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THERMOMETRIC TITRATION OF MONO- AND POLY-PROTIC ACIDS IN WATER—METHANOL MEDIUM

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ABSTRACT

Several mono- and poly-carboxylic acids are determined in aqueous and methanol—water (50% v/v) media by thermometric titrimetry. The titration errors are evaluated and compared in terms of some structural aspects of the acids tested. Their neutralisation enthalpies are also determined; in most cases the absolute values of these enthalpies decrease as the methanol content of the medium increases.

INTRODUCTION

Thermometric titrimetry has been widely used in the titration of acids in aqueous [1—9] as well as in non-aqueous [10—13] media, not only to evaluate the applicability, accuracy and precision of the technique, but also because it is a rapid way to obtain accurate values of ΔH^0, ΔG^0 (pK_a) and ΔS^0 for the acid ionisation process.

For a long time, only pK_a values were known with sufficient accuracy and comparison of acid strengths was thus made on the basis of these values. However, knowledge of accurate values of ΔH^0 and ΔS^0 allows for a new explanation of the acid dissociation process and acid strength. In this sense, carboxylic acids are a good model to study the relationship $\Delta G^0 = -RT\ln K = \Delta H^0 - T\Delta S^0$ for the acid dissociation.

Of special importance are the contributions from Christensen et al. to the development of entropic titrimetry [14—17], the determination of the currently accepted value for the ionisation enthalpy of water, $\Delta H^0 = -13.340$ kcal mole^{-1} at 25°C [18,19], and the improvement of the instrumentation [26—29].

Besides the well known characteristic of aqueous or mixed solvents in the titration of acids and bases, their use is very encouraging in thermometric titrimetry as their lower heat capacity gives rise to titration graphs with higher slopes, if reaction enthalpy is not unfavorably affected by the change in solvent.

Results obtained by Harries [10] in the titration of carboxylic acids in aqueous and anhydrous methanolic media suggest the use of mixed water—methanol solvents to overcome the insolubility in anhydrous methanol of the resulting salts, which can result in deformed enthalpograms that are unsuitable for extrapolation.

EXPERIMENTAL

Apparatus

The titration system has been previously described [24]. The measuring bridge has been calculated to use a miniaturised thermistor ($R_T = 100\ \mathrm{k\Omega}$, 25°C) as temperature sensor and a Omniscribe Recorder, Houston Instruments (imput impedance 1 MΩ in the whole sensitivity range). Radiometer ABU-12, 2.5 ml automatic burette and magnetic stirring were also used.

The adiabatic cell, Fig. 1, consists of a 100 ml polystyrene beaker with screw cap fitted in a poraspan block. The cap allows the entrance of the burette tip (B), the heating resistor R_c, and the thermistor R_T. The air-tight cell avoids thermal disturbances due to the evaporation of the solvent.

The neutralisation enthalpies have been calculated by the initial slope method using an electric calibration system [24] and applying the equation

$$\Delta H = -\frac{0.239 E_p E_c P_q}{F N R_p P_c}$$

where E_p is the voltage measured at the ends of a standard resistor R_p (9.992 ± 0.002 Ω, 18.8°C), E_c is the voltage at the ends of the heating resistor R_c, P_q and P_c the slopes at the origins of the titration and calibration

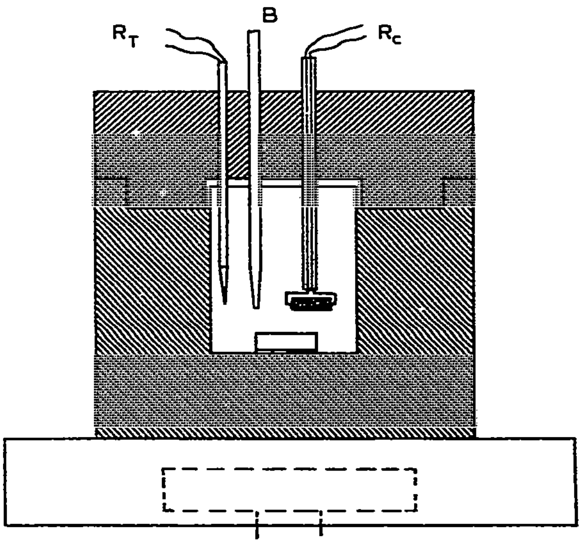


Fig. 1. Titration cell.

graphs, F the flow of titrant, and N its normality. E_c and E_p were measured with a Keithley 179TRMS digital voltmeter.

