3.71	5.06	1.1	21	This work
		3.75	5.11	0.1	17	[11]
Propionic	1	4.87	6.64	1.2	26	This work
		4.87	6.64	0.14	23	[12]
Malonic	1	5.75	7.84			
	2	8.56	11.68			
Succinic	1	5.67	7.73			
	2	9.85	13.44			
Phthalic	1	5.41	7.38	1.6	30	This work
		5.35	7.30	0.6	27	[13]
		5.36	7.31	0.5	26	[14]
	2	8.32	11.35	2.1	45	This work
		8.31	11.34	1.1	42	[13]
		8.29	11.31	1.2	42	[14]
Itaconic	1	5.58	7.61	0.5	27	This work
	2	9.42	12.86	−0.5	41	This work
Malic	1	5.10	6.96	0.5	25	This work
		5.11	6.97	0.33	24.5	[15]
	2	8.57	11.69	−0.3	38	This work
		8.58	11.70	−0.31	38.2	[15]
Oxydiacetic	1	4.37	5.96			This work
	2	7.43	10.14			This work
Thiodiacetic	1	4.57	6.23	1.1	25	This work
		4.58	6.24	0.99	24.3	[16]
	2	7.85	10.71	1.6	41	This work
		7.93	10.81	1.22	40.4	[16]
Thiodipropionic	1	5.10	6.96	1.2	27	This work
		5.10	6.95	0.53	25.1	[16]
	2	9.23	12.59	1.8	48	This work
		9.20	12.54	0.77	44.7	[16]

[a] $\log \beta_1 \pm 0.015$, $\log \beta_2 \pm 0.025$; $\Delta G_1^0 \pm 0.02$, $\Delta G_2^0 \pm 0.035$ kcal mol^{-1}; $\Delta H_1^0 \pm 0.3$, $\Delta H_2^0 \pm 0.6$ kcal mol^{-1}; $\Delta S_1^0 \pm 1$, $\Delta S_2^0 \pm 2$ cal K^{-1} mol^{-1}; 1 cal = 4.184 J (SI units not used).

obtained in this work is 0.41, in good agreement with previous findings [4,7,8,17], i.e., 0.30 ± 0.13; (d) by considering the low accuracy of the ΔH values obtained here (the dependence on temperature based on three temperatures allows the calculation only of estimates of ΔH) the agreement (see Table 4) with literature is satisfactory. All these points (a–d) confirm that the procedure followed in this paper is correct.

REFERENCES

1 P.G. Daniele, C. Rigano and S. Sammartano, Talanta, 30 (1983) 81.
2 idem, Transition Met. Chem., 7 (1982) 109.
3 idem, Ann. Chim. (Rome), 73 (1983) 741.
4 P.G. Daniele, G. Ostacoli, C. Rigano and S. Sammartano, Transition Met. Chem., 9 (1984) 385.
5 P.G. Daniele, C. Rigano and S. Sammartano, Talanta, in press.
6 P.G. Daniele, A. De Robertis, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 75 (1985) in press.
7 A. De Robertis, C. Rigano and S. Sammartano, Thermochim. Acta, 74 (1984) 343.
8 A. De Robertis, C. De Stefano, S. Sammartano, R. Scarcella and C. Rigano, J. Chem. Res., in press.
9 A. De Robertis, C. De Stefano, R. Scarcella and C. Rigano, Thermochim. Acta, 80 (1984) 197.
10 C. Rigano, M. Grasso and S. Sammartano, Ann. Chim. (Rome), 74 (1984) 537.
11 J.J. Christensen, M.D. Slade, D.E. Smith, R.M. Izatt and J. Tsang, J. Am. Chem. Soc., 92 (1970) 4164.
12 J.J. Christensen, R.M. Izatt and L.D. Hansen, J. Am. Chem. Soc., 89 (1967) 213.
13 G. Arena, R. Calì, E. Rizzarelli and S. Sammartano, Transition Met. Chem., 3 (1978) 147.
14 P. Lumme and E. Kari, Acta Chem. Scand., Ser. A, 29 (1975) 117.
15 G. Arena, R. Calì, M. Grasso, S. Musumeci, S. Sammartano and C. Rigano, Thermochim. Acta, 36 (1980) 329.
16 R. Calì, E. Rizzarelli, S. Sammartano and L.D. Pettit, Thermochim. Acta, 35 (1980) 169.
17 P.G. Daniele, A. De Robertis, C. Rigano and S. Sammartano, work in progress.