Reagents

Carbonate-free hydroxide solutions, in water and in methanol—water (50% v/v), were standardised by thermometric titrimetry using potassium hydrogen phthalate as the standard. Hydrochloric acid solution in methanol—water (50% v/v), was standardised against the sodium hydroxide solution. Organic acids of the best quality available, were recrystallised when necessary. Analytical reagent grade chemicals were used throughout.

Titration procedure

Each sample was weighed into a polystyrene beaker and dissolved in 35 ml of the solvent used as titration medium. The beaker was then screwed to the cap, fitted in the insulating block, and allowed to reach thermal equilibrium. The automatic titration was performed with a titrant flow of 0.142 ml min^{-1} with magnetic stirring.

RESULTS AND DISCUSSION

Titration graphs and errors

Titration graphs of some acids in methanol—water are shown in Figs. 2 and 3.

Titration graphs obtained in aqueous medium for most of the acids titrated show well-defined end points. However, analytical results are not good for several of these acids, mainly due to their insolubility in water (Table 1). Benzoic and salicyclic acids can be taken as examples: both acids must be titrated as a suspension and although the titration of the dissolved portion slowly displaces the solubility equilibrium, even after the end of the titration, solid particles can be seen on the walls of the titration cell. Besides, the endothermal effect due to solubilisation causes a deformation on the titration graphs, especially with salicyclic acid. These problems are not found in the hydromethanolic medium where titration errors and precision are good. Phthalic acid and potassium hydrogen phthalate give very good results in both media. Thus, potassium hydrogen phthalate can be used as a standard for thermometric titrations in water as well as in methanol—water media, while benzoic acid can be used as a standard only in the methanol—water medium.

In Table 1, it is seen that in the methanol—water medium, the titration error is small and precision is good for all the monoprotic acids tested. The greater titration error for ascorbic acid is due to the anomalous curvature of the titration graph after the end point has been reached, as discussed below.

In the methanol—water medium, oxalic, malic and tartaric acids, among diprotic acids, show well-defined titration graphs whose end points corre-

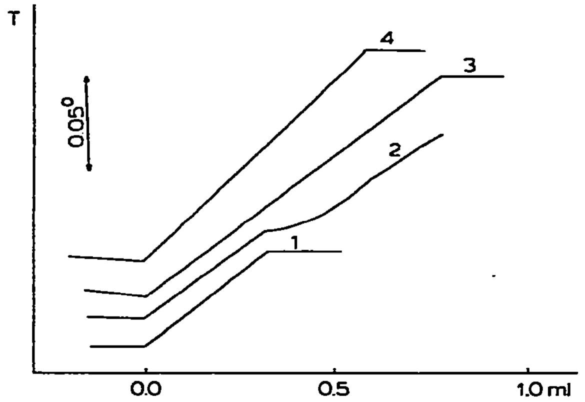


Fig. 2. Titrations graphs in methanol—water medium. 1, Anthranilic acid; 2, ascorbic acid; 3, nicotinic acid; 4, 2-thiophenecarboxylic acid.

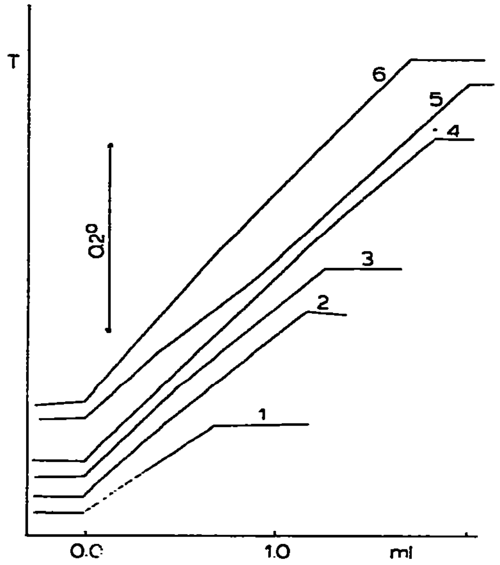


Fig. 3. Titration graphs in methanol—water medium. 1, Sulphanilic acid; 2, salicyclic acid; 3, benzoic acid; 4, hydrochloric acid; 5, phthalic acid; 6, potassium hydrogen phthalate.

spond to the simultaneous neutralisation of both acidities. On the other hand, malonic, succinic, maleic and phthalic acids show two end points, the slope before the first end point being lower than between the first and second. Only one proton is titrated in glutamic acid and the simultaneous titration of three protons is shown for citric and carboxymethylmercaptosuccinic acids. The fact that 4,5-imidazoledicarboxylic acid does not dissolve completely explains the poor results obtained in its thermometric titration.

Figure 4 shows titration graphs for several dihydroxybenzoic acids. Only one well-defined end point, corresponding to a one proton transfer, appears in the case of 2,5- and 2,6-dihydroxybenzoic acids. The other acids in this group give rise to two end points, the first better defined than the second, which can be located only by extrapolation. The slope corresponding to the neutralisation of the first proton is greater than that corresponding to the second, as opposed to the case in the titration of dicarboxylic acid, mentioned above.

Titration graphs for several amino-polycarboxylic acids in the methanol—water medium are shown in Fig. 5. On the iminodiacetic acid (IDA) titration graph, two end points are seen. But for nitrilotriacetic acid (NTA), whose pK_{a3} is very closed to pK_{a2} for IDA only one two-proton end point is present. For cyclohexanediaminotetracetic acid (CDTA) and diethylenetriaminepentacetic acid (DTPA), four protons are simultaneously neutralised. However, the insolubility of all of these acids in the water—methanol medium prevents good results being obtained. For EFTA, the analytical results are even worse.

TABLE 1

Results obtained in the thermometric titration of mono- and poly-protic acids in water and water—methanol media

Acid	Sample (mmole)	Found (mmole)	Error (%)	σ (%)
Benzoic	0.8171	0.8162	—0.11	0.35
	1.0363 [a]	0.8944	—13.69	15.82
Salicyclic	0.9153	0.9160	0.08	0.21
	0.9108 [a]	0.8892	—2.37	2.50
Sulphanilic	0.3318	0.3317	—0.04	0.19
Anthranilic	0.2205	0.2194	—0.51	0.17
Nicotinic	0.3363	0.3369	0.18	0.36
Ascorbic	0.2163	0.2135	—1.31	0.28
2-Thiophenecarboxylic	0.2874	0.2876	0.07	0.23
Oxalic	0.6301	0.5619	—10.82	6.82
Malonic	0.5641 [c]	0.5665	0.42	0.59
Succinic	0.4485 [c]	0.4401	—1.88	2.69
Maleic	0.9471	0.9421	—0.53	1.06
	0.5404 [c]	0.5343	—1.12	3.30
Phthalic	0.4221 [c]	0.4182	—0.02	0.72
	0.6426 [a]	0.6373	—0.83	0.55
Tartaric	0.4730	0.4853	2.59	1.38
Glutamic	0.2664	0.2621	—1.61	0.44
4,5-Imidazoledicarboxylic	0.2921	0.3257	11.59	6.73
Citric	0.3017	0.3021	0.14	0.16
Carboxymethylmercaptosuccinic	0.2058	0.2045	—0.65	0.24
2,4-Dihydroxybenzoic	0.1566	0.1554	—0.76	1.72
	0.1566 [c]	0.1482	—5.37	1.16
2,5-Dihydroxybenzoic	0.3359	0.3279	—2.39	1.12
2,6-Dihydroxybenzoic	0.2024	0.2070	2.26	2.66
3,4-Dihydroxybenzoic	0.2714	0.2472	—8.92	2.42
	0.2714 [c]	0.2713	—0.24	3.02
3,5-Dihydroxybenzoic	0.2507	0.2450	—2.26	0.57
	0.2507 [c]	0.2513	0.25	0.38
Iminodiacetic (IDA)	0.3025	0.2976	—1.63	0.53
	0.3025 [c]	0.3034	0.29	0.39
Nitrilotriacetic (NTA)	0.1564	0.1687	7.87	2.46
Cyclohexanediaminotetracetic (CDTA)	0.1309	0.1290	—1.49	0.19
Diethylenetriaminepentacetic (DTPA)	0.1459	0.1484	1.74	0.37
2-(2′-Thiazolylazo)-resorcinol (TAR)	0.7078	0.7571	6.96	6.49
	0.2257 [b]	0.2878	27.51	6.51
2-(2′-Pyridylazo)-resorcinol (PAR)	0.5697 [b]	0.5393	—5.34	3.04

[a] Titration in aqueous medium.

[b] Back titration of the sodium salt with hydrochloric acid.

[c] Neutralisation of the second proton.

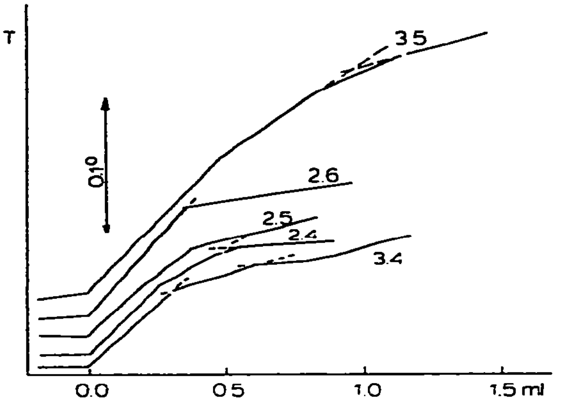


Fig. 4. Titration graphs in methanol—water medium for the dihydroxybenzoic acids.

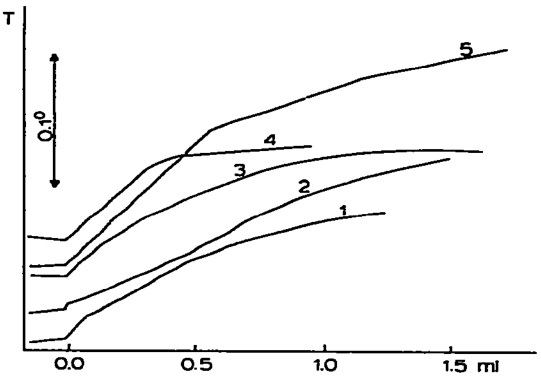


Fig. 5. Titrations graphs in methanol—water medium. 1, CDTA; 2, EGTA; 3, DTPA; 4, NTA; 5, IDA.

The greater error found in the thermometric titration of suspensions of 2-(2′-thiazolylazo)resorcinol (TAR) and 2-(2′-pyridylazo)resorcinol (PAR) is due not only to their very low solubilities in the medium, but also to anomalously low neutralisation enthalpies. The titration graph for a suspension of TAR in the water—methanol medium, Fig. 6, curve 2, shows an anomalous initial curvature related to the net result from two opposing thermal effects: the neutralisation of the dissolved portion and the solvation of the undissolved portion. The second effect initially predominates, resulting in a negative slope. Once the monosodium salt of TAR is formed, the slope takes a normal positive value for the neutralisation of the second proton. These phenomena are not found in the titration of a saturated solution of TAR in the hydromethanolic medium, where the titration graph, Fig. 6 curve 1, shows the same shape as for dihydroxybenzoic acids, allowing the separate identification of two end points. Solubility for TAR in the water—methanol (50% v/v) medium has been calculated to be 0.024 g 100 ml^{-1} at 25°C.

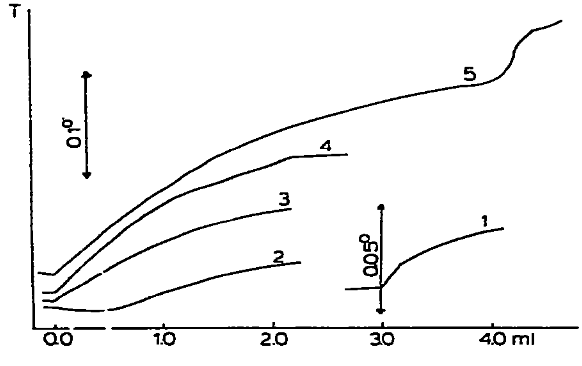


Fig. 6. Titration graphs in methanol—water medium. 1, TAR saturated solution; 2, TAR suspension; 3, back titration of PAR monosodium salt with HCl; 4 and 5, back titration of TAR disodium salt with HCl.

The back titration with hydrochloric acid of the disodium salt of TAR in water—methanol solution does not give better results, as no inflection point appears on the titration graph, Fig. 6 curves 4 and 5. Besides, a great deformation of the graph about the theoretical end point, increasing with TAR concentration, accounts for the precipitation of free TAR and prevents the location of the true end point. The same behavior is observed with PAR.

Neutralisation enthalpies

Examples of calculated neutralisation enthalpies in water are given in Table 2.

Table 3 shows that enthalpy changes for the neutralisation of acids in water—methanol are greater than in anhydrous methanol but smaller than in water. Boric acid is an exception.

As is known, neutralisation enthalpy can be written as $\Delta H_N = \Delta H_I + \Delta H_W$, where ΔH_W is the formation enthalpy for the solvent molecule from its ions in the neutralisation reaction, and ΔH_I is the total dissociation enthalpy for the weak acid, which in turn can be written as $\Delta H_I = \Delta H_i + \Delta H_d + \Delta H_s + \Delta H_r$, where ΔH_i is the ionisation enthalpy for the weak acid covalent molecule; ΔH_d is the dissociation enthalpy for the ionic pairs; ΔH_s is the solvation enthalpy for the ions; and ΔH_r is the resonance enthalpy stabilising the anion. Of these terms, ΔH_d and ΔH_s are dependent on the properties of the solvent (as well as ΔH_W) and, to some extent, on the ionic charge of the acid.

In the neutralisation of a strong acid, only ΔH_W has to be taken into account if the dielectric constant of the solvent is not too small. The decrease of the enthalpy change for the neutralisation of an acid on increasing the methanol content of the solvent ought to be attributed to a lower ΔH_W value, because on increasing the methanol content, the fraction of the basic titrant which is found as methoxide ion increases, and the neutralisation reaction is thus modified, becoming mainly

$$H^+ + CH_3O^- \rightleftharpoons CH_3OH$$

In the methanol—water (50% v/v) medium, the fraction of the base as methoxide ion is about 85% [34] and the values of neutralisation enthalpies of the acids are close to those obtained in anhydrous methanol [10]. This change in neutralisation enthalpies is not observed in a similar ethanol—water

TABLE 2

Neutralisation enthalpies calculated in aqueous medium

Acid	pK_a	$-\Delta H^0_{\text{calcd.}}$ (kcal mole^{-1})	$-\Delta H^0_{\text{lit.}}$ (kcal mole^{-1})
Hydrochloric		13.45	13.340 [18]
Benzoic	4.19	13.92	13.9 [10]
Salicyclic	2.97	13.20	13.4 [10]
Phthalic	2.89	14.22	14.4 [10]
Potassium hydrogen phthalate	5.51	13.76	13.7 [10]

TABLE 3

Neutralisation enthalpies in different media

Acid	pK_a [a]	$-\Delta H^0$ (kcal mole^{-1})		
		Water (this work and refs.)	Water—methanol (50% v/v) (this work)	Methanol [10]
Hydrochloric		13.45	10.81	
Boric	9.23	10.2 [10]	13.22	13.9
Benzoic	4.19	13.92	9.70	7.04
Salicyclic	2.97	13.20	10.06	7.1
Sulphanilic	3.23	8.90 [25]	8.40	
Anthranilic	4.96	10.55 [9]	8.67	
Nicotinic	4.81		9.99	
Ascorbic	4.37		11.14	
2-Thiophenecarboxylic	5.03	14.64 [3]	11.23	
Oxalic	1.46	13.5	10.81	8.4
	4.40	14.6		6.2
Malonic	2.85	14.6	9.29	6.5
	5.70	15.1	10.45	7.2
Succinic	4.21	13.2	8.76	6.3
	5.64	14.0	9.39	7.3
Maleic	1.83	13.48	10.57	8.8
	6.07	14.89		4.6
Malic	3.46		9.23	
	5.10		9.78	
Phthalic	2.89	14.22	9.19	6.5
	5.51	13.7	12.71	7.2
Hydrogen phthalate			11.33	
Glutamic	4.20		10.01	
Tartaric	3.04	12.89	10.07	6.6
	4.36	13.38		6.1
Citric	3.13			
	4.76		8.72	
Carboxymethylmercaptosuccinic	3.26			
	3.79		10.72	
2,4-Dihydroxybenzoic	3.13		10.91	
	8.60		6.44	
2,5-Dihydroxybenzoic	2.7		10.62	
2,6-Dihydroxybenzoic	1.08		11.68	
3,4-Dihydroxybenzoic	4.34		11.36	
	8.7		3.81	
3,5-Dihydroxybenzoic	4.12		10.74	
	9.08		6.78	
IDA	2.84		11.92	
	9.79		3.88	
NTA	1.8		12.16	
	2.48			
	9.71			
CDTA	2.41		11.12	
	3.52			
	5.87			
	9.30			
DTPA	2.3		10.61	
	2.6			
	4.17			
	8.26			

TABLE 3 (continued)

Acid	pK_a [a]	$-\Delta H^0$ (kcal $mole^{-1}$)		
		Water (this work and refs.)	Water—methanol (50% v/v) (this work)	Methanol [10]
TAR	6.53		6.91	
	10.76		3.13 [b]	
			3.07 [c]	
PAR	5.50		3.76 [c]	

[a] Values from refs. 3, 9, 10, 30—32.
[b] Titration of the suspension.
[c] Back titration of the sodium salt with hydrochloric acid.

(50% v/v) medium [36] in which more than 90% of the base is still found as hydroxyl ion and not as ethoxide ion [34].

In the neutralisation of weak acids, in addition to the changes in ΔH_W, changes in the terms included in ΔH_I can also influence the values of the neutralisation enthalpies. However, results obtained in this work, together with those of Harries [10] (Table 3), show that the change in ΔH_N with solvent composition is of the same order of magnitude for most of the weak acids tested. Therefore, the main effect is also due to changes in ΔH_W.

The anomalous behavior of boric acid can be attributed to its different neutralisation mechanism. Raman spectroscopy [43] suggests that, in aqueous neutralisation, $B(OH)_4^-$ is formed according to

$$H_3BO_3 + OH^- \rightleftharpoons B(OH)_4^-$$

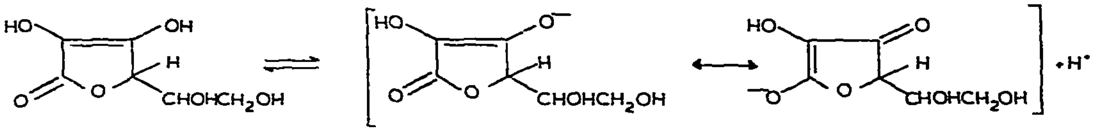
which involves OH^- addition and not the loss of one proton. In methanol-rich solvents, the predominant CH_3O^- ion will modify the course of the neutralisation reaction.

It is known that changes in solvent composition influence not only neutralisation enthalpies but also free energies. According to Grunwald et al. [37,38], pK_a values for monoprotic acids increase with a decreasing dielectric constant of the hydroalcoholic media. In Table 3, it is shown that values of ΔH_N for diprotic acids, and thus ΔH_I values, for the neutralisation of the second proton are quite similar to those for the first proton, while pK_a values are quite different. It can be deduced that differences in pK_a values can be partly balanced by variations in the ionisation entropy. On the other hand, as in non-aqueous media, ion pair formation and hydrogen bridging are enhanced [10], more relevant differences will be found for the changes in enthalpy and entropy in the successive steps of the neutralisation of polyprotic acids. These phenomena can be easily detected in cases where the anion can be stabilised by intramolecular hydrogen bridge formation, as in salicyclic acid.

The results obtained show that enthalpies for the neutralisation of the first and second proton show greater differences on increasing the methanol content of the solvent. In general, ΔH_N is greater for the second proton.

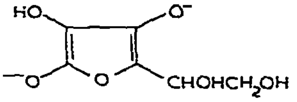
In the methanol—water medium, as in aqueous medium, neutralisation of phenolic groups gives ΔH_N values smaller than those for carboxylic acids. As for pK_a values, this phenomenon can be explained in term of the resonance stabilisation of the anions [44], which is greater for carboxylate anions. The solvent is not directly involved in the resonance mechanism.

In the same way, the higher acidity of ascorbic acid and its anomalous thermometric titration graph in the water—methanol medium can also be due to the resonance stabilisation of the successive anions formed during the titration. The titration of the first proton can be attributed to the process



which explains its pK_{a1} value of 4.17 (H_2O) and neutralisation enthalpy ($\Delta H_N = -11.14$ kcal mole^{-1} in methanol—water), very similar to those for carboxylic acids.

After the first proton has been neutralised and during a short part of the titration graph, ascorbic acid shows no apparent reaction, Fig. 2, curve 2. Afterwards, a new increase in the slope of the graph appears. It can be supposed that in a sufficiently basic medium the proton of the carbon atom which holds the side chain is lost and the dianionic resonant form, among others, is stabilised by the aromatisation of the system, in accordance with the high slope of the titration graph during the neutralisation of the second proton, and with ^{13}C-NMR [45], which shows that the neutralisation of ascorbic acid does not involve furanic ring opening.



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